DISTRIBUTION OF ARSENIC & FLUORIDE IN GROUND WATER FROM SEVERAL PARTS OF NORTH & SOUTH 24 PARGANAS DISTRICTS OF WEST BENGAL

AND

REMEDIAL MEASUREMENTS BY USING SUITABLE ADSORBENTS

Thesis submitted for the partial fulfilment of the degree of
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To Whom It May Concern

It is hereby recommended that this thesis entitled "**Distribution of arsenic & fluoride contaminated groundwater in several parts of North & South 24 parganas districts in West Bengal and Remedial measurements by using suitable adsorbents**" is prepared and submitted for the partial fulfilment of the continuous assessment of Master of Technology in Environmental Biotechnology course of Jadavpur University by **Bishal Ghosh** (Examination Roll No. M4EBT19006; Registration No. 141032 of 2017-2018; Roll No. 001730904008), a student of the said course for the session 2017 – 2019, under my supervision and guidance. It is also declared that no part of this thesis has been presented or published elsewhere.

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CERTIFICATE OF APPROVAL

This foregoing thesis is hereby approved as a credible study of an engineering subject carried out and presented in a manner satisfactorily to warranty its acceptance as a prerequisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not endorse or approve any statement made or opinion expressed or conclusion drawn therein but approve the thesis only for purpose for which it has been submitted.

Final Examination for evaluation of Thesis

(Signature of the Examiners)

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Abstract

The contamination of arsenic and fluoride in groundwater is one of the most concern areas among global water community. This present study mainly deals with the removal of arsenic and fluoride from aqueous solution by thermally activated adsorbents prepared from dolomite, sea shell and their mixtures (cheap and easily available). Atomic adsorption spectrophotometer (AAS) and Ion Selective Electrode (ISE) has been used for measuring and monitoring the total arsenic [As(V)] and fluoride(F-). Batch experiments has been conducted to establish the optimal conditions like effective pH, adsorbent dose, initial adsorbate concentration, contact time, contact speed and effective activated temperature. The maximum removal of arsenic (more than 90%) with adsorption capacity of 9.403 μg/gm is optimized at pH of 12, contact time of 20 mins, adsorbent dose of 5 gm/L, initial concentration of 100 ppb arsenic [As (V)] with a contact speed of 50 RPM on thermally activated adsorbents with 600ºC. Whereas maximum removal of fluoride (more than 90%) with adsorption capacity of 96 μg/gm is optimized at pH of 7, contact time of 60 mins, adsorbent dose of 50 gm/L, initial concentration of 5 ppm fluoride with a contact speed of 40 RPM on pretreated thermally activated adsorbents with 2(M) HCL and 800ºC. For both cases Pseudo second order kinetic model is best suited and Isotherm analysis shows that Freundlich is best for adsorption.

This study also shows the status of groundwater (mainly arsenic and fluoride) in some areas of north and south 24 parganas in West Bengal which are still unreported.

This research work that has been provided could be used for further studies. The results of this study could be used in designing a filtering unit that can efficiently remove the contaminants from groundwater to provide the safe drinking water. The development of such technology could help us with a cost effective and efficient remedy for both arsenic and fluoride removal.

Key Words: Arsenic, Fluoride, sea shell, Dolomite, Adsorption, isotherm, kinetics

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CHAPTER - 1

INTRODUCTION

Water is a scarce resource and most essential for the human survival. The quantity of potable water on earth is limited and its availability per person is reducing day by day due to increase in global population and damage to the environment. Access of safe drinking water was declared as a human right by the United Nations but remains a challenge for India.

The total amount of water available on the earth has been estimated at 1.37 billion cubic km, enough to cover the planet with a layer of about 3 km deep (Garrison, 2005). More than two-third of the earth surface is covered with water, but 97.5% of this is saline water. This leaves only 2.5% as fresh water. Adding to the paradox, only a tiny fraction of the total fresh water resource is available for human use. About 70% of the fresh water on the planet is blocked up in ice at the pole, and most of the remainder is retained as soil moisture or deposited in deep underground aquifers. In the final tally less than 0.5% of all the fresh water on the earth is technologically and economically accessible for human use (Chart 1.1).

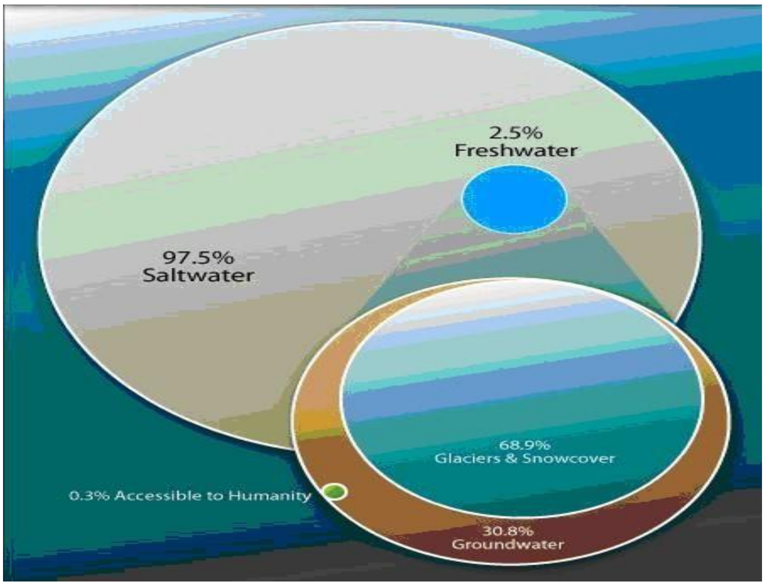


Fig 1: Global Water Scenario (source: Shiklomanov, 1999)

But still we are unable to use that much of water as they are getting contaminated or polluted by natural or manmade causes. Even the safe drinking water is getting endangered. There are mainly two sources of drinking water, one is groundwater another is surface water. Groundwater has been widely used for drinking purpose by the majority people (especially in rural areas). But nowadays groundwater is also contaminated either due to some natural calamities or some anthropogenic activities of human. The major contaminants include mainly heavy metals such as iron, arsenic, lead, mercury, chromium, cadmium and many more, inorganic ions such as fluoride, nitrate, chloride, perchlorate and sulfate and different colouring effluents coming from dye industry, textile and paper industries. All these contaminants impart severe health effects on human. Among all these contaminants, arsenic and fluoride are considered the most harmful and toxic contaminant present in water. Therefore, it is essential to remove these contaminants from groundwater to provide safe drinking water.

1.1 GROUND WATER RESOURCE: AN OVERVIEW

Ground water is a critical resource in India. It accounts for over 65% of irrigation water and 85% of drinking water supplies (World Bank, 2010) 33% of the country's groundwater resources are unfit for consumption (The Times of India, March 12, 2010) and estimates about 60% of ground water resource will be in critical state of degradation within next twenty years (Kumar and Raj, 2013).

Over the past several decades, a large number of both anthropogenic and geogenic contaminants have emerged as serious threat for ground water use. The primary anthropogenic sources of groundwater pollution in India are from sewage disposal, agriculture, and industry. Indian cities are estimated to generate 20 million m3 of sewage per day, and only 10% of this sewage is treated prior to reaching groundwater or surface water resources (Chakroborty et al., 2011). Furthermore, the majority of Indian domestic waste is improperly disposed. Rapid urbanization compounds these problems. Recent research conducted on Ganga plain finds roughly 70% of rural populations utilize tube wells (~10 m) and ~40% of them were contaminated with bacteria (Chakroborty et al., 2011).

In recent years ground water is considered as the major source of safe and potable water throughout the world. (Zektser and Everett, 2004) It is widely used and considered as a primary source of drinking water as it is less susceptible to contamination and pollution in comparison to surface water resource. (Kumar and Shah, 2004) Groundwater plays a crucial role in mitigating rural-urban water demand in India. Presently, the country is experiencing population growth of about 1.4% per annum with greater economic growth rates (Bloom, 2011), which intensifies the demand and use of water. Recent studies revealed that India is extracting about 200 billion cubic meter of ground water reserve every year, which is highest on the earth. Nearly, about 80% of the rural domestic needs and 50% of urban water needs in India are fulfilled by ground water (Aguilar, 2011). Ground water is now facing a crisis in terms of quantity and quality too. During the past two decades, the water level in several parts of the country has been falling rapidly due to an increase in ground water development. The number of wells drilled for irrigation has increased rapidly and indiscriminately (Ahmad et al., 2007). Thus rising population, urbanization and industrialization coupled with intense competition among agriculture, industry, and domestic sectors are pushing the groundwater table lower and lower. As a result, quality of groundwater is getting severely affected because of the overdraft. Discharge of untreated industrial wastewater and unscientific disposal of solid wastes contaminate groundwater. Thus, the quality of fresh Ground water resource is reducing.

CHAPTER – 2
ARSENIC: THE WORLDWIDE CONCERN

The greatest threat to public health from arsenic originates from contaminated groundwater. Inorganic arsenic (i.e. high toxic and carcinogenic, causes major health issues).is naturally present at high levels in the groundwater of a number of countries, including Argentina, Bangladesh, Chile, China, India, Mexico, and the United States of America. Drinking-water, crops irrigated with contaminated water and food prepared with contaminated water are the sources of exposure.

The United States Environmental Protection Agency states that all forms of arsenic are a serious risk to human health. The United States Agency for Toxic Substances and Disease Registry ranked arsenic as number 1 in its

2001 Priority List of Hazardous Substances at Superfund sites. Arsenic is classified as a Group-A carcinogen (Wikipedia, arsenic).

2.1 ARSENIC AND ITS OCCURRENCE

Arsenic is a naturally occurring metalloid that is widely distributed in the Earth's crust. It is found in water, air, food, soil, in plants and animals. People can also be exposed to arsenic in the environment from some agricultural and industrial sources.

There are two general forms of arsenic:

- Organic (arsenic combined with carbon and other elements): These compounds tend to be much less toxic than the inorganic arsenic compounds and are not thought to be linked to cancer. Organic compounds are found in some foods, such as fish and shellfish.
- Inorganic (arsenic combined with elements other than carbon): These compounds are found in industry, in building products (such as some "pressure-treated" woods), and in arsenic-contaminated water. This tends to be the more toxic form of arsenic and has been linked to cancer.

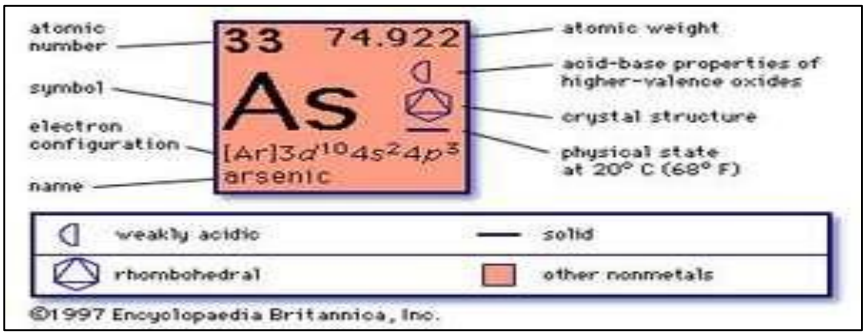


Fig 2: Arsenic and its features

2.2 CHEMISTRY AND TOXICITY OF ARSENIC

Arsenic is a chemical element that occurs in Group V of the periodic table. Chemically it is a metalloid, showing the properties of both metals and nonmetals. Elemental arsenic usually occurs in brittle form with silver grey colour. However, in nature three allotropic forms of arsenic are found, viz. yellow, black & grey (Carapella, 1978). Commonly, it is found in association with oxides, chlorides & sulfate/sulfides. In water arsenical compounds are partly soluble to completely insoluble (Budavari, 1996). The solubility properties of some arsenical compounds are mentioned below.(Table: 1)

Arsenic occurs in two oxidation states: a trivalent form, arsenite [As_2O_3; As (III)] and a pentavalent form, arsenate [As_2O_5; As (V)]. As (III) is 60 times more toxic than As (V). Organic arsenic is non-toxic whereas inorganic arsenic is toxic.

Arsenic toxicity inactivates up to 200 enzymes, most notably those involved in cellular energy pathways and DNA replication and repair, and is substituted for phosphate in high energy compounds such as ATP.

Unbound arsenic also exerts its toxicity by generating reactive oxygen intermediates during their redox cycling and metabolic activation processes that cause lipid peroxidation and DNA damage.29 As III, especially, binds thiol or sulfhydryl groups in tissue proteins of the liver, lungs, kidney, spleen, gastrointestinal mucosa, and keratin-rich tissues (skin, hair, and nails) and many other toxic effects due to arsenic are being determined and are detailed (Abernathy et al in 1999).

Table 1: Physical Properties of Arsenic Compounds (source: Merck, 1989; Sax, 1989)

Compound Name	Molecular Formula	Synonyms	Solubility in Water (PerLiter)
Arsenic Pent oxide	As_2O_5	Arsenic acid, Arsenic oxide	65.8g (20^0 C)
Arsenic tri oxide	As_2O_3	Arsenous acid, crude arsenic	21g (25^0 C)
Arsenic acid hemi hydrate	$H_3AsO_41/2H_20$	Ortho arsenic Acid	170g (20^0 C)
Arsenic sulfide	As_2S_3	Arsenious sulfide	Insoluble
Arsine gas	AsH_3	Hydrogen arsenide	200ml (20^0 C)
Calcium arsenate	$Ca_3(AsO_4)_2$	Calcium ortho arsenate pencal	0.13g (25^0 C)

2.3 SOURCES AND EXPOSURES OF ARSENIC

Arsenic is a widely dispersed element in the Earth's crust and occurs as a constituent in more than 200 minerals. Arsenic is mostly released in the environment through different natural processes such as weathering and volcanic eruptions, and transported over long distances as suspended particulates and aerosols through water or air. Arsenic emission from industrial activity also accounts for widespread contamination of soil and groundwater environment (Jacks and Bhattacharya, 1998; Juillot et al., 1999; Singh, 2006). Once introduced into the atmosphere, arsenic may circulate in natural ecosystems for a long time depending on the prevailing geochemical environments (Boyle and Jonasson, 1973; Yan Chu, 1994). The source of arsenic in the groundwater is a controversial issue and has yet to be determined. But it is now widely believed that the high levels of arsenic in ground water of fluvio-deltaic environments are geogenic in nature (Kinniburgh and Smedley, 2001, Acharyya et al., 1993, 2000; Acharyya and Saha, 2005). The quaternary confined and semi-confined alluvial aquifers release arsenic through a number of bio- geo-chemical processes of oxidation, reduction, adsorption, precipitation, methylation and volatilization (Polizzotto, 2007; Naidu, 2013).

Arsenic exposure occurs from inhalation, absorption through the skin and, primarily, by ingestion of, for example, contaminated drinking water. Arsenic in food occurs as relatively non-toxic organic compounds (arsenobentaine and arsenocholine). Seafood, fish, and algae are the richest organic sources.These organic compounds cause raised arsenic levels in blood but are rapidly excreted unchanged in urine. Arsenic intake is higher from solid foods than from liquids including drinking water.Organic and inorganic arsenic compounds may enter the plant food chain from agricultural products or from soil irrigated with arsenic contaminated water.Arsenic is one of the most toxic metals derived from the natural environment. The major cause of human arsenic toxicity is from contamination of drinking water from natural geological sources rather than from mining, smelting, or agricultural sources (pesticides or fertilizers).Arsenic trioxide (As2O3) is now widely used to induce remission in patients with acute promyelocytic leukaemia, based on its mechanism as an inducer of apoptosis (programmed cell death).Arsenic continues to be an essential constituent of many non-western traditional medicine products. Some Chinese traditional medications contain realgar (arsenic sulphide) and are available as pills, tablets, and other preparations. In India, herbal medicines containing arsenic are used in some homoeopathic preparations.

Biological sources contribute very little amounts of arsenic into soil and sub-surface aquatic systems. However, plants and microorganisms affect the redistribution of arsenic through their bioaccumulation (e.g., biosorption), biotransformation (e.g., biomethylation), and transfer (e.g., volatilization).

Arsenic accumulates readily in living tissues because of its strong affinity for proteins, lipids, and other cellular components (Ferguson and Gavis, 1972). Aquatic organisms are particularly known to accumulate arsenic, resulting in considerably higher concentrations. Arsenic could be transferred from soil to plants and then to animals and humans, involving terrestrial and aquatic food chains. For example, poultry manure addition is considered to be one of the major sources of arsenic input to soils. (Christen, 2001).

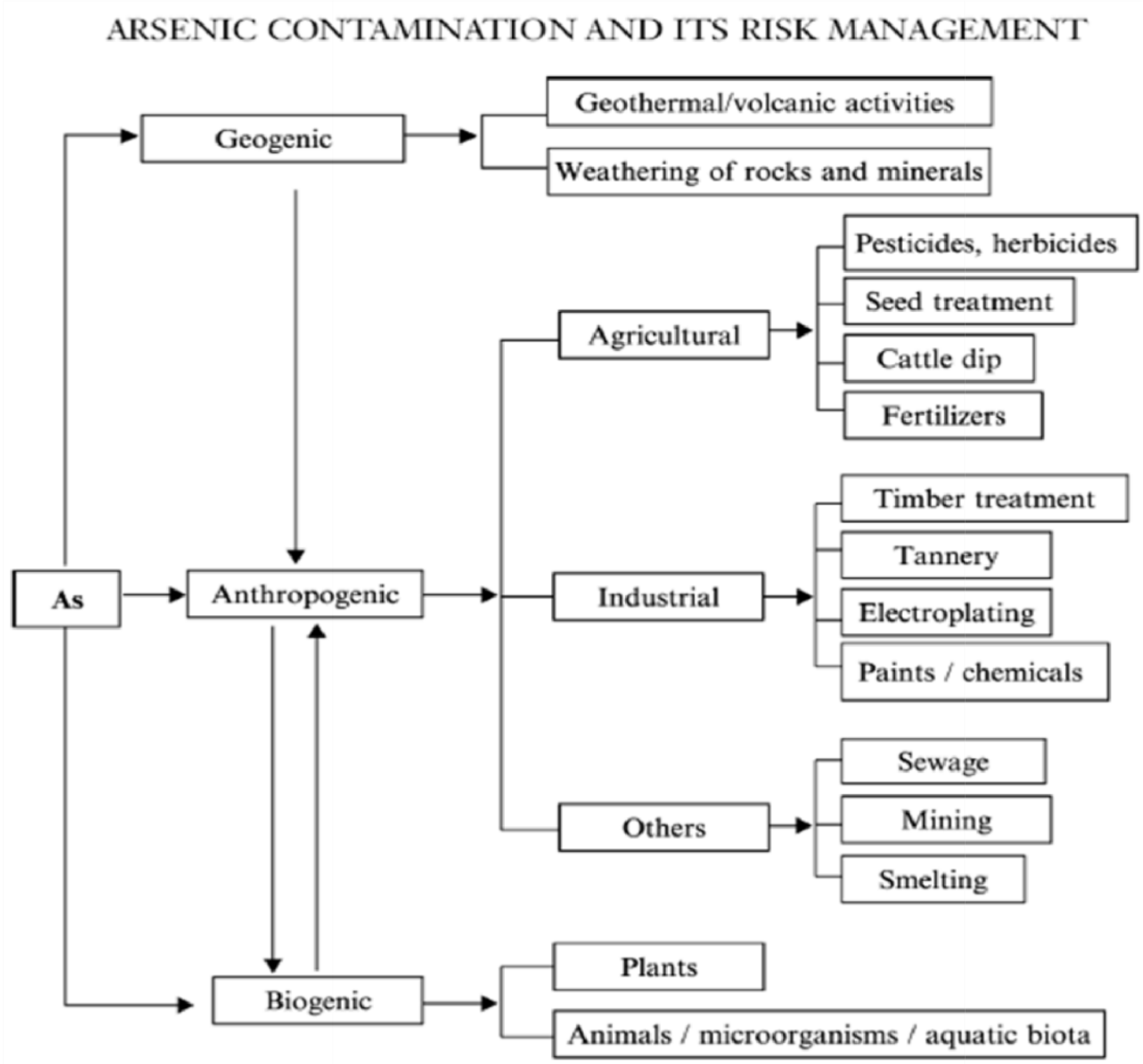


Fig 3: Sources of Arsenic Contamination (Source: Mahimairaja et. al., 2005)

2.4 ARSENIC IN GROUNDWATER

The earliest measurement of arsenic in natural water was done by a German chemist at Wiesbaden Spa in 1885 (Schwenzer et al., 2001). But, this water was not consumed in sufficient quantities to cause illness. The earliest report of arsenic poisoning from well-water that caused skin cancer, was from Poland in 1898 (Mandal and Suzuki, 2002), The first major case of endemic disease caused by arsenic in drinking water was reported in the 1920s in Cordoba Province of Argentina (Bado, 1939), where it is associated with skin cancer also. From the 1930s to the 1970s, there were few incidents of natural arsenic contamination were noticed in Canada (Wyllie, 1937) and New Zealand (Grimmett and McIntosh, 1939). In the 1960s, arsenic poisoning has been reported from southwest Taiwan and became well known tragedy in Taiwan. Until 1980s, the picture did not attract international attention (Ravenscroft, 2009). In 1980s the biggest Geo-environmental hazard was recognized from west Bengal India. In tropical Asia, drinking water was traditionally drawn from surface water and dug wells, but, wide spread bacterial pollution of these water sources gave rise to epidemics of diarrheal diseases and accelerates the child-mortality rate (Falkenmark, 1980). In the 1990s, arsenic pollution of groundwater burst from obscurity to receive the attention of the media (Bearak, 1998). This transformation essentially took place in India and Bangladesh by the efforts of School of Environmental Studies (SOES) who described arsenic pollution in six districts of West Bengal as the biggest arsenic calamity in the world' (Das et al., 1994) In February 1998 a conference took place in Dhaka organised by the joint venture of SOES and the Dhaka Community Hospital (DCH), which reiterated the magnitude of the problem in West Bengal, and Bangladesh.the current scientific explanation of the pollution in Bengal was presented (Ahmed et al., 1998), showing that the cause was geological, and not anthropogenic. In the coming years extensive pollution was discovered in the river basins of Nepal, Myanmar, Cambodia, Vietnam and Pakistan (Jain and Ali, 2000; Nordstrom, 2002). Gradually it was identified upstream from West Bengal in the States of Bihar, Uttar Pradesh and Assam on the Ganges and Brahmaputra floodplains. Since 2000, arsenic contamination has been found in several parts of the world (Ravenscroft, 2009).In groundwater, inorganic arsenic commonly exists as arsenate (As5+) and arsenite (As3+). Inter- conversion of As5+ and As3+ takes place by oxidation of As3+ to As5+ and reduction of As5+ to As3+(Singh, 2006). The other form of arsenic occurrence, is organic-arsenic, which is mostly less toxic than both As3+ and As5+. High concentration of arsenic tends to occur in sulphide minerals and metal oxides, especially iron oxides. Several studies suggest that the arsenic rich groundwater is mostly restricted to the alluvial aquifers of the Ganges delta comprising sediments carried from the sulphide-rich mineralized areas of Bihar and elsewhere surrounding the basin of deposition (Das et al., 1995; Bhattacharya et al., 1997; Singh, 2006). However, recent studies indicate that the vast tract of Indo-Gangetic alluvium extending further to the west and the Brahmaputra alluvium have elevated concentrations of As in wells placed in the late Quaternary and Holocene aquifers. Arsenic released during the weathering of sulphide minerals is generally adsorbed on to the surface of iron oxy hydroxides that precipitated under oxidizing conditions generally prevailing during the deposition of the Holocene sediments. However, redox processes in the sediments trigger the reductive dissolution of iron oxides that transfers substantial amounts of arsenic in aqueous phases through biogeochemical interactions (Acharyya, 2002; Smedley and Kinniburgh, 2002). Arsenic containing groundwater in Ganges–Brahmaputra river basin is hosted by the sediments deposited by the rivers during the late Quaternary or Holocene age. Most environmental arsenic problems recognized today are the result of mobilization under natural conditions.

2.5 MECHANISM OF ARSENIC MOBILIZATION

Geochemical and hydro-geological characteristics of alluvial sediments govern the mobility of arsenic in shallow aquifer system, and the source of arsenic in the sediments depends on the geology of the source terrain (Juillot et al., 1999). The retention or mobility of arsenic under varying redox (oxidation–reduction) conditions is based on the interaction of the aqueous phase with different mineral phases in the sediments (Singh, 2006). It has also been reported that mineralogical characteristics of the sediments reflect differential concentrations of arsenic (Bhattacharya, et al., 2001). The mechanism of arsenic release and mobilization in groundwater has been a subject of considerable controversy. Detailed discussions on three contrasting hypotheses have been published (Bhattacharya et al., 2001; Nickson et al., 2000; Das et al., 1996; Roy Chowdhury et al., 1999; Chakroborti et al., 2001). They are:

- Release of As following the oxidation of As-rich pyrite
- Reductive dissolution of iron hydroxides and release of sorbed As into the groundwater, and
- Anion exchange of sorbed arsenic with phosphate from fertilizers.

Oxidation of sulphide minerals (pyrite-$FeS2$) has been advocated strongly by many workers in West Bengal as the cause of groundwater arsenic problems (Das et al., 1994; Singh, 2006). The oxidation processes could be possible in some parts of the aquifers, particularly at the shallowest levels. However, it is not considered to be the main cause of groundwater arsenic problems in the GDP. While, the chemical reaction can be stated as,

$$2\ FeS_2 + 9\ O_2 + 4\ H_2O \rightarrow 8\ H+ + 4\ SO4^{2-} + 2\ Fe(OH)_3$$

The reduction of arsenic from its oxidized (As5+) form to its reduced (As3+) form is less strongly adsorbed to iron oxides than As5+ and reduction should therefore involve a net release of As3+ from adsorption sites. The chemical reaction can be given as-

$8FeOOH – As_{(s)} + CH_3COOH + 14\ H_2CO_3 \rightarrow 8\ Fe3+ + As_{(d)} +16\ HCO_3 - + 12\ H_2\ O$

Where As (s) is sorbed As, and As (d) is dissolved As.

Under aerobic and acidic to neutral conditions, adsorption of arsenic (As5+) to iron oxides is normally strong and aqueous concentrations are therefore usually low. However, the sorption is less strong at high pH level. Increases in pH (especially above pH 8.5 or so) will therefore result in desorption of arsenic from oxide surfaces and a resultant increase in dissolved concentrations. Such processes are considered to have been responsible for the release of arsenic in oxidizing Quaternary sedimentary aquifers.

The surface reactivity of iron (Fe) and aluminum (Al) plays an important role in adsorbing the bulk of arsenic in the sedimentary aquifers in the Ganga Delta Plain. However, it was reported that the theory does not explain increasing arsenic concentration in existing tube-wells, previously safe but now progressively contaminated (Roy Chowdhury et al., 1999). Sediment analyses showed that extensive groundwater withdrawal for agricultural purposes favours the oxidation of arsenic rich iron sulphide and thereby mobilizes arsenic in the Bengal basin (Nickson et al., 2000; Das et al., 1996; Roychowdhury et al., 1999).

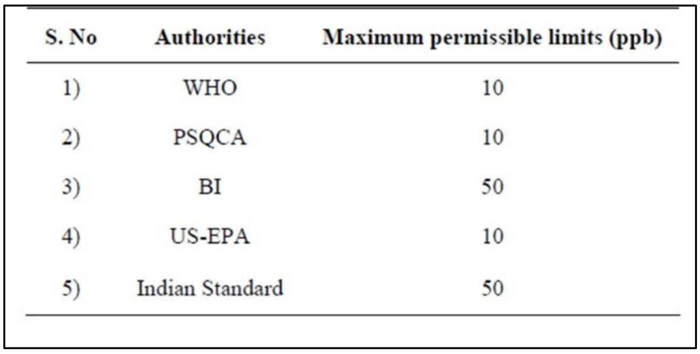
Increased use of water for irrigation and use of fertilizers have caused mobilization of phosphate from fertilizers down to the shallow aquifers, which have resulted in the mobilization of arsenic due to anion exchange onto the reactive mineral surfaces. Since phosphate is bound strongly on to these surfaces, As5+ can be mobilized in groundwater (Acharyya et al., 1993) However, it confirmed that phosphorus in groundwater cannot contribute to arsenic pollution by experimental desorption by phosphate of arsenic sorbed to mineral surfaces (Manning and Goldberg, 1997). However, microbiological and chemical processes might increase the natural mobility of arsenic (Acharyya et al., 1999).

2.6 PERMISSIBLE LIMIT OF ARSENIC

WHO’s provisional guideline value for arsenic in drinking water is 0.01 mg/l (10 μg/l) (Source: Guidelines for drinking water quality, 4th edition, WHO, 2011). Permissible limit of arsenic in India in absence of an alternative source - 0.05 mg/l (50 μg/l). (Source: Indian Standards for Drinking Water, second revision of IS 10500, 2004).

This permissible limit varies according to the climatic condition of a place. Hence every country of the world has different permissible limits based on their geography, temperature and humidity.

Table 2: Authorities and their permissible limits of arsenic



S. No	Authorities	Maximum permissible limits (ppb)
1)	WHO	10
2)	PSQCA	10
3)	BI	50
4)	US-EPA	10
5)	Indian Standard	50

2.7 HEALTH IMPACTS OF ARSENIC

The acute impacts of arsenic are mainly drowsiness, headaches, confusion, severe diarrhea, a metallic taste in the mouth and garlicky breath, swallowing blood in the urine, cramping muscles, hair loss, stomach cramps, excessive sweating, vomiting, diarrhea. Chronic exposure to inorganic arsenic affects different systems with in the body. Some of these systems and their associated toxic effects from chronic arsenic exposure are listed below.

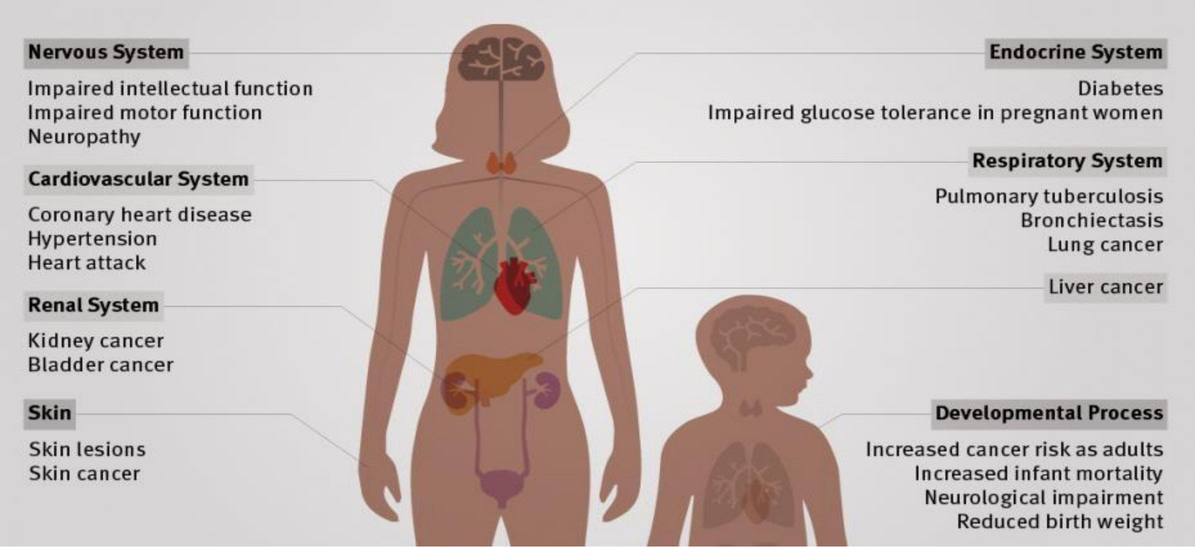


Fig 4: Arsenic's Effects on the Human Body
(source: Richard Pearshouse, Environment and Human Rights Division)

Multiple skin cancers **Kerasotes of the foot** **Skin cancers**

Fig 5: Arsenic Toxicity in Humans (source: https://scialert.net/fulltextmobile/?doi=tasr.2012.331.349)

2.8 GLOBAL SCENARIO OF ARSENIC

Distribution of high concentration of arsenic has been detected in groundwater all round the world in recent times. Due to geological and climatic variations, the concentration of arsenic in groundwater is not similar all round the world. Nowadays a great concern has been diverted to the contamination of groundwater with geogenic arsenic (i.e. high toxic and carcinogenic), as it causes major health issues.

Arsenic has penetrated into the groundwater over 70 countries, affecting more than 140 million humans (Herath et al.,2016). Arsenic contamination in the south eastern part of Asia has gained a lot

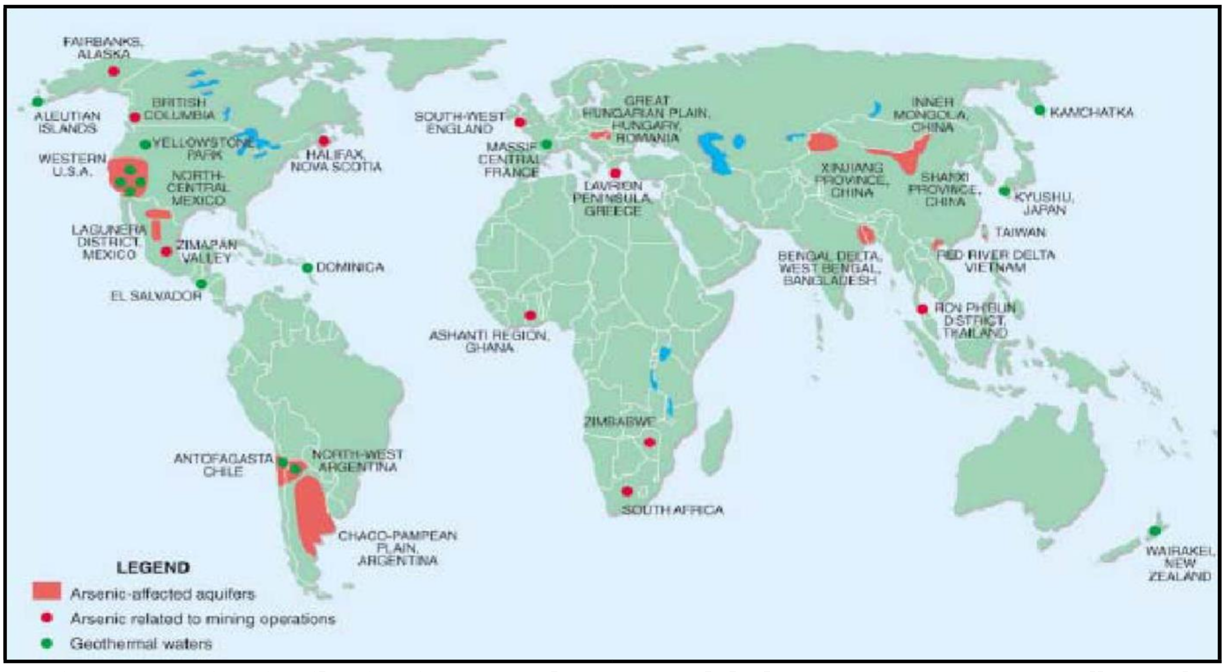


Fig 6: Arsenic Distribution in Groundwater at Global Scenario (Source: Smedley and Kinniburgh,2002)

of attention from researchers and medical experts in the recent years (Chakraborty et al.,2015). The natural contamination of arsenic has been seen in the belt of Ganga-Bhramaputra -Meghna basin (Herath et al.,2016). Over 100 million people in the part of world are effected by arsenic and ove 700000 people have been reported tsuffering from arsenic related diseases (Kim et al.,2011)

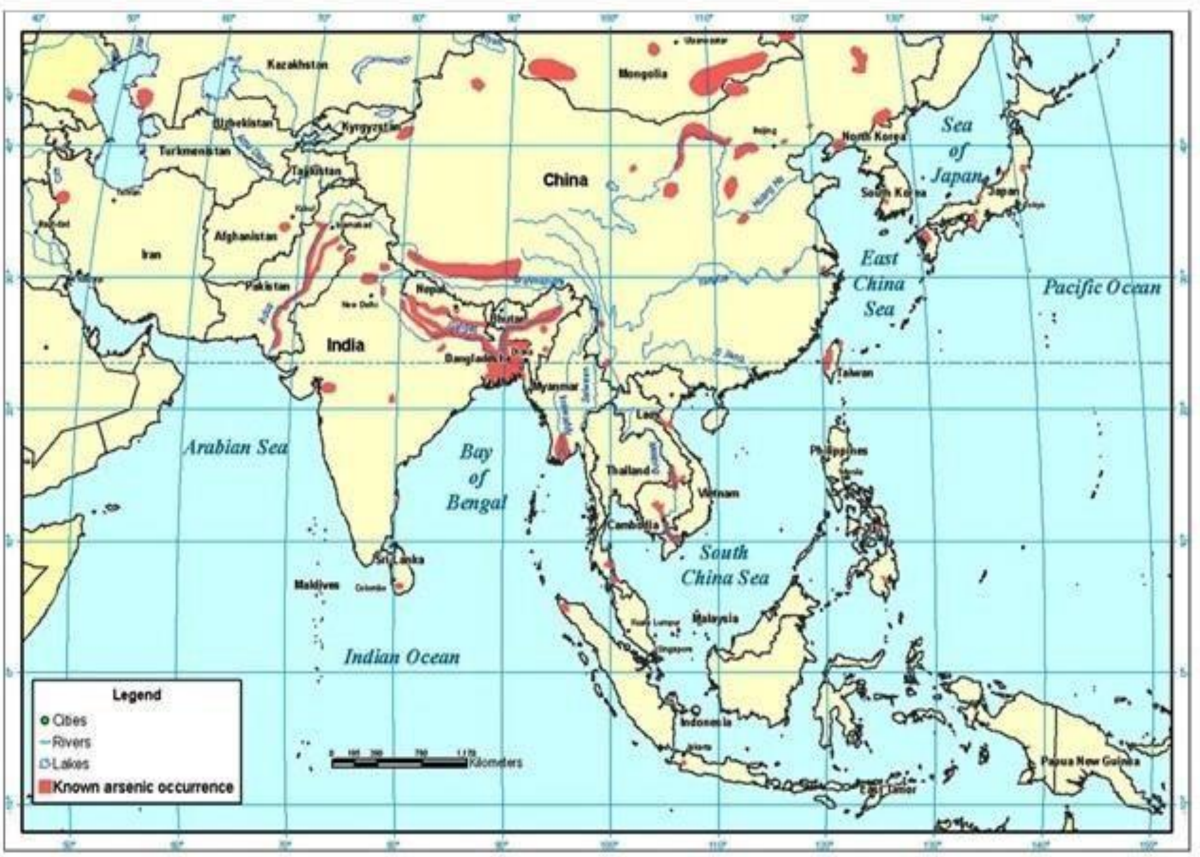


Fig 7: Arsenic distribution map of South-East Asia (source: Ravenscroft, 2007)

In Asia several countries are in lime light due to contamination of ground water of shallow depth by arsenic viz. Bangladesh, (SOES, 1995; Dhar, 1997) Afghanistan, (Sengupta et al., 2003 ; Saltori, 2004) India, (Garai et al., 1984; Chaktoborti et al., 2002) Cambodia, (Berg et al., 2007)China (Sun et al., 2001) Indonesia (Winkel et al., 2008) Myanmar (UNDP-UNCHS, 2001) Taiwan (Yeh, 1963 ; Tseng et al., 1968) Vietnam (Berg et al., 2001,2007; Agusa et al., 2006; Shinkai et al., 2007)Nepal (Tandukar et al., 2001, 2006; Shrestha et al., 2003) Pakistan (Iqbal, 2001; Nickson et al., 2005) etc. The incidence of Arsenic toxicity in South-East Asian countries is shown in the below figure.

2.9 SCENARIO OF BANGLADESH AND INDIA

In India, the states of West Bengal, Jharkhand, Bihar, Uttar Pradesh, Assam, Manipur and Chhattisgarh are reported to be most affected by arsenic contamination of groundwater above the permissible level. Most of Bangladesh and the state of west Bengal (lies in the Ganga-Meghna-bhramaputra basin) has been reported for the chronic arsenic toxicity, according to the recent reviews, 50 district of Bangladesh and 9 districts of west Bengal has been identified for arsenic contamination. Over 22% of the population of Bangladesh consumes at least 50 µg/ml of arsenic and over 4% of entire population consumes water with more than 200 µg/L of arsenic (bhattacharya et al., 2009). Arsenic has penetrated into the groundwater over 70 countries, affecting more than 140 million humans (Herath et al.,2016). Arsenic contamination in the south eastern part of Asia has gained a lot of attention from researchers and medical experts in the recent years (Chakraborty et al.,2015). The natural contamination of arsenic has been seen in the belt of Ganga-Bhramaputra -Meghna basin (Herath et al.,2016).

Over 100 million people in the part of world are effected by arsenic and ove 700000 people have been reported tsuffering from arsenic related diseases (Kim et al.,2011).

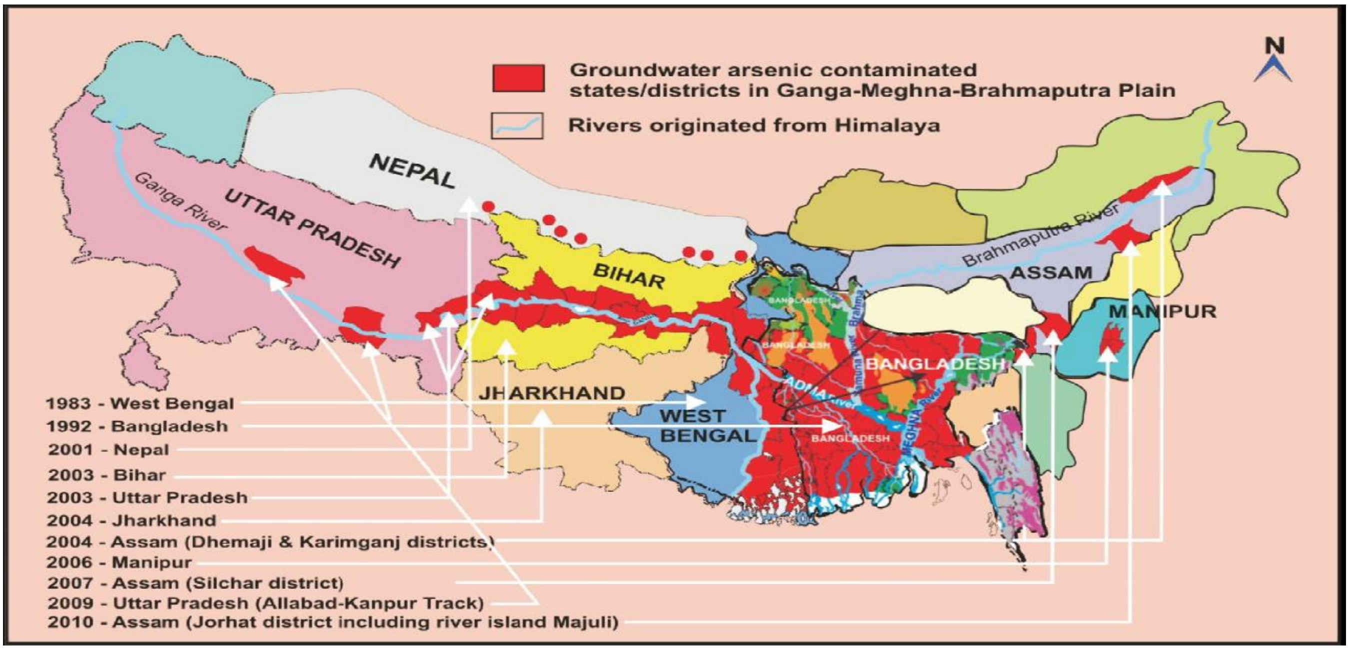


Fig 8: Arsenic contamination in Ganga-Meghna-Brahmaputra Plain (GMB) with dates of Identification (source: Chakraborti et. al., 2013)

70.4 million Populations of India have chronically been exposed to drinking Arsenic contaminated hand tube-wells water (Chakroborty et al., 2011) which is indicated in below Figure. With every new survey, more Arsenic affected villages and people suffering from Arsenic related diseases are being reported, and the issues are getting complicated by a number of unknown factors.

2.10 SCENARIO OF WEST BENGAL

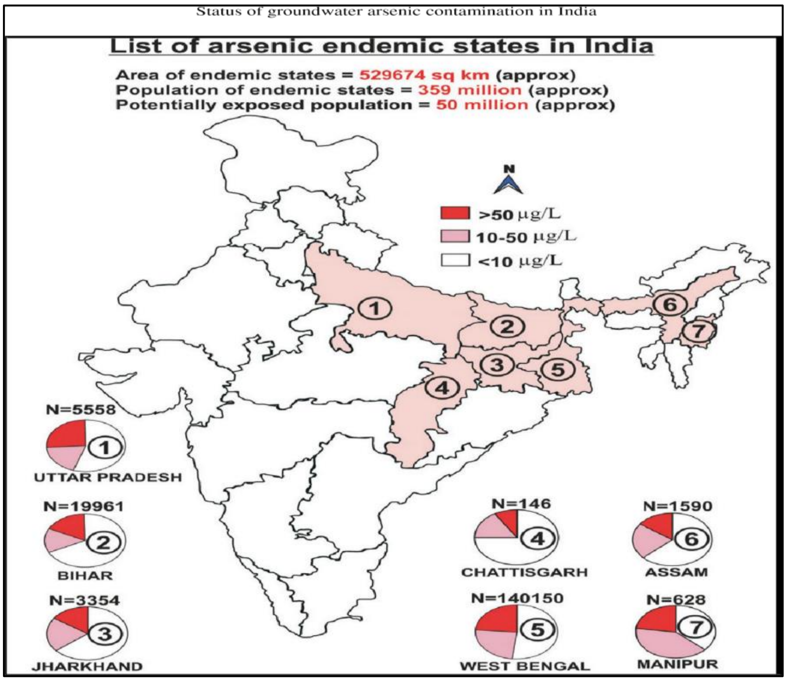


Fig 9: **S**tatus of Groundwater Arsenic Contamination in India (Source:Chakraborti et al., 2013)

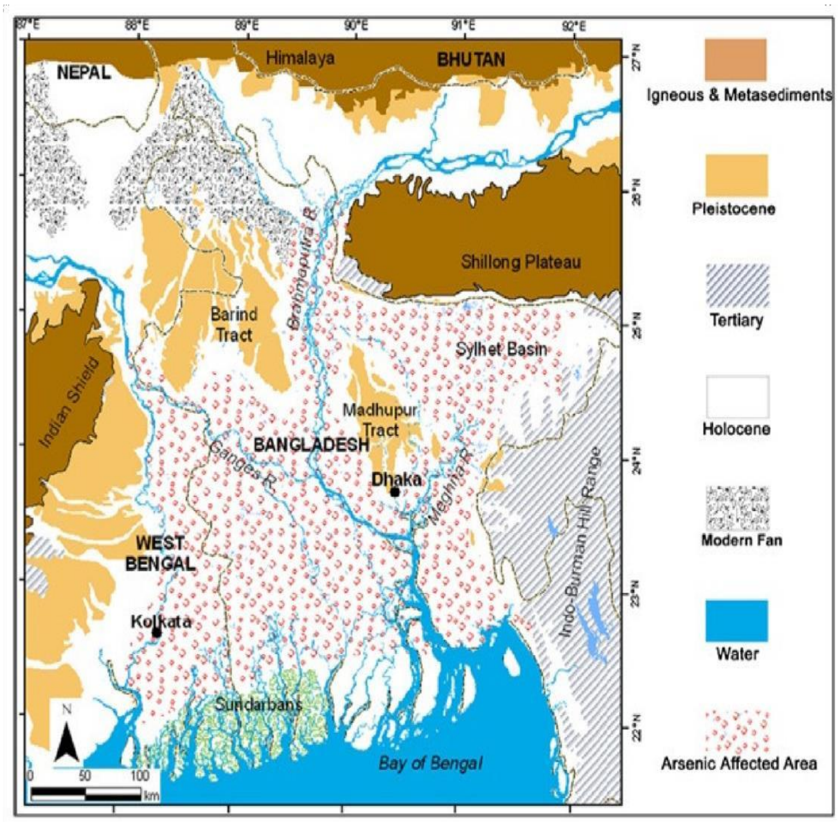


Fig 10: Spatial distribution of arsenic contamination in Bengal Basin (Source: Haque et al., 2011)

The Bengal Basin is composed of West Bengal (WB) in India and Bangladesh and includes the delta of the Ganges, Brahmaputra and Meghna Rivers. It is initially recognized with sub-surface arsenic contamination (Acharyya et al., 2000; Adel, 2000a). The extensive alluvial plain of the basin covering 569,749km2 areas (Chakraborti et al., 2004) and About 75 million people are now live with the risk of arsenic poisoning (Adel, 2005). The areal extension of arsenic contamination in Bengal Basin is depicted in below Fig. 10.

Arsenic problem in groundwater in West Bengal was first reported in the year 1978 (ACIC, 2000). The first arsenicosis patients had been identified from a village of South 24-Parganas district in 1983 and 16 were found with arsenical skin manifestations (Garai et al., 1984). During 1988, groundwater in 22 villages from five districts of West Bengal was reported as arsenic contaminated above 0.05mg/liter (Chakraborti et al., 2009); gradually its severity and health effects are reasonably well documented in recent publications. (WHO 1993; Acharyya et al., 1993; Chowdhury et al., 2000; Smith et al., 2000; Manahan 2001; Bhattacharya et al., 2002 Chakraborti et al., 2002, 2009).

The scenario of west Bengal is no longer far behind from Bangladesh.14 districts have been reported for amenable arsenic exposure in their drinking water (chakraborti et al.,2009). Accroding to the reports of school of environmental studies, Jadavpur university, india, tubewells with arsenic concentrations ≥ 50 µg/L in more than 3000 villages has been identified. West Bengal has been classified into three zones based on the arsenic concentrations:

1.Highly affected were the districts of south 24 parganas,north 24 parganas malda ,murshidabad nadia, , bardhaman, Howrah, Hooghly and Kolkata (mainly the eastern side of Bhagirathi river), where the average arsenic concentrations greater than 50 µg/L (up to 300 µg/L).

2.Moderately affected were the 5 districts in the northern parts of the state namely jalpaiguri,darjiling,Koch bihar,south and north Dinajpur where average arsenic concentrations are below 50 µg/L (a few above 50µg/L but all below 100 50µg/).

3.Arsenic safe 5 districts are purulia,bankura,birbhum,medinipur east and medinipur west (mostly below 10µg/L) in the western part.

From recent research it is apparent that ingestion of drinking water is not the only source of arsenic diet in the Bengal Basin, Staple crops grown and irrigated with arsenic contaminated water, also supplying arsenic to the inhabitants (Roychowdhury, 2010). Arsenic affected areas in West Bengal is shown in the below Figure.

Fig 11: Arsenic affected districts of West Bengal in India (Chakraborti et al., 2015)

2.11 Removal technologies of arsenic

There are a few treatment technologies for removal of arsenic from contaminated groundwater and they are mainly-

1. Coagulation by filtration
2. Ion – exchange
3. Membrane based separation process
4. Adsorption technologies
5. Microbial or enzymatic degradation

One of the most frequently used technology is coagulation followed by filtration. Even it requires a huge handling of generated sludge which is again challenging for us.

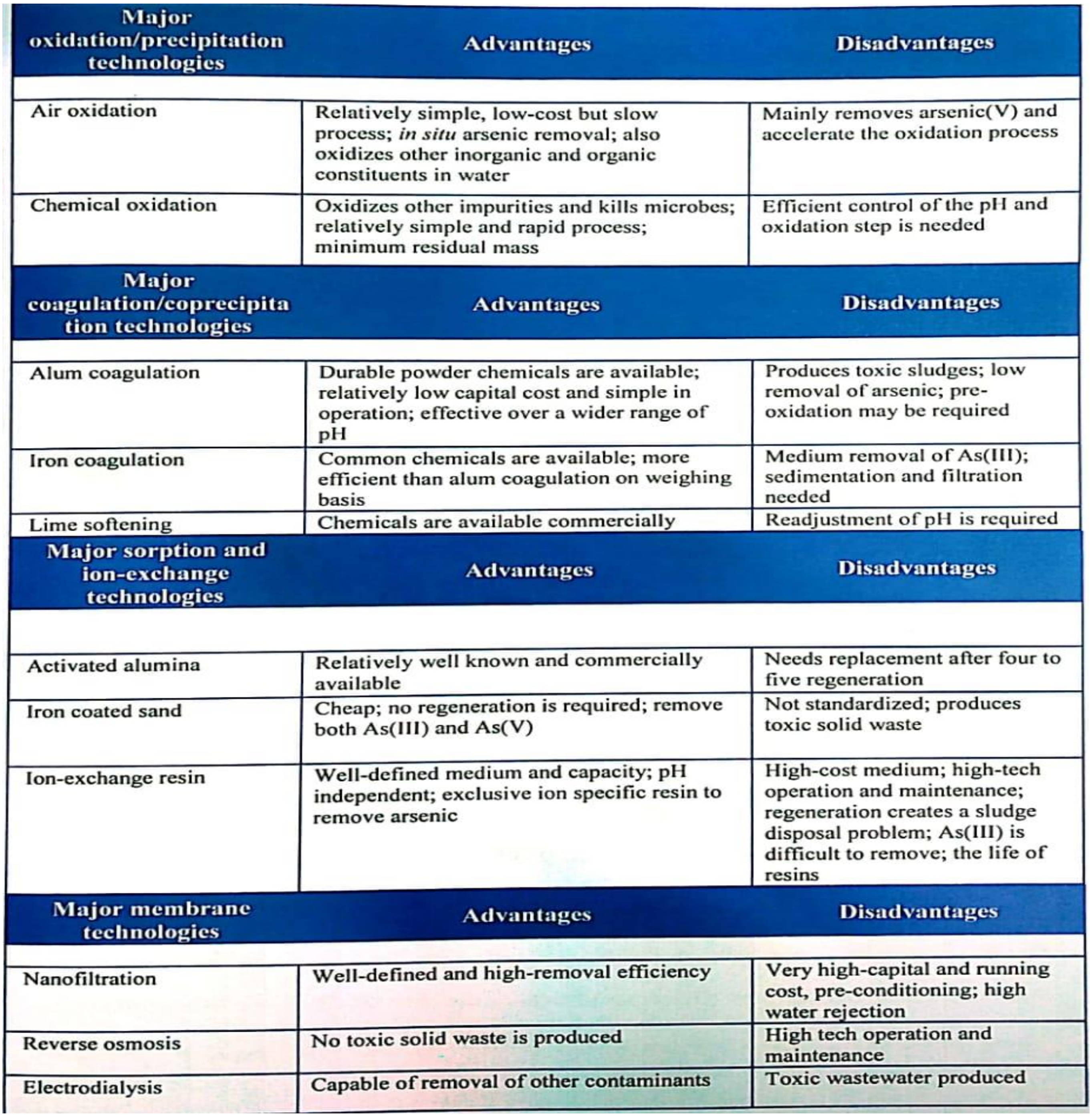
Again removal of arsenic with the help of Ion exchange resins has been effective, but groundwater usually contains arsenite or As (III) (Korte and fernanado, 1991).

There are also very expensive methods as compared to the others that use membranes in arsenic removal (Johnston et al., 2003).

There has been the effective removal of arsenic aided by adsorption on granular ferric hydroxide (GFH) (Thirunavukkarasu et al., 2003), manganese greensand (Viraraghavan et al.,1999) and activated alumina (Lin and Wu,1991) are found effective.But some of these technologies must requires careful pretreatment of the support media and skilled manpower.

Whereas arsenic removal at lower levels was achieved by slight modification in the sand filters with immobilized iron or manganese oxidizing bacteria depending upon the presence of iron, manganese and arsenic concentration. It was studied that iron based biological treatment was efficient enough on removing As(III) without a peroxidation step (Katsoyiannis and Zouboulis, 2006 a,b).

Table 3: Comparison of arsenic Removal methods (Source: Mohan Pittman, 2007)



Major oxidation/precipitation technologies	Advantages	Disadvantages
Air oxidation	Relatively simple, low-cost but slow process; *in situ* arsenic removal; also oxidizes other inorganic and organic constituents in water	Mainly removes arsenic(V) and accelerate the oxidation process
Chemical oxidation	Oxidizes other impurities and kills microbes; relatively simple and rapid process; minimum residual mass	Efficient control of the pH and oxidation step is needed
Major coagulation/coprecipitation technologies	**Advantages**	**Disadvantages**
Alum coagulation	Durable powder chemicals are available; relatively low capital cost and simple in operation; effective over a wider range of pH	Produces toxic sludges; low removal of arsenic; pre-oxidation may be required
Iron coagulation	Common chemicals are available; more efficient than alum coagulation on weighing basis	Medium removal of As(III); sedimentation and filtration needed
Lime softening	Chemicals are available commercially	Readjustment of pH is required
Major sorption and ion-exchange technologies	**Advantages**	**Disadvantages**
Activated alumina	Relatively well known and commercially available	Needs replacement after four to five regeneration
Iron coated sand	Cheap; no regeneration is required; remove both As(III) and As(V)	Not standardized; produces toxic solid waste
Ion-exchange resin	Well-defined medium and capacity; pH independent; exclusive ion specific resin to remove arsenic	High-cost medium; high-tech operation and maintenance; regeneration creates a sludge disposal problem; As(III) is difficult to remove; the life of resins
Major membrane technologies	**Advantages**	**Disadvantages**
Nanofiltration	Well-defined and high-removal efficiency	Very high-capital and running cost, pre-conditioning; high water rejection
Reverse osmosis	No toxic solid waste is produced	High tech operation and maintenance
Electrodialysis	Capable of removal of other contaminants	Toxic wastewater produced

CHAPTER - 3

FLUORIDE: A DOUBLE EDGED SWORD

Fluoride is a natural mineral that is found mainly in soil, foods and in water. It is an inorganic compound and chemical formula of F^- (i.e. ionic form of fluorine). It plays a vital role in dental health by strengthening the tooth enamel and making more resistant for tooth decay. Over the research of 60 years, the addition of fluoride to water (i.e. water fluoridation) has proven to reduce decay by 40 to 60 percent. Besides high exposure of fluoride causes various fatal disease like dental fluorosis, skeleton fluorosis. This dual character of fluoride makes its double edged sword.

3.1 SOURCES OF FLUORIDE

There are mainly two sources of fluoride in the environment i.e. natural and manmade sources.

- ### Natural Sources

Occurrence of fluoride in groundwater is a natural phenomenon which is mainly influenced by local and regional hydro-geological geologic conditions of the region. Fluoride occurs abundantly in the earth's crust as a component of rocks and minerals. Natural constituent of rocks like fluorite, fluorspar or calcium fluoride ($CaF2$), Apatite or Rock Phosphate [$Ca3F(PO4)3$], Cryolite ($Na3AlF6$), Magnesium Fluoride ($MgF2$), mica and many other minerals is the main natural sources of fluoride (Das et al., 1998) (Das et al.,1999). Groundwater is mainly contaminated with fluoride maily by the slow dissolution and leaching of such rocks and mineral (Goswami et al., 2011).

Fig. 12: Fluorospar

Fig. 13: Cryolite

Thus it is released into the groundwater by slow dissolution of such rocks and minerals (Biswas et al., 2009) (Goswami et al., 2011). Chemically, fluoride and OH ions are negatively charged and also have almost similar ionic sizes. Hence, during the chemical reaction, fluoride ion can easily replace OH ions present in rocks and enriched its concentration in rocks and minerals. Whenever carbonate and bicarbonate rich water passed through such type of rocks, fluoride ion is released due to some chemical reactions (Reaction 1.1 and 1.2) and percolates to the ground water and increases its concentration (Saxena et al., 2001)

$CaF_2 + Na_2 CO_3 \rightarrow CaCO_3 + 2F^- + 2Na^+$……………………………….(1)

$CaF_2 + 2NaHCO_3 \rightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2$ ………………..(2)

The dissolution of fluoride from geologic formations occurs through the rain water and repeated irrigation of agricultural lands. As rain water percolates through the soil, it comes in contact with the rocks and minerals in the aquifer materials. Due to the acid in the soil, dissolution of fluoride from the country rocks occurs. Dissolution of fluoride in groundwater itself may also contribute to the fluoride contamination phenomenon. The fluoride content in groundwater becomes higher in summer season due to a drop in the water level. The higher concentration of fluoride in the summer may be further attributed to the higher dissolution of fluoride, which may be due to the presence of air in the minerals/rocks cavities, which indicates that oxygen in the cavities of the geologic formation catalyses the fluoride dissolution process. The evidence suggests that, as the groundwater level gradually drops below the earth's crust, a greater concentration of fluoride is found in the water because of greater dissolution of fluoride from rocks and soil.

- **Manmade Sources**

Groundwater is contaminated with fluoride widely by the various anthropogenic activities. The effluents or by-products of industries like, ceramic, cement, gasoline production and manufactures of coke, surface heating operations, metal etching, enamel, fiber glass, electronics, pesticides and fertilizers. wood preservatives (Chand D, 1999) often release large quantities of fluoride in process waste streams including fluorosilicate acid and hydrofluoric acid or in the form of silicon tetra fluoride causes fluoride contamination. Power plant boiler, steel making industry, aluminum processing industry (Das et al., 1998; Sun et al., 1998)., glass manufacturing process, by-products of brick kilns (Malhotra et al., 1998) are also responsible for fluoride contamination.

Again nonpoint sources of groundwater contamination like modern agricultural practices which involves the large application of fertilizers and pesticides plays a vital role (about 1–3% fluoride) (Suresh T., 1996). Thus agricultural crops are getting also contaminated with fluoride. Extensive use of medicines, drugs, toothpaste are also responsible for this.

3.2 FLUORIDE IN GROUNDWATER

High fluoride bearing groundwater is from an active geothermal system which can have dissolved fluoride concentrations exceeding 1000mg/l (Ozsvath, 2009, Edmunds and Smedley, 2005). However, the most common type that Edmunds and Smedley (2005) report, is the high fluoride bearing groundwater that occurs in areas of active geothermic activity, is alkali-chloride solutions with neutral pHs and fluoride concentrations of between1-10mg/l. The other cause of high fluoride bearing groundwater is the geological system in which it occurs. In this case the concentration of fluoride in groundwater will be limited by the source mineral, the contact time in the system and temperature of the solution (Ozsvath, 2009). Ozsvath (2009) also points out that pH, hardness and ionic strength can also play a part in terms of its influence on a mineral's solubility. Fluorite is one of the most common fluoride bearing minerals, and while usually stable, fluorite's solubility can be affected by the calcium concentrations in the water where the absence of calcium encourages dissolution of fluorite and so allows higher concentrations of fluoride (Edmunds and Smedley, 2005). The solubility of fluorite also increases with an increase in temperature, so in arid areas with low rainfall, high concentrations of fluoride are more likely (Edmunds and Smedley, 2005). Edmunds and Smedley (2005) also report that arid regions decrease the flow rate of groundwater thus allowing more contact time with the rocks and, in turn, allow more chemical transfer to take place.

3.3 CHEMISTRY OF FLUORIDE IN GROUNDWATER

In general, the concentration of fluoride in groundwater depends on the concentration of fluoride bearing minerals in rock types and mainly on their decomposition and dissolution activities through rock-water interactions. An alkaline environment (within a pH range 7.6–8.6) with a high bicarbonate concentration is more conducive for fluoride dissolution in groundwater (Saxena et al., 2001), suggesting that the pH of groundwater is more important in determining the concentration of fluoride. Thus, it is the weathering of primary minerals in rocks and leaching of fluoride-containing minerals that yields fluoride in solution (Saxena et al., 2003). The mineral that predominantly determines the concentration of fluoride in natural water is fluorite. Since solubility product of fluorite is very low (Eq. 9), waters with low content of calcium should have high fluoride concentration (Apambire et al., 1997). Groundwater in the sodium bicarbonate and bicarbonate chloride types always has high fluoride concentrations. The water-soluble fluoride in sodic surface soil treated with gypsum increased with increasing exchangeable sodium percent (Chhabra et al., 1980). These observations together with the exchange mechanism suggested in Eq. 1 are significant in the context of the reported excess fluoride in groundwater due to high sodicity of soil near the major south Indian irrigation schemes inducing fluorosis amongst the nearby populations (Datta & K.K., 2000; Singh & R.B., 2000; Umar et al., 2000). The rain water falling on the land gets enriched in CO2 from soil, air and biochemical reactions of bacteria and organic matter during its downward movement. Secondary salts present in the soil (mixture of varying content of NaHCO3, NaCl and Na2SO4) are also getting leached out. If phosphate fertilizers are applied, soil may contain varying proportions of fluoride-bearing compounds. Simultaneously an ion exchange reaction goes on with exchangeable cations present in the soil clay complex as (Handa & B.K., 1975):

$CaX_2 + 2\,Na^+(aq) \leftrightarrow 2\,NaX + Ca_2+(aq)$ (1) where X is the clay mineral.

The dissolution of CO2 tends to enhance the hydrogen ion concentration in groundwater. The calcareous minerals particularly CaCO3, if present, also getting dissolved as (Saxena et al., 2003; Handa & B.K., 1975; Subba et al., 2003):

$CO_2 + H_2O \rightarrow H_2CO_3$ (2)

$H_2CO_3 \rightarrow H^+ + HCO_3^-$ (3)

$HCO_3^- \rightarrow H^+ + CO_3^{-2}$ (4)

$CaCO_3 + H^+ + 2F^- \rightarrow CaF_2 + HCO_3^-$ (5)

$CaF_2 \rightarrow Ca_2+ + 2F^-$ (6)

The alkaline water can mobilize F− from soils, weathered rocks and CaF_2 precipitating $CaCO_3$ as:

$CaF_2 + 2HCO_3^- \rightarrow CaCO_3 + 2F^- + H_2O + CO_2$ (7)

In presence of excessive sodium bicarbonates in ground water, the dissolution activity of fluoride will be high and this can be expressed as:

$CaF_2 + 2NaHCO3- \rightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2$ (8)

The CaF_2 has a solubility product of $Ksp = [F^-]2[Ca^{+2}] = 4.0 \times 10^{-11}$ (9)

3.4 PERMISSIBLE LIMITS OF FLUORIDE

Since fluoride has dual significance on human health, World Health Organization (WHO) recommends that water containing a minimum of 0.6 mg/L fluoride and a maximum of 1.5 mg/L fluoride is considered safe for drinking purposes (WHO, 2008). This permissible limit varies according to the climatic condition of a place. Hence every country of the world has different permissible limits based on their geography, temperature and humidity. The standard of the United States is between 0.6 and 0.9 mg/L and that of India is 0.6 and 1.2 mg/L in drinking water (ISI, 1983).

Therefore, by considering the climatic and other above said conditions the World Health Organization (WHO) has set a limit range between 0.5 to 1.5 mg/L (WHO, 2008). According to Indian standards the safe limit is 0.6 - 1.2 mg/L and it is the same in China and Bangladesh. According to United States standards it is in between 0.6 and 0.9 mg/L (WHO, 2008).

Table 4: permissible limits of fluoride in drinking water (Source: Roy et al.,2018)

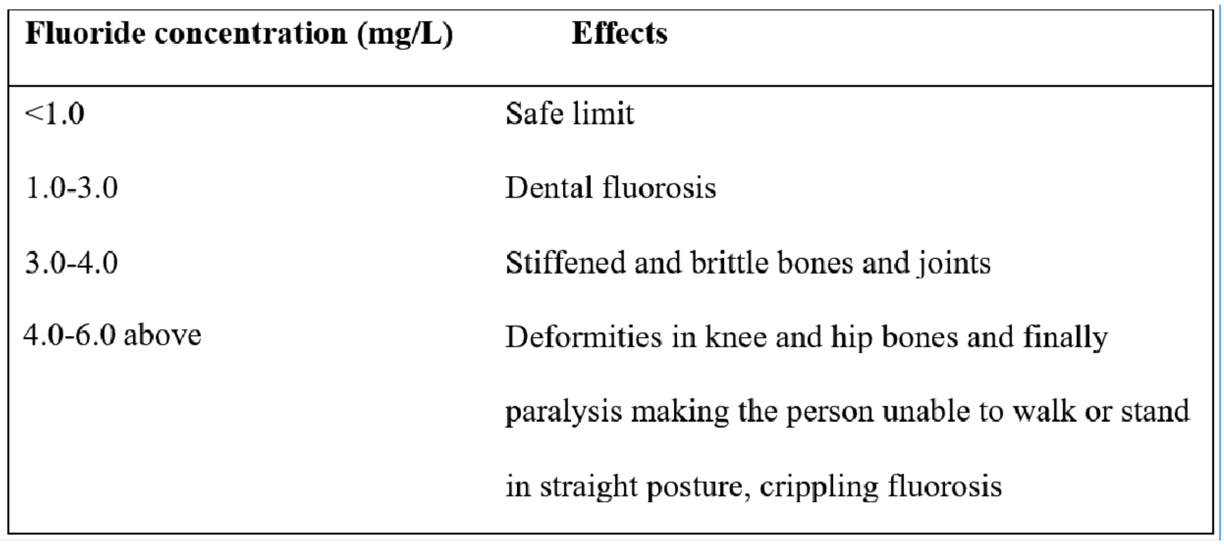
Name of organization	Desirable limit (mg/L)	Sources
Bureau of Indian Standards	0.6–1.2	IS 10500: 2012
Indian Council of Medical Research	1.0	Kumar and Puri (2012)
The Committee on Public Health Engineering Manual and Code of Practice, Government of India	1.0	Bhagan et al. (1996)
World Health Organization (International Standards for Drinking Water)	1.5	Fawell et al. (2006)

3.5 HEALTH IMPACTS OF FLUORIDE

Fluoride in drinking water has appeared as serious problem and around 200 million people, from 25 nations of the world over, are under the dreadful fate of fluorosis (Garg et al., 2008). Fluorosis is an endemic disease due to long term intake of excessive fluoride. So far two main kinds of fluorosis, namely dental fluorosis and skeletal fluorosis have been identified. Fluorosis occurs due to the presence of fluoride in both high (>1.5 mg/L) and low (<0.6 mg/L) concentration in drinking water, with identified health effect and benefits for human beings. Teeth mottling which is characterized initially by opaque white patches on the teeth and in advanced stages leads to dental fluorosis (teeth display brown to black staining) followed by pitting of teeth surfaces (Rwenyonyi et al., 2000; Vieira et al., 2005). High manifestations of dental fluorosis are mostly found in children up to the age of 12 years.

Skeletal fluorosis is a bone disease exclusively caused by consumption of fluoride more than 3 mg/L (Krishnamachari & K.A., 1986). Mild cases of skeletal fluorosis cause slight problems. However, in serious cases, skeletal fluorosis results in unbearable pain as well as severe damage to bones and joints (Teotia, 1988). Crippling skeletal fluorosis can occur when the water supply contains more than 10 mg/L of fluoride. The severity of fluorosis depends on the concentration of fluoride in the drinking water, daily intake, continuity and duration of exposure and climatic conditions.

Table 5: Effects of fluoride in water on human health (Meenakshi et al., 2006)



Fluoride concentration (mg/L)	Effects
<1.0	Safe limit
1.0-3.0	Dental fluorosis
3.0-4.0	Stiffened and brittle bones and joints
4.0-6.0 above	Deformities in knee and hip bones and finally paralysis making the person unable to walk or stand in straight posture, crippling fluorosis

Fig 14: Dental Fluorosis

Fig 15: Crippling Fluorosis

3.6 GLOBAL SCENARIO OF FLUORIDE

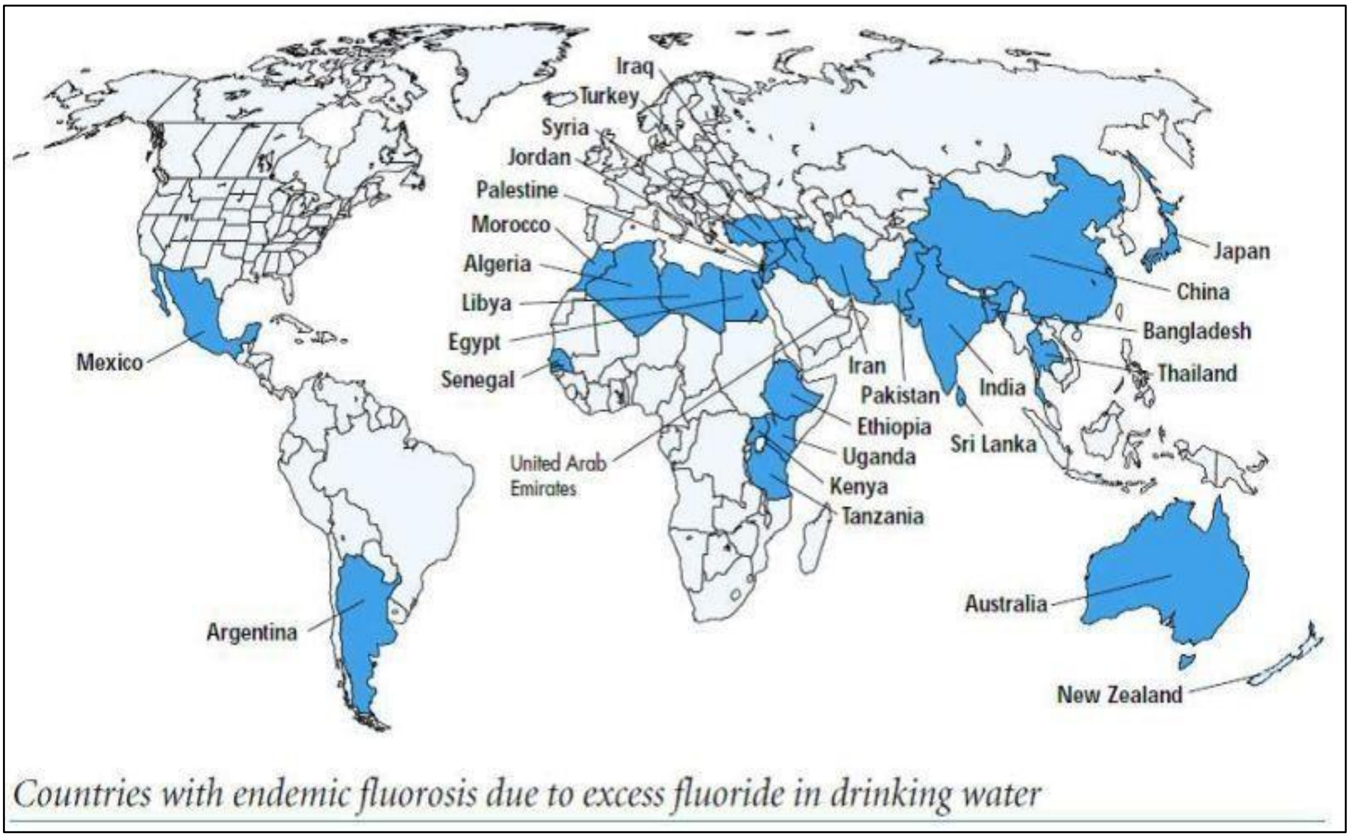


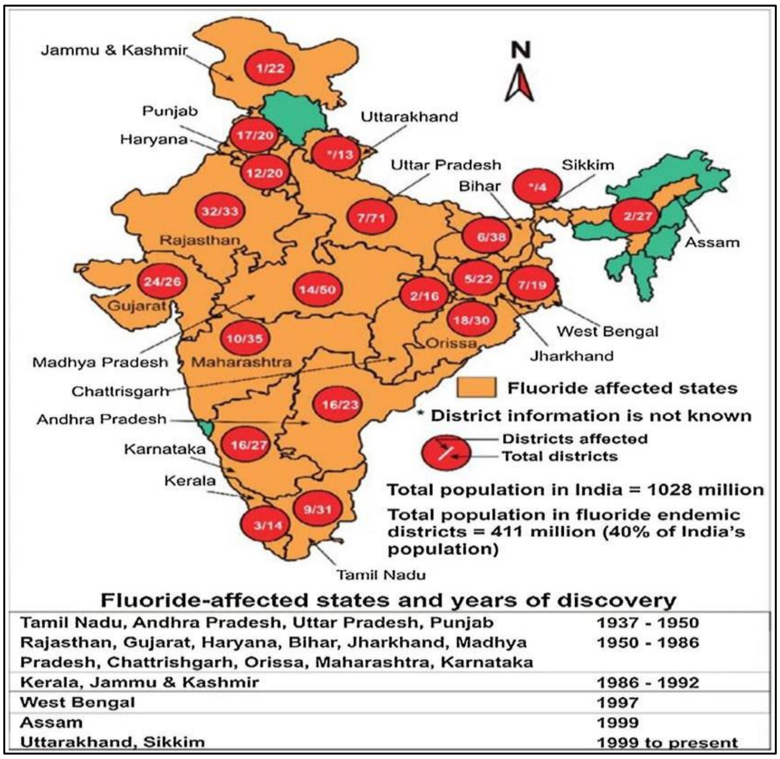
Fig 16: Fluoride Distribution in Groundwater at Global Scenario

(source:https://link.springer.com/chapter/10.1007/978-81-322-2298-9_1)

It is estimated that more than 200 million people worldwide (Kumar et al., 2009) rely on drinking water with fluoride concentrations that exceed the present WHO guideline of 1.5 mg /L (Aiteken et al., 2004). In some areas food stuffs and/or indoor air pollution due to the burning of coal may make significant contributions to the daily intake of fluoride (Pathak et al., 2009; Chen et al., 2009). Excess fluoride intake causes different types of fluorosis, primarily dental and skeletal fluorosis, depending on the level and period of exposure. Fluorosis, associated with elevated fluoride concentrations in drinking water, has been reported in various countries (Subho et al., 2011) around the world such as India, China, Tanzania, Mexico, Argentina, and South Africa, among others.

3.7 SCENARIO OF FLUORIDE IN INDIA

In India, Fluoride was first detected in Nellore district of Andhra Pradesh in 1937. Since then considerable work has been done in different parts of India to explore the fluoride laden water sources and their impacts on human as well on animals. At present, it has been estimated that fluorosis is prevalent in 17 states of India out of 29 States & 7 Union Territories. The fluoridated states include Andhra Pradesh, Assam, Bihar, Delhi, Gujarat, Haryana, Jammu and Kashmir, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh, and West Bengal (Rwenyonyi et al., 2000).



Fluoride-affected states and years of discovery

Tamil Nadu, Andhra Pradesh, Uttar Pradesh, Punjab	1937 - 1950
Rajasthan, Gujarat, Haryana, Bihar, Jharkhand, Madhya Pradesh, Chattrishgarh, Orissa, Maharashtra, Karnataka	1950 - 1986
Kerala, Jammu & Kashmir	1986 - 1992
West Bengal	1997
Assam	1999
Uttarakhand, Sikkim	1999 to present

Fig 17: Fluoride Distribution in Groundwater at Indian Scenario (source: Rwenyonyi et al., 2000)

3.8 SCENARIO OF FLUORIDE IN WEST BENGAL

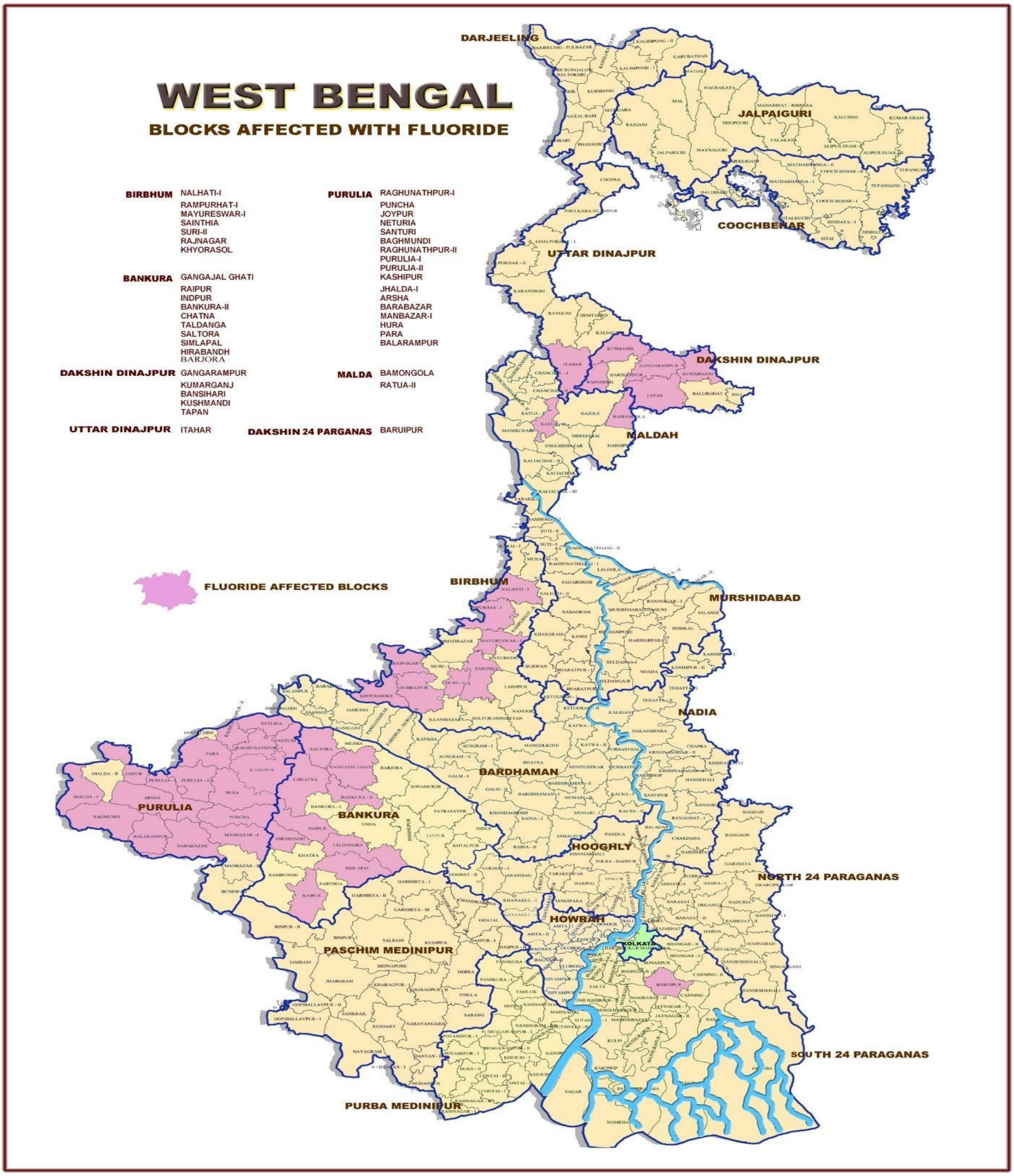


Fig 18: Fluoride Distribution in Groundwater at West Bengal Scenario (source: WBPHED)

3.9 Removal Technologies of fluoride

To maintain the WHO permissible limit, various defluoridation techniques are used to treat fluoride contaminated water. All the defluoridation techniques are mainly divided in two categories; physical process and chemical process. Physical process includes adsorption, ion exchange and membrane separation techniques. Chemical process includes chemical coagulation- precipitation and electro-coagulation techniques. A small overview of each process is discussed in the proceeding section.

Chemical Process

Chemical process includes chemical coagulation precipitation process which is also called Nalgonda technique and electro coagulation process.

Chemical Coagulation – Precipitation Method

Chemical precipitation method is the most common method of fluoride removal from water. This is a two-step process. In the first step, precipitation occurs by adding lime which is followed by a second step where alum is added to cause coagulation. When alum is added to water, essentially two reactions occur. In the first reaction, alum reacts with some of the alkalinity to produce insoluble aluminum hydroxide [Al(OH)3]. In the second reaction, alum reacts with fluoride ions present in the water. The best fluoride removal is accomplished at pH range of 5.5–7.5 (Potgeiter, 1990). The process undergoes the following reactions:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^{-} \quad (1)$$

$$Ca^{2+} + 2F^{-} \rightarrow \downarrow CaF_2 \quad (2)$$

Electro – Coagulation Method

In electrocoagulation process, an applied potential generates the coagulant species in situ as the sacrificial metal anode (aluminum or iron) dissolves, while hydrogen is simultaneously evolved at the cathode. Coagulant species aggregate the suspended particles or precipitate and adsorb dissolved contaminants. Tiny bubbles of hydrogen and oxygen that are formed during electrolysis of water, collide with air bubbles which compel to float the pollutant particles. Choice of electrode material depends on various_criteria such as low-cost, low-oxidation potential, inertness towards the system under consideration, etc. Different electrodes were reported in the literature like carbon (Gallegos et al., 1999), mild steel (Golder et al., 2005), iron (Yildiz et al., 2007), graphite titanium (Hernandez et al., 2007) and aluminum (Bi et al., 2004; Ghosh et al., 2008). Aluminium was reported to be very effective and successful in fluoride removal at favorable operating conditions (Ghosh et al., 2008).

Physical Process

This category includes adsorption, ion exchange and membrane based technology. The summary of each technique is described below.

Ion – Exchange Method

Ion exchange is a physical process similar to adsorption. In this technique, fluoride can be removed from water supplies with a strongly basic anion-exchange resin containing quaternary ammonium functional groups. The removal takes place according to the following reaction:

$\text{Matrix-NR3+Cl}^- + \text{F}^- \rightarrow \text{Matrix-NR3+F}^- + \text{Cl}^-$

The fluoride ions replace the chloride ions of the resin. This process continues until all the sites on the resin are occupied by fluoride. The resin is then backwashed with water that is supersaturated with dissolved sodium chloride salt. New chloride ions then replace the fluoride ions leading to recharge of the resin and starting the process again. The driving force for the replacement of chloride ions from the resin is the stronger electro negativity of the fluoride ions. Meenakshi and Viswanathan (Meenakshi et al., 2007) studied Indion FR10 and Ceralite IRA 400 resin as defluoridating agent. The same author also studied metal ion incorporation in ion exchange resin (Vishwanathan et al., 2009) used as fluoride removing agent from water.

Adsorption Method

Adsorption is a physical process and it is considered as cheap and easy handling process. The selection of adsorbents should be economic, easily available, easy handling and must have good fluoride adsorption behavior. Lots of adsorbents are reported in the literature such as some biological materials, natural clay materials, agricultural waste materials, metal oxides and hydroxides, calcium and iron based adsorbents. The adsorbents like plaster of paris (Gopal et al., 2007), granular red mud (Tor et al., 2009), pyrophyllite, PCB (Viswanathan et al., 2009), γ – alumina (Lee et al., 2010), acidic alumina (Goswami et al., 2012), calcium aluminate (Sakhare et al., 2012), protonated cross-linked chitosan particles (Huang et al., 2012), hydroxyapatite (Nie et al., 2012), granular ceramic (Chen et al., 2010) and many other adsorbents are employed for fluoride removal. Apart from these adsorbents, nano sized adsorbents such as nano alumina (Kumar et al., 2011), Fe–Al–Ce nano-adsorbent (Chen et al., 2011) and others are some of the nano adsorbents which are used in defluoridation of water. Although lot of adsorbents were reported in the literature, researchers are still finding for a better, efficient and cost effective adsorbent which will helpful in treating fluoride contaminated water. Hence, in this study, we concentrate mainly on the adsorption process of defluoridation

Membrane Based Technologies

Membrane based techniques mainly comprise of reverse osmosis (RO), nanofiltration (NF), dialysis and electro-dialysis which are getting attractive in separation and purification technology. In the recent years, RO membrane process has emerged as a preferred alternative to provide safe drinking water without posing the problems associated with other conventional methods. RO is a physical process in which the contaminants are removed by applying pressure on the feed water to direct it through a semipermeable membrane. The process is the reverse of natural osmosis as a result of the applied pressure to the concentrated side of the membrane, which overcomes the natural osmotic pressure. RO membrane rejects ions based on size and electrical charge. RO produces water of extremely high purity. Some applications of reverse osmosis to purification of water are discussed by Schneiter and Middlebrooks (Schnieter et al., 1983), Fu et al. (Fu et al., 1995) and Arora et al. (Arora et al., 2004). Ndiaye et al.(Ndiaye et al., 2005) studied fluoride removal from effluents using RO technique. It was observed that the rejection of fluoride ion was typically higher than 98%, considering that the RO membrane was fully regenerated after each set of experiments. The factors influencing the membrane selection are cost, recovery, rejection, raw water characteristics and pretreatment. Efficiency of the process is governed by different factors such as raw water characteristics, pressure, temperature and regular monitoring and maintenance

Table 6: Advantages and disadvantages of different fluoride removal techniques

	Adsorption	Ion Exchange	Coagulation-Precipitation	Membrane Process
Technique	**Adsorbents:** Activated alumina, Activated carbon, calcite, Activated saw dust, Activated coconut shell carbon and Activated fly ash, groundnut shell, coffee husk, rice husk, bone charcoal, Activated soil sorbent, etc	Strongly basic anion-exchange resin containing quaternary ammonium functional groups is used.	**Nalgonda technique:** In first step, precipitation occurs by lime dosing which is followed by a second step in which alum is added to cause coagulation.	**NF** (Nano Filtration) and **RO** (Reverse Osmosis) is generally used for fluoride removal
Advantages	The process can remove fluoride up to 90%. Treatment is cost-effective. Easily available	Removes fluoride up to 90–95%. Retains the taste and colour of water intact.	The two-step process has been claimed as the most effective technique by NEERI Under Rajiv Gandhi Drinking Water Mission several fill and draw (F&D) type and hand pump attached (HPA) plant based on Nalgonda technique have come up in rural areas,	The process is highly effective for fluoride removal. Membranes also provide an effective barrier to suspended solids, all inorganic pollutants, Organic micro pollutants, Pesticides. It works under wide pH range.
Disadvantages	The process is highly dependent on pH Presence of sulfate, phosphate or carbonate results in ionic competition.	Efficiency is reduced in presence of other ions. The technique is expensive because of the cost of resin	The process removes only a smaller portion of fluoride (18–33%) in the form of precipitates and converts a greater portion of ionic fluoride (67–82%) into soluble aluminium fluoride complex ion, and therefore this technology is erroneous. Silicates have adverse effect on defluoridation by Nalgonda Technique.	The process is expensive in comparison to other options.

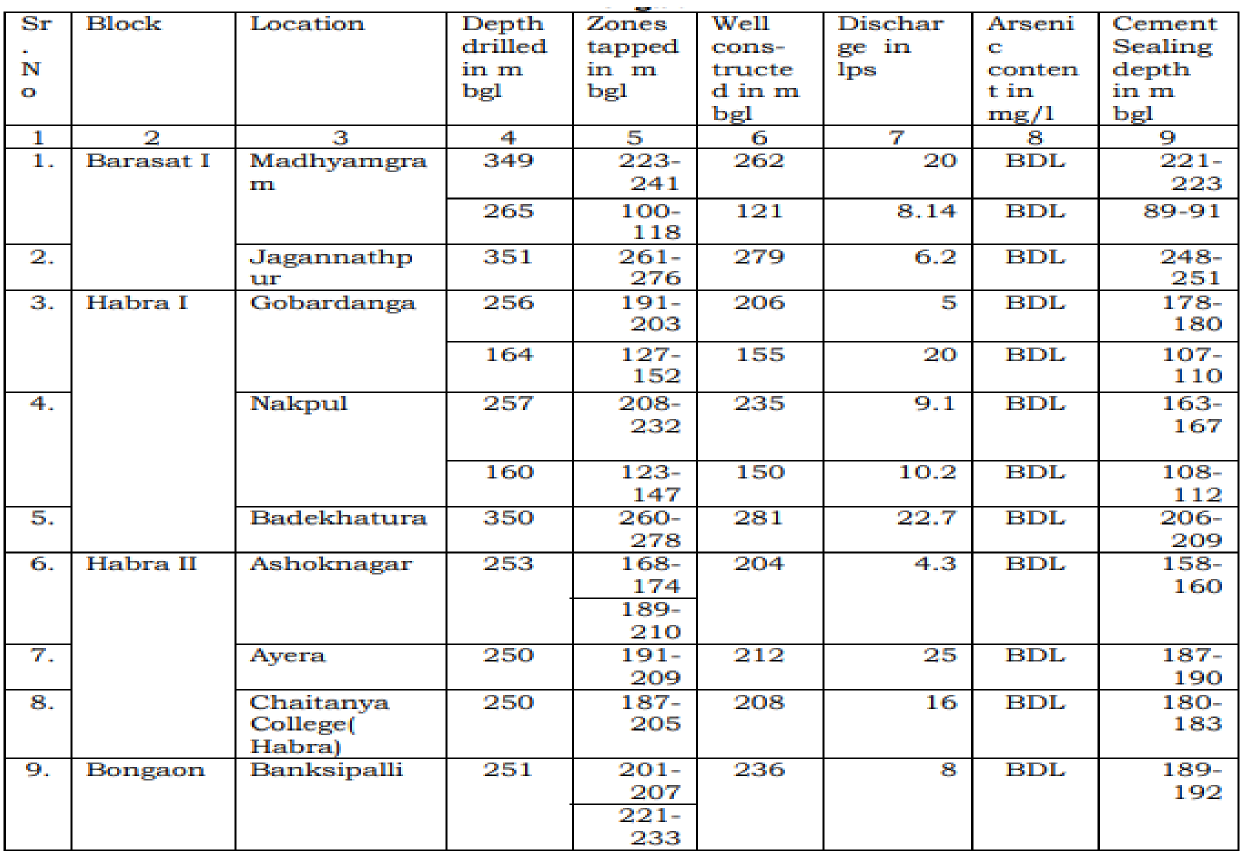
SECTION - 1

DISTRIBUTION OF ARSENIC AND FLUORIDE IN SEVERAL PARTS OF NORTH AND SOUTH 24 PARGANAS DISTRICTS OF WEST BENGAL

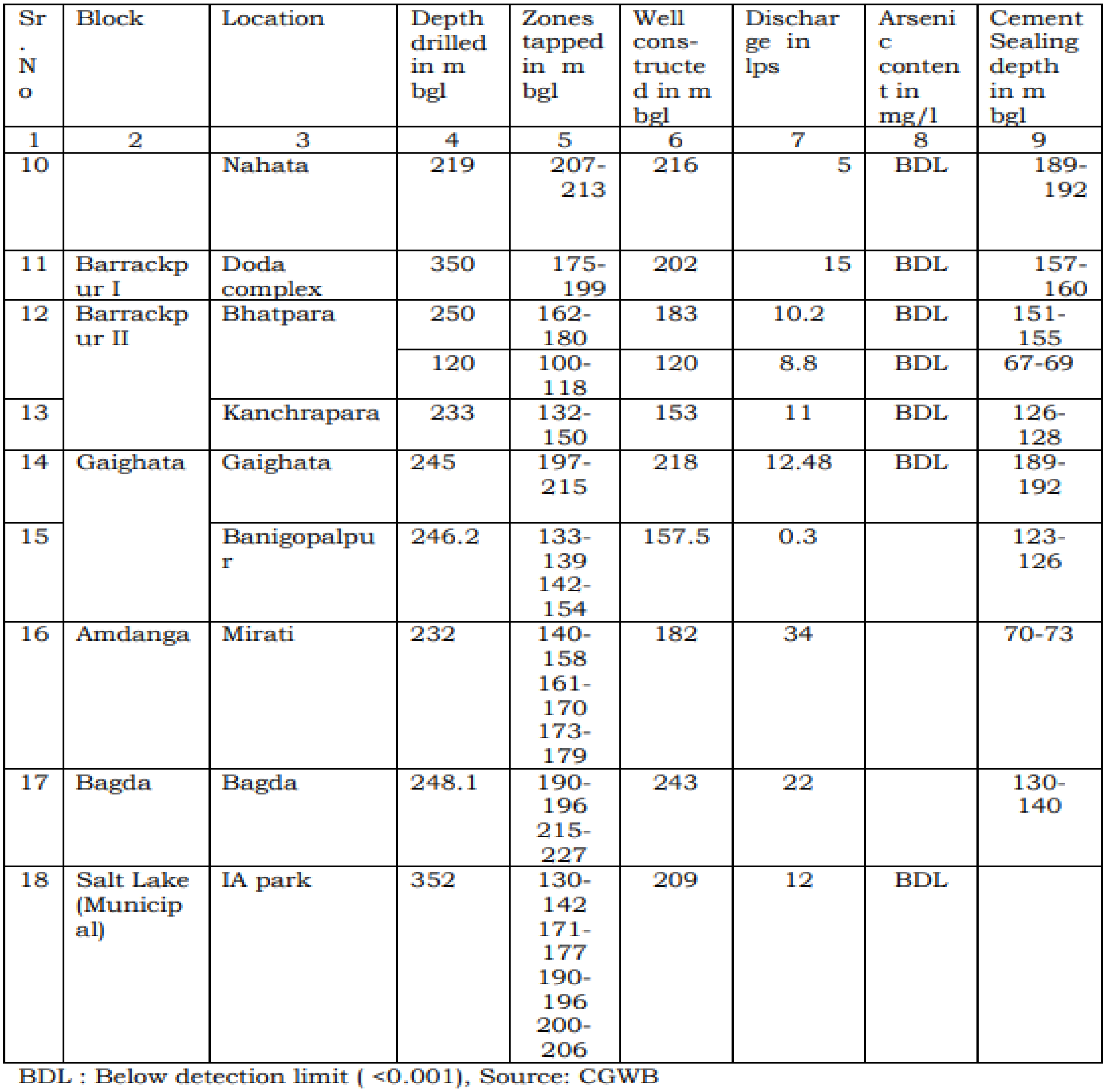
CHAPTER – 4

LITERATURE REVIEW

Since 1988, 150 water samples have been analysed from tube wells in all 19 districts of West Bengal for arsenic; 48.1% had arsenic above 10 μg/L (WHO guideline value), 23.8% above 50 μg/L (Indian Standard) and 3.3% above 300 μg/L (concentration predicting overt arsenical skin lesions). Based on arsenic concentrations, West Bengal has been classified into three zones: highly affected (9 districts mainly in eastern side of Bhagirathi River), mildly affected (5 districts in northern part) and unaffected (5 districts in western part). The estimated number of tube wells in 8 of the highly affected districts is 1.3 million, and estimated population drinking arsenic contaminated water above 10 and 50 μg/L were 9.5 and 4.2 million, respectively. In West Bengal alone, 26 million people are potentially at risk from drinking arsenic-contaminated water (above 10 μg/L). Studying information for water from different depths from 107 253 tube wells, it was noted that arsenic concentration decreased with increasing depth. Measured arsenic concentration in two tube wells in Kolkata for 325 and 51 days during 2002–2005, showed 15% oscillatory movement without any long-term trend (Chakraborti et al., 2009). Groundwater As concentrations in parts of North 24 Parganas, West Bengal is given in the following table (Talukdar et al, 2009).



Sr. No	Block	Location	Depth drilled in m bgl	Zones tapped in m bgl	Well cons-tructed in m bgl	Discharge in lps	Arsenic content in mg/l	Cement Sealing depth in m bgl
1	2	3	4	5	6	7	8	9
1.	Barasat I	Madhyamgram	349	223-241	262	20	BDL	221-223
			265	100-118	121	8.14	BDL	89-91
2.		Jagannathpur	351	261-276	279	6.2	BDL	248-251
3.	Habra I	Gobardanga	256	191-203	206	5	BDL	178-180
			164	127-152	155	20	BDL	107-110
4.		Nakpul	257	208-232	235	9.1	BDL	163-167
			160	123-147	150	10.2	BDL	108-112
5.		Badekhatura	350	260-278	281	22.7	BDL	206-209
6.	Habra II	Ashoknagar	253	168-174 189-210	204	4.3	BDL	158-160
7.		Ayera	250	191-209	212	25	BDL	187-190
8.		Chaitanya College(Habra)	250	187-205	208	16	BDL	180-183
9.	Bongaon	Banksipalli	251	201-207 221-233	236	8	BDL	189-192



Sr. No	Block	Location	Depth drilled in m bgl	Zones tapped in m bgl	Well constructed in m bgl	Discharge in lps	Arsenic content in mg/l	Cement Sealing depth in m bgl
1	2	3	4	5	6	7	8	9
10		Nahata	219	207-213	216	5	BDL	189-192
11	Barrackpur I	Doda complex	350	175-199	202	15	BDL	157-160
12	Barrackpur II	Bhatpara	250	162-180	183	10.2	BDL	151-155
			120	100-118	120	8.8	BDL	67-69
13		Kanchrapara	233	132-150	153	11	BDL	126-128
14	Gaighata	Gaighata	245	197-215	218	12.48	BDL	189-192
15		Banigopalpur	246.2	133-139 142-154	157.5	0.3		123-126
16	Amdanga	Mirati	232	140-158 161-170 173-179	182	34		70-73
17	Bagda	Bagda	248.1	190-196 215-227	243	22		130-140
18	Salt Lake (Municipal)	IA park	352	130-142 171-177 190-196 200-206	209	12	BDL	

BDL : Below detection limit (<0.001), Source: CGWB

A study was conducted to understand the hydrogeological processes dominating in the North 24 Parganas and South 24 Parganas based on representative 39 groundwater samples collected from selected area. The abundance of major ions was in the order of $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+} > Fe^{2+}$ for cations and $HCO_3^{-} > PO_4^{3-} > Cl^{-} > SO_4^{2-} > NO_3^{-}$ for anions. Piper trilinear diagram was plotted to understand the hydrochemical facies. Most of the samples are of Ca-HCO_3 type. Based on conventional graphical plots for (Ca + Mg) vs. (SO_4 + HCO_3) and (Na + K) vs. Cl, it is interpreted that silicate weathering and ion exchange are the dominant processes within the study area. Previous studies have reported quartz, feldspar, illite, and chlorite clay minerals as the major mineral components obtained by the XRD analysis of sediments. Mineralogical investigations by SEM and EDX of aquifer materials have shown the occurrence of arsenic as coating on mineral grains in the silty clay as well as in the sandy layers. Excessive withdrawal of groundwater for irrigation and drinking purposes is responsible for fluctuation of the water table in the West Bengal. Aeration beneath the ground surface caused by fluctuation of the water table may lead to the formation of carbonic acid. Carbonic acid is responsible for the weathering of silicate minerals, and due to the formation of clay as a product of weathering, ion exchange also dominates in the area. These hydrogeological processes may be responsible for the release of arsenic into the groundwater of the study area, which is a part of North 24 Parganas and South 24 Parganas (Singh et al, 2014). In India, several states are endemic for hydrofluorosis due to the high F content in drinking water. It is well known that F contamination is present in the ground water in the western part of West Bengal (Birbhum, particularly Nalhati, Bankura, Purulia, parts of Midnapore, and Bardhaman districts). Recently, an escalation of the groundwater F in the Ganga alluvial plain of India has also been reported. Thus, a study was made of the F concentrations in different parts of West Bengal to give a preliminary assessment of the extent of F contamination (Datta et al, 2014).

CHAPTER - 5

AIMS AND OBJECTIVE

We have already discussed about the serious public health concern in recent years worldwide for the arsenic and fluoride contamination in groundwater due to its toxic and carcinogenic health effects. We have initially started the research work with the field work by selecting some areas and their present groundwater status by finding the tubewells (or sometimes the pump) which are the source of drinking water for people. The main objectives are as follows:

- To identify or characterize the fluoride and arsenic contaminated tubewells.

- Quantify the other physico-chemical water quality parameters and their correlation.

- Identification of source of fluoride and arsenic contamination in groundwater.

- Mobility and mechanism of fluoride and arsenic leachability into the aquifer and investigation of co-existence of fluoride and arsenic in groundwater, if any and mechanism of release from source to aquifer.

CHAPTER - 6

METHODOLOGY

For the fulfillment of the mentioned objectives in Chapter – IV, my present work pursues five stage process to achieve the goal. A brief scheme have been illustrated in **Chart 5.1.**

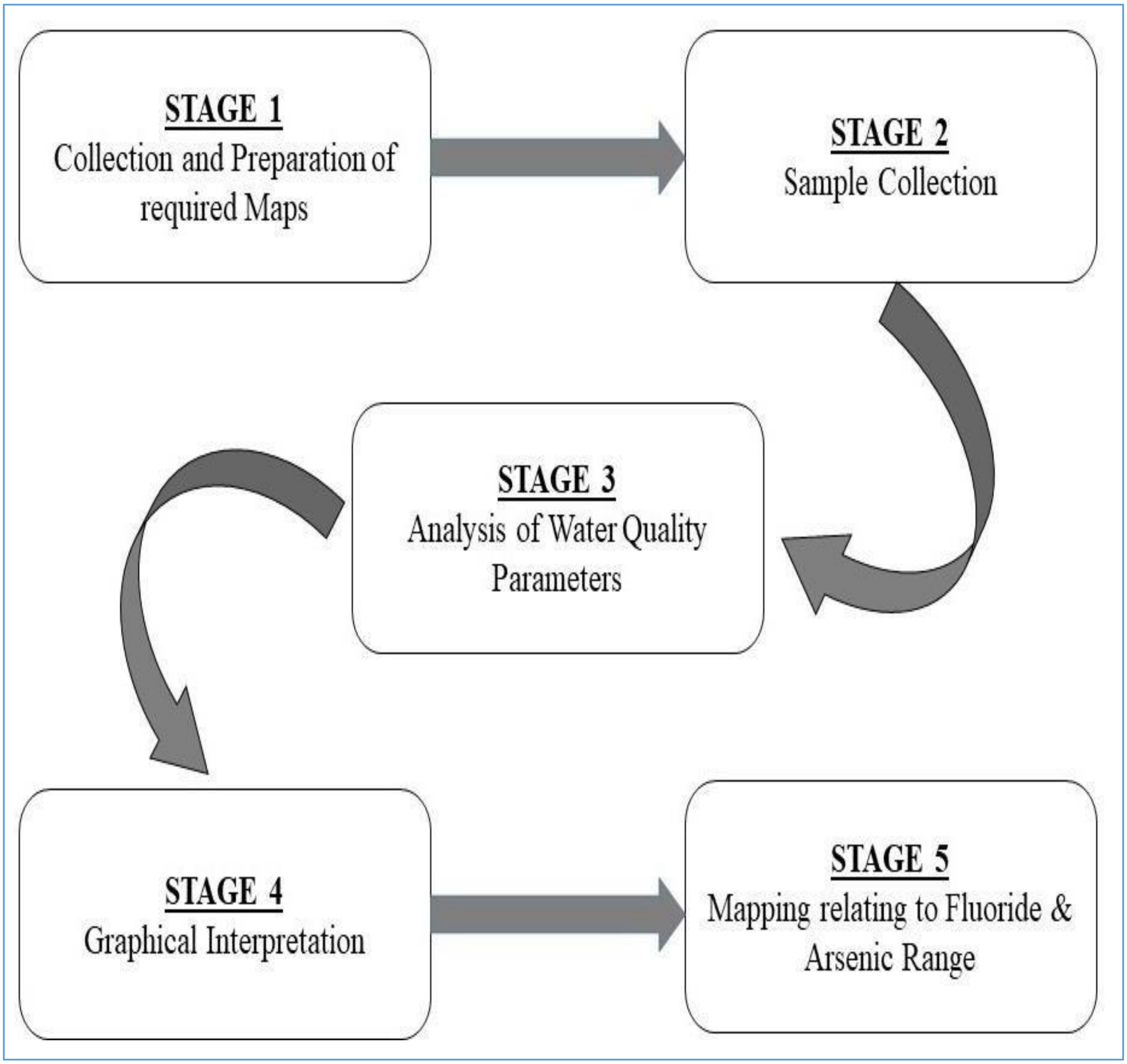


Fig 18: Methodology Scheme

CHAPTER - 7

MATERIAL AND METHODS

7.1 COLLECTION AND PREPARATION OF SAMPLE

Water samples was collected from domestic tube well, pump, deep tube well and pipeline supplied.GPS Coordinates was noted down using GARMIN GPSMAP 64S.

Each and every water sample has been collected in two containers (given by the water test laboratory, Jadavpur university).one container is acidified and other one in non-acidified. Diluted (nearly 1:10) commercially available nitric acid (69%) has been used here. Water sample has been collected carefully so that it cannot contaminated to each other. Mainly arsenic and iron has been analyzed through Acidified water sample. other parameters can be done through non-acidified water samples. Acid has been used so that iron and arsenic in that sample cannot co-precipitate.

Fig 19: Collected samples from field

Fig 20: GARMIN GPSMAP 64S

The material and method of every water quality parameter (i.e. how we measured the parameters in our laboratory) has been discussed as follows.

7.2 Fluoride Estimation

- **Chemicals Used:** Fluoride Standard 100 ppm [or mg/L] (Thermo Scientific)
- TISAB III [Total Ionic Strength Adjustment Buffer] (Thermo Scientific)
- **Reagents:** 10 and 1 mg/L of standard fluoride solution was prepared from the 100 mg/L Fluoride Standard solution
- **Instruments Used:** Orion Star A214 pH / ISE Meter
- **Calibration:** Calibration curve was prepared using 1, 10 & 100 mg/L F- Soln.
- **Preparation of Samples:** To every water sample TISAB III was added at 1 : 10 ratio

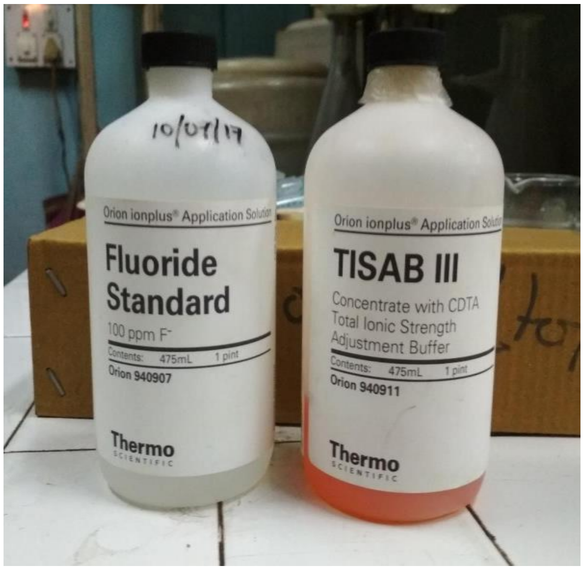


Fig 21: Chemicals Used for Fluoride Estimation

Fig 22: Orion Star A214 pH / ISE Meter

7.3 Arsenic Estimation

- **Chemicals Used:** Sodium Borohydride [$NaBH_4$] (Merck Life Science Pvt. Ltd.), Potassium Iodide [KI] (Merck Life Science Pvt. Ltd.), Hydrochloric Acid [HCl] about 35% (Merck Life Science Pvt. Ltd.) and Sodium Hydroxide Pellets [NaOH] (Merck Life Science Pvt. Ltd.).
- **Reagents:** For 500 ml of Reductant Solution – 3 gm of NaBH4 + 2.5 gm NaOH for 500 ml of Acid

Solution – 200 ml conc. HCl + 300 ml dd H2O for 100 ml of 10 % KI – 10 gm KI + 90 ml dd H_2O.

- **Instruments Used:** AA140 FI – HG – AAS (Flow Injection Hydraulic Generation Atomic Absorption Spectrophotometer).
- **Calibration:** Calibration curve was prepared using Blank, 10, 20, 30, 40 and 50 µg/L Arsenic Solution.
- **Preparation of Samples:** To every 5 ml of water sample add 0.6 ml 10% KI and 0.4 ml HCl.

Fig 23: Chemicals Used for Arsenic Estimation

Fig 24: AA140 FI – HG-AAS

7.4 Iron Estimation

- **Chemicals Used:** Iron Standard Soln 1000 ppm [or mg/L] (Merck Life Science Pvt. Ltd.), Acetic Acid Glacial 100% [CH3COOH] (Merck Life Science Pvt. Ltd.), Sodium Acetate Anhydrous extra pure AR [C2H3NaO2] (Sisco Research Laboratories Pvt. Ltd.), Hydroxyl Ammonium Chloride [(NH2OH).HCL] (Merck Life Science Pvt. Ltd.) & 1,10 – Phenanthroline monohydrate [C12H8N2.H2O] (Merck Life Science Pvt. Ltd.).
- **Reagents:** From the Iron Standard Stock solution 10 mg/L was prepared, from that 0.25, 0.50 and 1.0 mg/L was prepared. Iron Buffer per 1000 ml – 3.8 gm Sodium Acetate + 48 ml Acetic Acid then volume was made up to the mark with dd H2O. Hydroxyl Ammonium Hydrochloride – 10% of total volume Ortho-phenanthroline – 0.25% of total volume.
- **Calibration:** Calibration curve was prepared using Blank, 0.25, 0.50 & 1.0 mg/L Iron standard solution.
- **Preparation of Samples:** In a 25 ml volumetric flask for every 5 ml of water sample add 10 ml of Iron Buffer, 2.5 ml of Hydroxyl Ammonium Hydrochloride and 2 ml of Ortho- phenanthroline then the volume was made upto the mark with dd H2O.

- **Instruments Used:** Orion Aquamate 8000 UV – VIS Spectrophotometer at 510 nm Wavelength.

Fig 25: Orion Aquamate 8000 UV – VIS Spectrophotometer

Fig 26: Chemicals Used in Iron estimation

7.5 Total Calcium Estimation

- Chemicals Used: Calcium Carbonate Precipitated [$CaCO_3$] (Merck Life Science Pvt. Ltd.), and Hydrochloric Acid about 35% (Merck Life Science Pvt. Ltd.).
- Reagents: For preparation of 250 ml 1000 ppm [or mg/L] Calcium Standard Solution – 0.624 gm $CaCO_3$ + 1:1 HCl (dropwise), then volume made up to the mark by dd H_2O.
- From 1000 mg/L Standard soln. 10, 20, 30, 40 & 50 mg/L was prepared.
- Instruments Used: HPG Systems Microcontroller Flame Photometer G-301
- Calibration: Calibration Curve was prepared using Blank, 10, 20, 30, 40 & 50 mg/L Calcium Standard Solution.
- Preparation of Samples: Filter the sample water using a filter paper before measuring

Fig 27: HPG Systems Microcontroller Flame Photometer G-301

CHAPTER - 8

STUDY AREA

• KALUPUR GP, BONGAON

Bangaon is a city,block and a municipality in North 24 Parganas district in the state of West Bengal, Bangaon is located at 23.07°N 88.82°E. It has an average elevation of 7 metres (22 feet). Arsenic contamination is a major concern in this area. Bongaon block have mainly 15 gram panchayats (GP) ,out of them kalupur is the largest gram panchayats. A map of that area and a list of tube wells has been collected from Kalupur Gram Panchayat Karjalaya.

Fig 28: Location of bongaon in West Bengal (source: wikpedia)

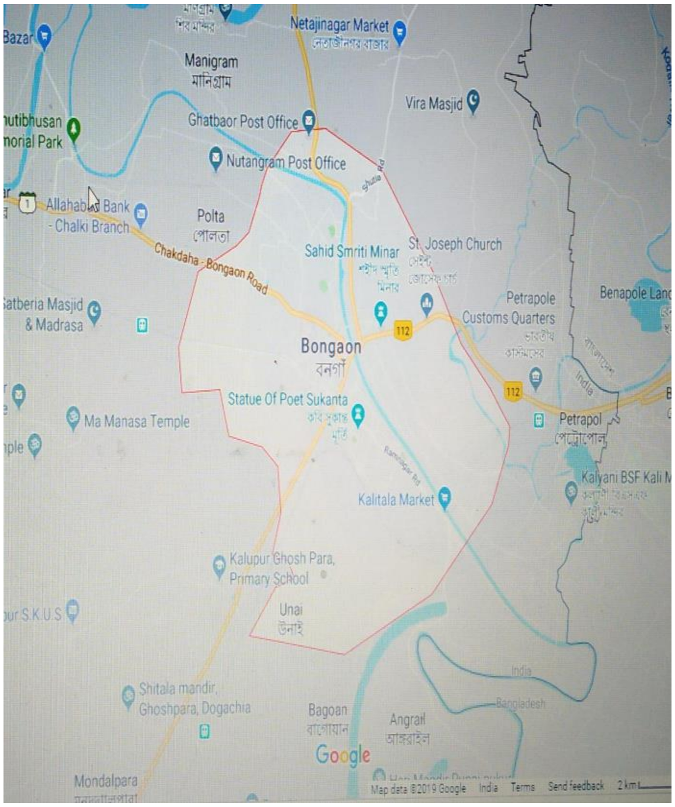
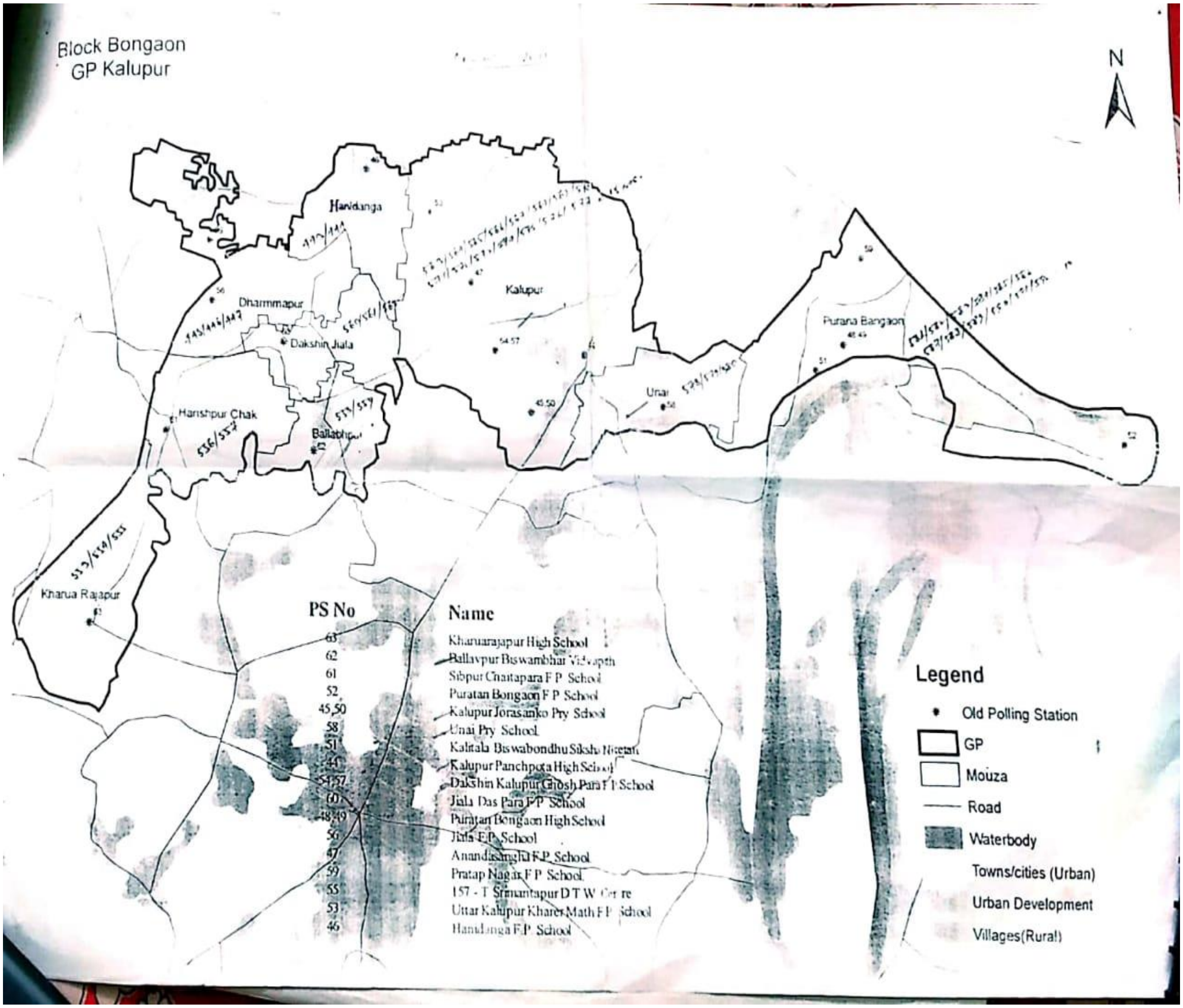


Fig 29: Bongaon block (source: google map)



PS No	Name
63	Kharuarajapur High School
62	Ballavpur Biswambhar Vidyapith
61	Sibpur Chaitapara F P School
52	Puratan Bongaon F P School
45,50	Kalupur Jorasanko Pry School
58	Unai Pry School
51	Kalitala Biswabondhu Siksha Niketan
44	Kalupur Panchpota High School
54,57	Dakshin Kalupur Ghosh Para F P School
60	Jiala Das Para F P School
48,49	Puratan Bongaon High School
56	Jiala F P School
47	Anandasangha F P School
59	Pratap Nagar F P School
55	157 - T Srimantapur D T W Centre
53	Uttar Kalupur Kharer Math F P School
46	Hanidanga F P School

Fig. 30: Map of Kalupur GP (source: Kalupur GP karjalaya office)

Fig 31: Tubewell of South Kalupur State Free F.P school

Fig 32: Tubewell in Ghoshpara, Kalupur **Fig 33:** Sampling pictures of tubewells in Kalupur GP

RAJPUR SONARPUR MUNICIPILATY, BARUIPUR, SOUTH 24 PARGANAS, WEST BENGAL

South 24 parganas is a very significant district in West Bengal, India. It is the largest district in this state in terms of area while it's a second largest in population. This districts has a vast diversity as one side is in urban fringe (i.e. Kolkata) other one is in remote riverine villages of Sundarbans.

This districts mainly contains five subdivisons .Baruipur is one of them. Baruipur has three municipilaties.Rajpur sonarpur is one of them.In this study we have mainly targeted some areas of Rajpur Sonarpur municipilaty.

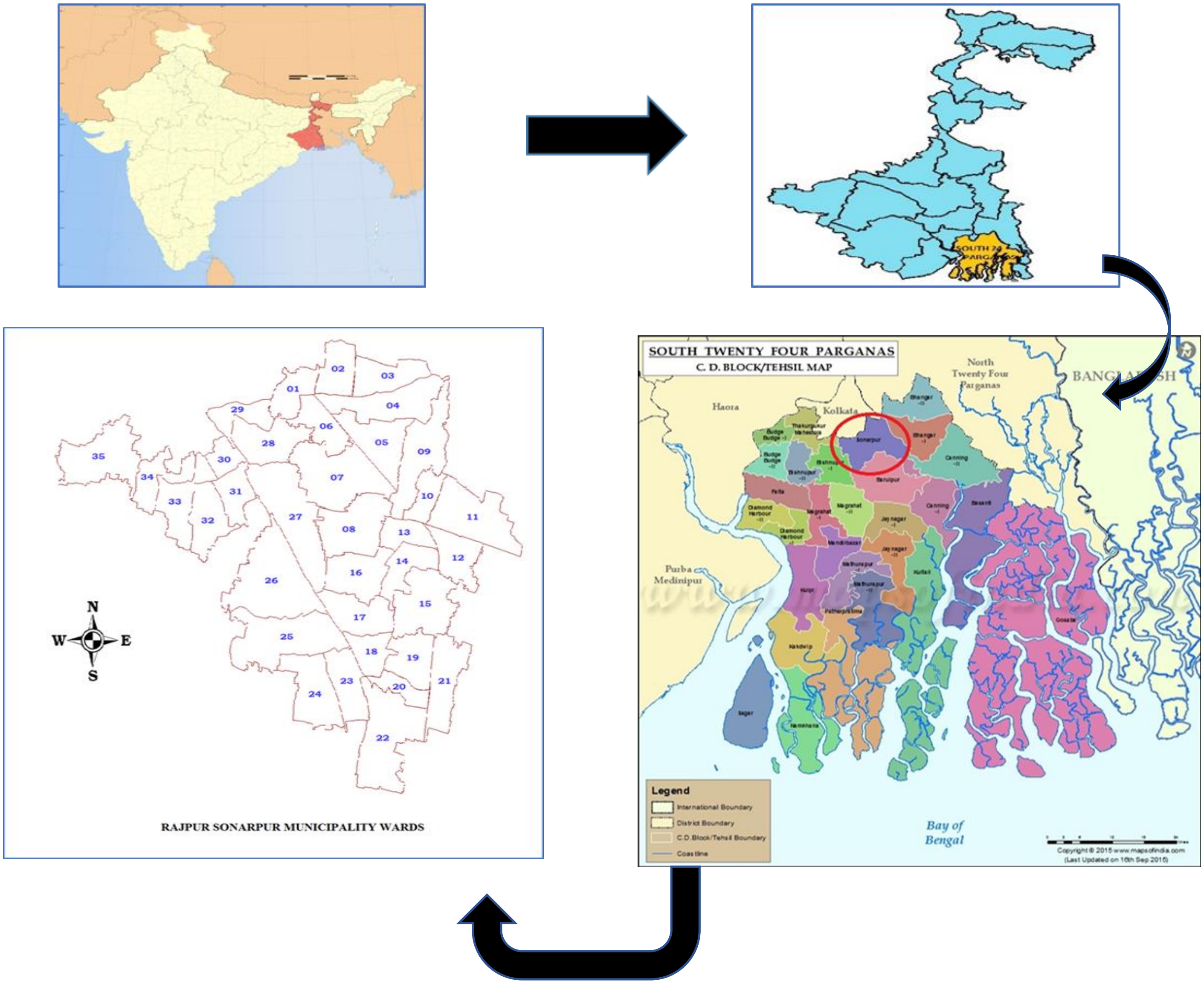


Fig 34: Rajpur sonarpur study area in Indian Map

We have mainly collected the sample from Boalia (word no 6) and Narendrapur (word no 7)from rajpur sonarpur municipilaty.

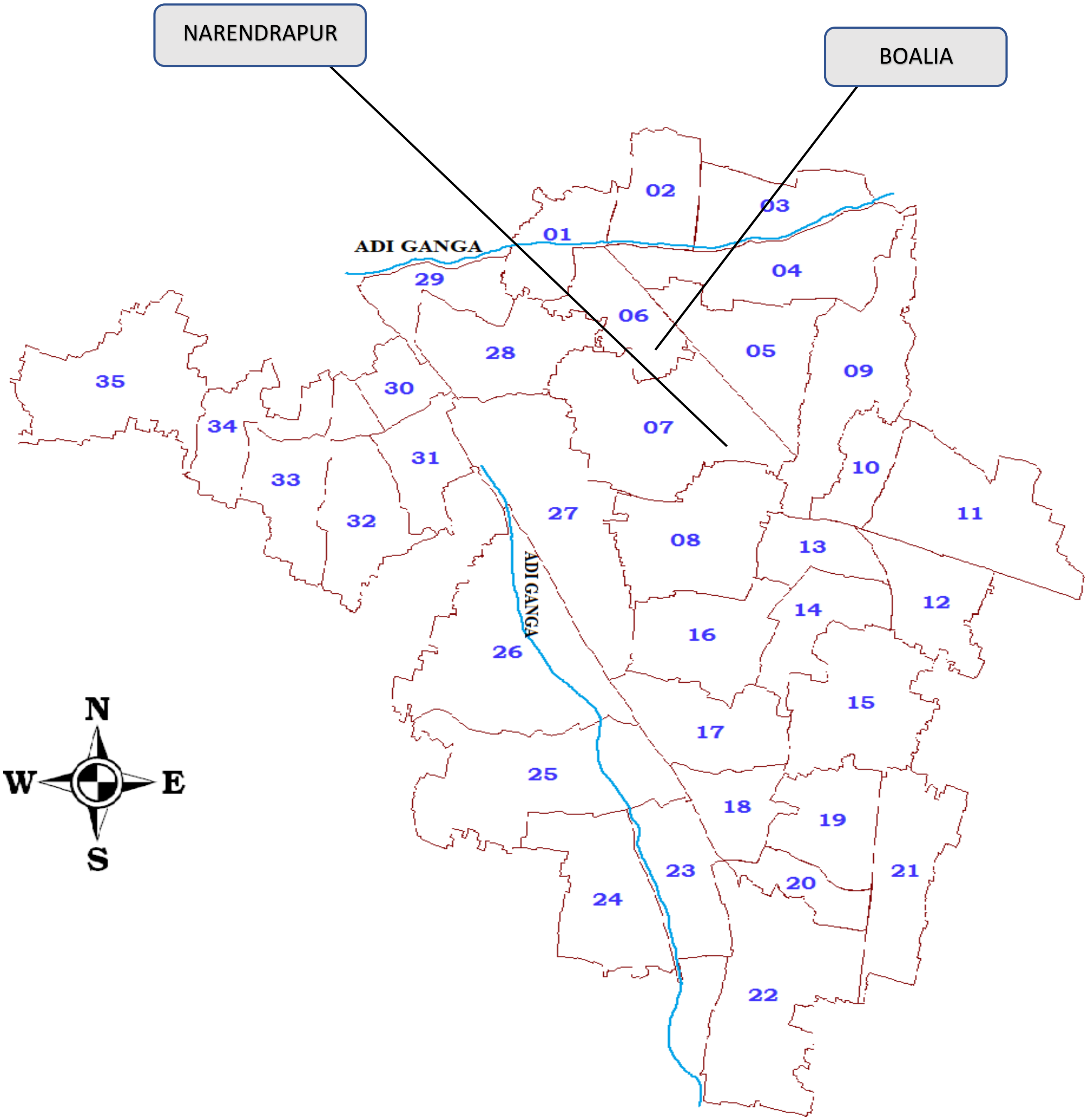


Fig 35: Rajpur Sonarpur Sonarpur Municipality Ward Map indicating the Adi Ganga Flow

(Source: Rajpur Sonarpur Municipality Office, Harinavi)

Fig 36: Tubewell used by students of primary school for drinking

Fig 37: Primary school in Narendrapur

Fig 38: Tubewell used in household for drinking

BARUIPUR AND CANNING BLOCK, SOUTH 24 PARGANAS

We have also collected the drinking water samples from several areas of baruipur and canning sub division. South 24 parganas. Many Gram panchayat like Kalabaru, Tagarbaria, Tangtala, Bansra, Gourdaha, piyali , Begampur have been included in our study which gives us an idea of the status of the drinking water of the locality.

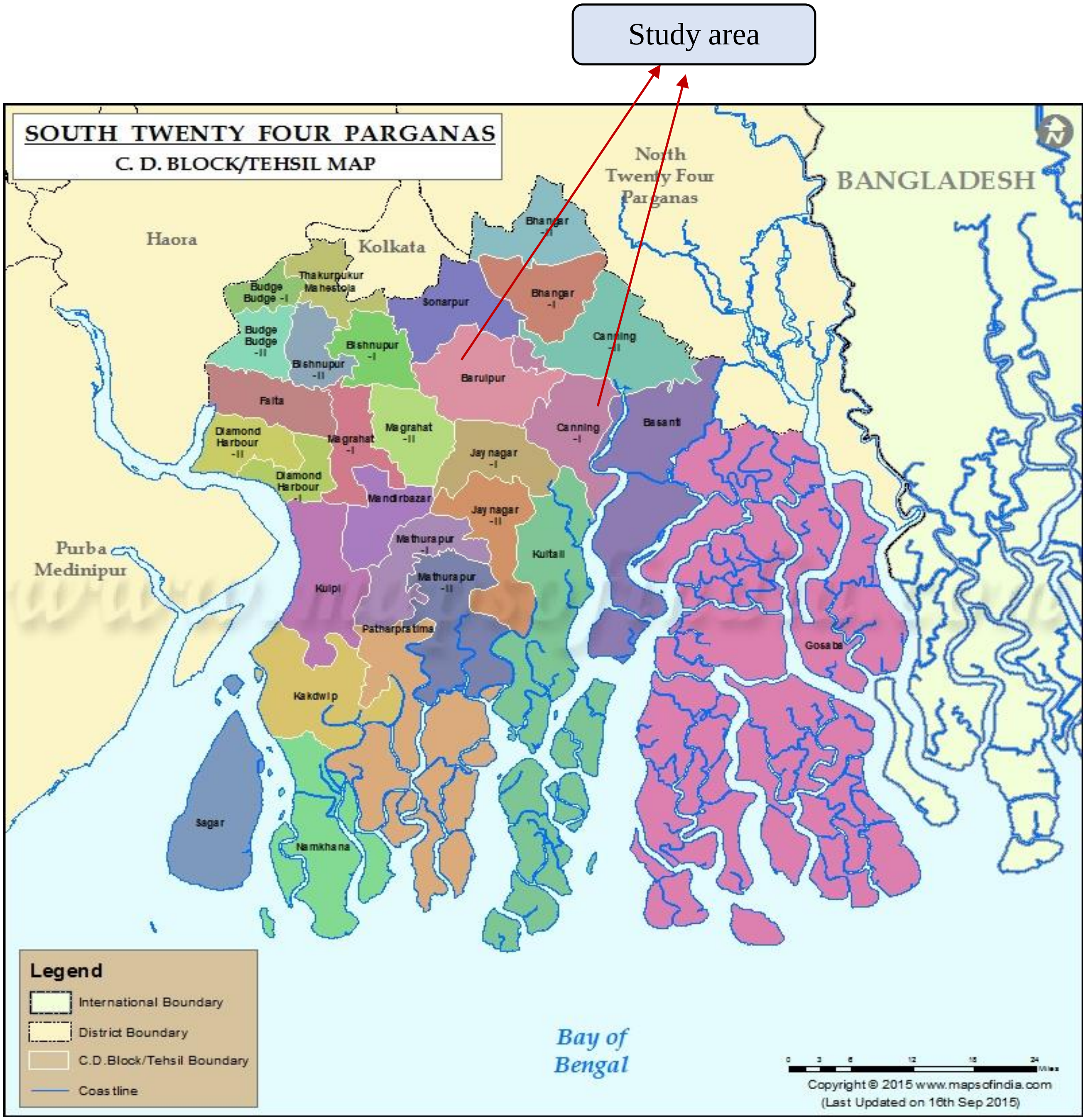


Fig 39: Block wise map of South 24 Parganas (source: Google images)

Fig 40: GP wise map of Baruipur block (source: Google images)

Fig 41: View of Canning-I

Fig 42: Piyali River

CHAPTER – 9

RESULTS AND DISCUSSION

KALUPUR GRAM PANCHAYAT, BONGAON, NORTH 24 PARGANAS:

We have collected total 48 water samples from various tube wells from that area which have been used regularly wise for drinking purpose by the people.

We can easily see from the tables that almost 80% of the collected samples have been crossed the permissible limit of arsenic (> 10 ppb). Even 52% of the samples have the arsenic concentration of greater than 50 ppb which can be very harmful for the people.

Almost 94% of samples have crossed the permissible limit of iron (i.e.0.3 ppm) in drinking water.

Each tube wells are in the permissible limit of fluoride (1-1.5 ppm). Even each samples have fluoride concentration below 0.5 ppm.

Table 7: KALUPUR GRAM PANCHAYAT (BONGAON, NORTH 24 PARGANAS, WEST BENGAL) SAMPLING DATA SHEET

DAY-1 **DATE - 08/10/2018**

Sample No	Place	Type	Coordinates	Iron [Fe] (mg/L)	Arsenic [As] (µg/L)	Fluoride [F] (mg/L)
1.	Near railgate, Unai, Kalupur	Govt. tubewell	N 23º00'41.59" E 88º48'43.68"	0.635	7.6	0.45
2.	Unai Satate Plan Abaitanik Prathamik Vidyalaya	Govt. tubewell	N 23º00'41.59" E 88º49'03.04"	0.81	3.27	0.35
3.	Battala, Unai, Kalupur	Govt. tubewell	N 23º00'36.62" E 88º48'54.44"	0.885	1.11	0.015
4.	Girja More, Unai, Kalupur	Govt. tubewell	N 23º00'28.17" E 88º48'52.27"	2.035	1.05	0.17
5.	Unai Cygnet Day School, 32 pipe	Govt. tubewell	N 23º00'46.62" E 88º48'42.05"	0.22	1.1	0.17

6.	Kalupur Bazar, Gholar Pukur	Govt. tubewell	N 23°00'55.05" E 88°48'34.55"	3.335	11.105	0.12
7.	Kalupur Bazar, Gholar Pukur	Govt. tubewell	N 23°00'55.05" E 88°48'34.55"	4.315	21.5	0.17
8.	Kalupur Jorasako F.P. School	Govt. tubewell	N 23°00'37.41" E 88°48'22.23"	2.5	63.1	0.01
9.	Kalupur, Panchpota	Govt. tubewell	N 23°01'19.14" E 88°48'49.90"	0.37	5.24	0.23
10.	Kalupur Panchpota High School	Govt. tubewell	N 23°01'21.16" E 88°48'49.81"	2.525	40.87	0.01
11.	Kalupur Panchpota Prathomik Vidyalaya	Govt. tubewell	N 23°01'21.05" E 88°48'50.74"	1.89	1.58	0.074
12.	Beler math, near High School	Govt. tubewell	N 23°01'20.41" E 88°48'41.42"	0.685	51.8	0.061
13.	New Beler Math Club	Govt. tubewell	N 23°01'20.28" E 88°48'39.78"	0.465	1.725	0.01
14.	Kalupur Majerpara Sishu Sikhshakendra	Govt. tubewell	N 23°01'20.72" E 88°48'03.52"	12.505	97.2	0.046
15.	Kalupur, Sakher Bazar	Govt. tubewell	N 23°01'35.13" E 88°47'59.87"	3.43	52.8	0.065
16.	Kalupur (Uttar), Karmakar para	Govt. tubewell	N 23°01'48.52" E 88°47'56.12"	0.37	2.69	0.2
17.	Kalupur Ananda Sangha F.P. School	Govt. tubewell	N 23°01'58.61" E 88°47'58.12"	1.055	12.98	0.43
18.	Shibshakti Sangha, Shibtala, Kalupur	Govt. tubewell	N 23°01'06.93" E 88°48'16.26"	1.325	53.8	0.01
19.	Ramkrishna Pally, Kalupur	Govt. tubewell	N 23°01'03.28" E 88°48'14.52"	0.86	49.8	0.11
20.	Near Amra Sabai Sangha, Ghoshpara , Kalupur	Govt. tubewell	N 23°01'09.93" E 88°48'04.47"	3.75	46.65	0.16
21.	Asharnagar, Kalupur	Govt. tubewell	N 23°00'55.52" E 88°47'20.29"	4.045	47.7	0.32
22.	Ballavpur High School, Ballavpur	Govt.	N 23°00'41.51"	2.77	76.65	0.087

		tubewell	E 88º46'43.61"			
23.	Ghoshpara, near Bazar More, Kalupur	Govt. tubewell	N 23º00'59.63" E 88º48'32.63"	1.08	**3.3**	0.13
24.	South Kalupur State free Primary School	Govt. tubewell	N 23º01'00.87" E 88º48'22.78"	0.195	16.55	0.49
25.	South Kalupur State free Primary School	Govt. tubewell	N 23º01'00.77" E 88º48'23.30"	1.79	14.88	0.081

Table 8: KALUPUR GRAM PANCHAYAT (BONGAON, NORTH 24 PARGANAS, WEST BENGAL) SAMPLING DATA SHEET

DAY-2 **DATE - 10/10/2018**

Sample No	Place	Type	Coordinates	Iron [Fe] (mg/L)	Arsenic [As] (µg/L)	Fluoride [F] (mg/L)
1.	Dakhin Jiala F.P. School	Govt. tubewell	N 23º00'54.18" E 88º46'52.47"	1.8	32.46	0.49
2.	Jiala F.P. School	Govt. tubewell	N 23º01'27.14" E 88º46'29.78"	2.715	60.42	0.43
3.	Sulka Durgapur F.P. School	Govt. tubewell	N 23º02'00.68" E 88º46'06.52"	<0.1	19.35	0.35
4.	Khaldar Para,Sulka	Govt. tubewell	N 23º02'02.86" E 88º46'38.30"	4.435	88.85	0.23
5.	Hanidanga F.P. School	Govt. tubewell	N 23º02'05.37" E 88º46'49.33"	4.99	62.32	0.17
6.	Mathpara,Hanidanga	Govt. tubewell	N 23º01'49.82 " E 88º47'07.70"	4.97	64.86	0.2
7.	Haritala Milan Sangha ,Hanidanga	Govt. tubewell	N 23º01'43.61" E 88º47'16.34"	2.52	47.65	0.32
8.	Beside Road,Dharampur,Jiala	Govt. tubewell	N 23º01'29.86" E 88º46'38.80"	1.69	51.86	0.17
9.	Inside Home,Dharampur..Jiala	Govt.	N 23º01'28.02"	4.935	63.35	0.47

		tubewell	E 88°46'35.00"			
10.	Beside Road,Dharampur,Jiala	Govt. tubewell	N 23°01'28.02" E 88°46'35.00"	6.04	53.49	0.12
11.	Boropara , Shibpur	Govt. tubewell	N 23°00'57.94" E 88°46'86.94"	1.36	105.95	0.16
12.	Shibpur F.P.School	Govt. tubewell	N 23°00'53.78" E 88°45'49.44"	0.775	102.75	0.13
13.	Chaiytapara	Govt. tubewell	N 23°00'53.76" E 88°45'49.49"	2.52	94.37	0.32
14.	Beside Kali Mandir,Chaiytapara	Govt. tubewell	N 23°00'00.46" E 88°45'31.72"	3.215	90.55	0.42
15.	Gournagar,Harishpur Chawk	Govt. tubewell	N 23°00'13.18" E 88°45'36.70"	3.715	108	0.37
16.	Kharaua Rajapur High School	Govt. tubewell	N 22°49'40.97" E 88°45'14.46"	0.44	50.32	0.09
17.	Uttarpara,Kharua Rajapur	Govt. tubewell	N 23°00'03.97" E 88°45'21.14"	3.825	104.67	0.23
18.	Dakhhinpara,Kharua Rajapur	Govt. tubewell	N 22°59'17.37" E 88°44'57.67"	2.66	79.68	0.29
19.	Near School Math,Ghoshpara	Govt. tubewell	N 23°01'00.77" E 88°48'22.71"	8.145	10.675	0.11
20.	Dakhin Kalupur F.P. School	Govt. tubewell	N 23°01'00.87" E 88°48'22.78"	0.14	27.15	0.01
21.	Kamarpara ,Kalupur	Govt. tubewell	N 23°00'53.23" E 88°48'22.70"	1.22	33.15	0.04
22.	Nilkuthi Math,Kalupur	Govt. tubewell	N 23°00'58.68" E 88°48'14.26"	12.36	53.32	0.12
23.	Mathpara,Kalupur	Govt. tubewell	N 23°00'56.56" E 88°48'07.30"	0.5	23.57	0.19

BOALIA (WORD NO 6), RAJPUR SONARPUR MUNICIPILATY, SOUTH 24 PARGANAS

We have collected total 71 water samples from various tube wells and pumps from that area which have been used regularly wise for drinking purpose by the people.

We can easily see from the tables that near about 85% of the collected samples have been crossed the permissible limit of fluoride. Even 40% of the samples have the fluoride concentration of greater than 1.5 ppm which can be very harmful for the people.

Almost 58% of samples have crossed the permissible limit of iron (i.e.0.3 ppm) in drinking water.

Each tube wells or pump are almost in the permissible limit of arsenic (<10 ppb). Only 2 samples of the collected samples have crossed the permissible limit of arsenic (> 10 ppb).

Table 9: BOALIA (WORD NO 6), RAJPUR SONARPUR MUNICIPILATY, SOUTH 24 PARGANAS,SAMPLING DATA SHEET

DAY-1 **DATE - 13/01/2019**

SL NO	Place	GPS N…… E…….	Depth (ft´)	Type	Fluoride conc. (mg/L)	As Conc. (µg/L)	Iron Conc (mg/L)	Calcium Conc. (mg/L)
1	Dev das Ganguli (1)	22º27´04´´ 88º24´43´´	100	Pump	1.47	1.51	<0.1	22.5
2	Sandha Ganguli	22º27´30´´ 88º24´36´´	100	Pump	1.63	1.28	0.42	22.3
3	Ameo Barui	22º27´29´´ 88º24´37´´	250	Pump	1.34	5.06	1.98	23.1
4	Amit Baram Mishra	22º27´29´´ 88º24´38´´	265	Pump	0.99	3.08	<0.1	23.6
5	Ashim kr.Das	22º27´29´´ 88º24´37´´	100	Pump	1.49	1	0.34	22.7
6	Jagannath Das	22º27´30´´ 88º24´38´´	100	Pump	1.43	0.72	<0.1	21.1
7	Amalesh Gantai	22º27´29´´ 88º24´38´´	100	Pump	1.07	1.65	3.4	22.9
8	Subhankar Naskar	22º27´28´´ 88º24´40´´	100	Tube well	1.72	0.91	<0.1	23.0
9	Dibakar Jana	22º27´29´´ 88º24´40´´	100	Tube well	1.92	0.61	0.24	31.2
10	Sujit Chatterjee	22º27´28´´ 88º24´40´´	100	Tube well	2.04	0.51	1.45	32.4
11	Sankar Biswas	22º27´28´´ 88º24´41´´	250	Pump	1.16	0.92	<0.1	29.9
12	Dipankar Biswas	22º27´27´´ 88º24´41´´	250	Pump	1.01	1.18	<0.1	32.5

13	Pradip kr. Samanta	22º27´30´´ 88º24´40´´	240	Pump	0.854	1.01	2.01	33.5
14	Pulakesh Bhunia	22º27´29´´ 88º24´40´´	150	Tubewell	1.59	0.13	0.31	28.4
15	Shirshendu Maity	22º27´29´´ 88º24´41´´	150	Tubewell	0.91	2.77	0.32	34.9
16	Uttam Das	22º27´29´´ 88º24´41´´	250	Pump	0.92	2.04	<0.1	32.3
17	Suman S. Sasmal	22º27´30´´ 88º24´41´´	250	Pump	0.84	2.19	<0.1	33.8
18	(Basati) Amal Mondal	22º27´30´´ 88º24´41´´	100	Tubewell	1.66	0.29	<0.1	32.0
19	Bapan Bera	22º27´31´´ 88º24´40´´	100	Tubewell	1.56	0.15	<0.1	26.9
20	Anup Banerjee	22º27´32´´ 88º24´40´´	100	Tubewell	1.59	<3	<0.1	29.8
21	Sishir Mondal	22º27´31´´ 88º24´38´´	100	Tubewell	1.75	0.22	0.26	27.2
22	Kartik Biswas	22º27´32´´ 88º24´40´´	100	Tubewell	1.39	0.02	2.16	35.4
23	Sapan Sarkar	22º27´33´´ 88º24´41´´	250	Tubewell	0.68	0.82	1.85	31.4
24	Ratan Saha	22º27´33´´ 88º24´41´´	100	Pump	1.24	0.22	4.12	29.2
25	Bidyut Das	22º27´33´´ 88º24´40´´	100	Pump	1.46	<3	0.97	29.1
26	Tapan Giri	22º27´33´´ 88º24´40´´	100	Pump	1.53	<3	0.70	24.5
27	Surajit Sarkar	22º27´33´´ 88º24´41´´	250	Pump	0.69	1.39	<0.1	30.1
28	Gopal Biswas	22º27´30´´ 88º24´41´´	100	Tubewell	0.68	3.75	<0.1	31.4
29	Shayamal kayal	22º27´33´´ 88º24´41´´	100	Tubewell	1.07	0.01	<0.1	24.7
30	Shamal Naskar	22º27´33´´ 88º24´41´´	250	Pump	0.67	0.27	<0.1	27.9
31	Bakul Talamore	22º27´29´´ 88º24´35´´	250	Tubewell	1.16	4.59	0.34	26.7
32	Jatin Naskar	22º27´27´´ 88º24´35´´	250	Tubewell	1.05	2.81	<0.1	27.2
33	Arun Naskar	22º27´29´´ 88º24´31´´	250	Tubewell	1.02	2.19	<0.1	27.3
34	Sujit kayal	22º27´29´´ 88º24´38´´	230	Pump	1.31	3.92	2.51	29.3
35	Pranab Naskar	22º27´29´´ 88º24´38´´	250	Pump	1.31	10.73	4.81	31.2
36	Bhrigu Ram Mondal	22º27´35´´ 88º24´51´´	220	Tubewell	0.676	0.41	1.17	31.2

37	Devkumar Naskar	22º27´29´´ 88º24´33´´	250	Pump	1.30	5.02	0.23	26.8
38	Krishna Ghosh	22º27´29´´ 88º24´31´´	240	Pump	1.69	0.7	<0.1	28.3
39	Govt. Tubewell Shamapally More	22º27´29´´ 88º24´31´´	250	Tubewell Govt.	1.13	3.28	<0.1	25.1
40	Tunu Rakshit	22º27´29´´ 88º24´35´´	100	Tubewell	1.77	0.3	0.33	20.0
41	Kamal Senapati	22º27´29´´ 88º24´31´´	100	Tubewell	1.76	<3	<0.1	26.4
42	Billapada Mondal	22º27´5´´ 88º24´45´´	130	Pump	1.99	0.08	0.28	28.9
43	Ramen Naskar	22º27´30´´ 88º24´32´´	230	TubeWell	2.13	0.16	0.23	27.8
44	Niranjan Naskar,Pump	22º27´29´´ 88º24´35´´	100	Pump	1.93	0.03	1.13	29.8
45	Santu Kayal	22º27´1´´ 88º24´46´´	250	Pump	1.12	10.33	0.31	18.8
46	Ranjan Kayal	22º27´4´´ 88º24´12´´	250	Pump	1.74	1.06	1.06	21.8
47	Subhankar kayal	22º27´45´´ 88º23´28´´	100	Pump	1.84	<3	1.30	18.1
48	Nitai kr. Jana	22º27´55´´ 88º24´51´´	100	Tubewell	1.73	0.03	0.4	22.2
49	Krisna Kundu	22º27´32´´ 88º24´22´´	100	Tubewell	1.52	<3	0.21	19.9
50	Samar Kayal	22º27´32´´ 88º24´22´´	100	Pump	1.76	0.18	<0.1	21.6
51	Raju Mandal	22º27´33´´ 88º24´22´´	100	Tubewell	1.70	0.33	1.26	20.6
52	Jhuma Dutta	22º27´26´´ 88º24´23´´	100	Tubewell	1.06	0.61	<0.1	24.2
53	Prasanta Haldar	22º27´26´´ 88º24´22´´	100	Pump	1.78	<3	<0.1	23.0
54	Shibu Chaterjee	22º27´26´´ 88º24´22´´	100	Pump	1.52	<3	0.1	24.6
55	Nritya Gapal Garu	22º27´26´´ 88º24´22´´	100	Tubewell	1.09	0.4	0.08	27.2
56	(2)Dipayan kayal	22º27´27´´ 88º24´34´´	100	pump	1.68	0.03	0.09	27.5
57	(1)Dipayan kayal	22º27´27´´ 88º24´34´´	100	Tubewell	1.84	0.18	0.1	24.2
58	Durga bhaban	22º27´31´´ 88º24´35´´	100	Pump	1.27	<3	0.25	24.5
59	Sujit kayal	22º27´30´´ 88º24´38´´	Pump	Pump	1.36	5.33	1.28	20.5
60	Jugal das Nakal	22º27´34´´ 88º24´32´´	240	Pump	0.91	3.22	1.17	27.2

61	Mohan Prasad	22º27´33´´ 88º24´34´´	100	Tubewell	1.35	0.23	<0.1	20.7
62	Samir Biswas	22º27´38´´ 88º24´37´´	100	Pump	1.34	<3	<0.1	20
63	Rajat jana	22º27´33´´ 88º24´34´´	100	Tubewell	0.91	1.75	0.25	25.2
64	Babu ghosh	22º27´35´´ 88º24´20´´	100	Tubewell	1.21	<3	1.02	18.6
65	Roghu majumder	22º27´38´´ 88º24´37´´	100	pump	1.20	<3	0.21	19.9
66	Subrata ghosh pal	22º27´35´´ 88º24´35´´	100	Tubewell	1.21	<3	<0.1	18.8
67	Tapan bidh	22º27´36´´ 88º24´35´´	110	pump	1.02	1.17	1.37	19.2
68	Kalidas pal	22º27´36´´ 88º24´36´´	250	Pump	1.45	0.05	0.25	21.6
69	Kantilal das	22º27´36´´ 88º24´38´´	110	Pump	1.05	<3	1.05	19.2
70	Niranjan naskar	22º27´30´´ 88º24´38´´	100	Tubewell	1.93	0.19	<0.1	24.2
71	Dulal das	22º27´31´´ 88º24´37´´	100	Pump	1.13	0.23	<0.1	19.6

NARENDRAPUR, KADARAT (WORD NO 7), RAJPUR SONARPUR MUNICIPILATY, SOUTH 24 PARGANAS:

We have collected total 59 water samples from various tube wells and pumps from that area which have been used regularly wise for drinking purpose by the people.

We can easily see from the tables that near about 73% of the collected samples have been crossed the permissible limit of fluoride. Even 46% of the samples have the fluoride concentration of greater than 1.5 ppm which can be very harmful for the people.

Almost 60% of samples have crossed the permissible limit of iron (i.e.0.3 ppm) in drinking water.

Each tube wells or pump are almost in the permissible limit of arsenic (<10 ppb). Only 1 samples of the collected samples have crossed the permissible limit of arsenic (> 10 ppb).

Table 10: NARENDRAPUR, KADARAT (WORD NO 7), RAJPUR SONARPUR MUNICIPILATY, SOUTH 24 PARGANAS SAMPLING DATA SHEET

DAY-2 **DATE - 14/01/2019**

SL NO	Place	GPS N…… E…….	Depth (ft´)	Type	Fluoride conc. (mg/L)	As Conc. (µg/L)	Iron Conc (mg/L)	Calcium Conc. (mg/L)
1	In front of Shani Mandir	22°27´31´´ 88°24´46´´	800	Tubewell	0.27	1.51	0.16	17.9
2	Asha Lata Mukherjee	22°27´31´´ 88°24´45´´	100	Pump	1.5	10.11	1.86	19.3
3	Subal Saha	22°27´31´´ 88°24´44´´	100	Tubewell	1.71	0.78	0.67	19.4
4	Sridam Das	22°27´30´´ 88°24´44´´	250	Pump	0.825	0.7	0.30	21.2
6	Dhiren Sen (1)	22°27´30´´ 88°24´46´´	250	Pump	0.732	1.37	0.39	22.5
8	Harshankar Monadal	22°27´29´´ 88°24´46´´	250	Pump	0.84	0.76	0.49	21.8
9	Panchanan Chatterjee	22°27´29´´ 88°24´45´´	100	Pump	1.59	1.02	2.37	18.2
10	Ranjan Khatua	22°27´29´´ 88°24´45´´	100	Pump	1.49	1	3.33	18.2
11	Anil Roy	22°27´29´´ 88°24´45´´	100	Pump	1.66	0.95	0.30	19.7
13	Monoranjan Tati	22°27´28´´ 88°24´45´´	250	Pump	1.55	1.13	1.30	22.1
14	Pradip Kr. Khatua	22°27´28´´ 88°24´45´´	250	Tube well	1.62	0.93	<0.1	18.7
16	Rajib Kr. Mandal	22°27´28´´ 88°24´46´´	250	Pump	1.48	1.06	0.37	18.2
18	Mamata Majhi	22°27´27´´ 88°24´45´´	250	Pump	0.98	2	<0.1	21.0
19	Sk Saha naunaj	22°27´27´´ 88°24´44´´	250	Pump	0.99	1.52	1.07	21.2
20	Keshab Patra	22°27´27´´ 88°24´46´´	100	Pump	1.58	1.2	<0.1	19.7
21	Somnath Barik	22°27´27´´ 88°24´44´´	100	Pump	1.62	1.92	0.21	21.8
22	Shankar Giri	22°27´26´´ 88°24´44´´	250	Pump	0.98	1.58	1.54	24.9
24	Kurumba G.P.	22°27´26´´ 88°24´45´´	800	Tube well	0.3	1.85	1.86	15.5
25	Sailen Das	22°27´26´´	100	Pump	1.66	0.95	1.05	21.4

		88º24´46´´						
26	Lalit Mandal	22º27´26´´ 88º24´46´´	250	Pump	0.87	1.25	1.49	25.2
27	Kartick Sarkar	22º27´26´´ 88º24´46´´	250	Pump	1.07	5.4	0.7	23.5
28	Joydeb Sardar	22º27´26´´ 88º24´45´´	250	Pump	1.67	1.26	1.24	21.8
29	Prasanta Mandal	22º27´26´´ 88º24´45´´	250	Pump	1.08	2.31	<0.1	21.4
30	Temathar More	22º27´24´´ 88º24´46´´	800	Tube well	1.07	4.1	2.56	22.8
32	Himanshu Giri	22º27´25´´ 88º24´46´´	250	Pump	1.11	1.62	0.56	23.3
34	Jagadish Manna	22º27´24´´ 88º24´43´´	250	Pump	1.05	3.81	0.56	20.4
35	Ashok Shit	22º27´24´´ 88º24´43´´	250	Pump	2.26	1.25	1.77	22
37	Manoj Dutta	22º27´23´´ 88º24´43´´	250	Pump	1.09	3.76	1	21.2
38	Basudev Naskar	22º27´24´´ 88º24´43´´	250	Pump	1.09	5.4	0.49	19.6
39	Rabindranath Mandal	22º27´23´´ 88º24´43´´	250	Pump	0.96	3.12	1.56	20.9
40	Vidyasagar Palli More	22º27´24´´ 88º24´48´´	1000	Tube well	0.25	1.36	<0.1	46.2
41	Shanti Kr. Mondal	22º27´23´´ 88º24´42´´	250	Pump	0.78	0.93	0.93	26.6
42	Parimal Das	22º27´28´´ 88º24´47´´	250	Tubewell	1.30	1.5	0.14	22.3
43	Susanta Gayen	22º27´28´´ 88º24´47´´	100	Tubewell	1.79	3.46	0.44	22.9
44	Asim Bhunia	22º26´55´´ 88º24´51´´	250	Pump	1.24	2.93	<0.1	22.7
45	Surajit Basu	22º27´24´´ 88º24´44´´	110	Tubewell	1.92	0.62	2.03	20.6
46	Animesh Chowdhury	22º27´24´´ 88º24´44´´	250	Pump	1.08	1.77	1.07	25.3
47	Nibas Halder	22º27´36´´ 88º24´57´´	100	Pump	1.65	0.35	0.53	20.2
48	Nibas Halder	22º27´36´´ 88º24´57´´	100	Tubewell	1.64	0.3	0.67	20.9
49	Ashok Halder	22º27´39´´ 88º24´38´´	250	Pump	1.39	0.53	<0.1	25.6
50	Salub Halder	22º27´23´´ 88º24´45´´	100	Tubewell	2.14	0.38	1.02	20.3
52	Biplab Mandal	22º27´35´´ 88º24´51´´	250	Pump	1.16	2.91	1.33	22.7

53	Kadarat Gopalchandra Abaitanik Primary School	22º27´19´´ 88º25´4´´	250	Tubewell	0.32	1.37	1.35	16.5
54	Kadare gram Naredrapur Stn.	22º27´24´´ 88º24´48´´	250	Tubewell	0.95	1.32	0.53	26.9
55	Doltala Math, in front of Radha Krishna Temple	22º27´9´´ 88º25´3´´	800	Tubewell	0.34	1.07	0.11	14.1
56	Mohan Sarkar	22º27´9´´ 88º25´10´´	250	Pump	1.99	0.23	<0.1	22.7
57	Kodarak R.K. palli	22º27´10´´ 88º25´4´´	800	Tubewell	0.357	1.1	0.95	15.7
58	Paschim para Sulekha Mandal	22º26´55´´ 88º24´51´´	120	Tubewell	1.02	0.72	1.61	25.1
59	Narendrapur stn.	22º27´24´´ 88º24´48´´	800	Tubewell	0.35	2.58	0.46	14.7

CANNING – I BLOCK, SOUTH 24 PARGANAS:

We have collected total 29 water samples from various tube wells from that area which have been used regularly wise for drinking purpose by the people.

We can easily see from the tables that maximum percentage of collected samples are within the permissible limit of arsenic and fluoride. only 4 samples have crossed crossed the permissible limit of arsenic (> 10 ppb). While one sample have the arsenic concentration of greater than 50 ppb.

Almost 80% of samples have crossed the permissible limit of iron (i.e.0.3 ppm) in drinking water.

Almost every tube wells are in the permissible limit of fluoride (1-1.5 ppm). Even 83% samples have fluoride concentration below 0.5 ppm.

Table 11: CANNING – I BLOCK, SOUTH 24 PARGANAS, WEST BENGAL SAMPLING DATA SHEET

DAY-1 **DATE - 08/09/2018**

SLNO	Block	Gram/ Gram Panchayate / Municipality	Place	Type	Coordinates	Iron [Fe] (mg/L)	Arsenic [As] (µg/L)	Fluoride [F] (mg/L)
1.	Canning-1	Piyali	Bivash Mondal, Piyali, Chatuipara	Tubewell	22º22'24.86" 88º32'12.07"	2.91	3.4875	0.759
2.	Canning-1	Piyali	Beside Road	Tubewell	22º22'21.51" 88º32'12.71"	4.37	8.6	0.352

3.	Canning-1	Tangtala	Tangtala Pukurpar, Beside Road	Govt. tubewell	22°20'20.12" 88°32'13.01"	2.865	0.475	0.264
4.	Canning-1	Bansra	Bansra Natun Abaitanik Primary School	Govt. tubewell	22°21'28.03" 88°32'15.90"	0.66	<3	0.352
5.	Canning-1	Bansra	Bansra Natun Abaitanik Primary School	Govt. tubewell	22°21'28.03" 88°32'15.90"	1.07	1.075	0.473
6.	Canning-1	Bansra	Beside road, Hirgor, Naskar Para	Govt. tubewell	22°21'33.37" 88°32'20.02"	<0.1	<3	0.517
7.	Canning-1	Bansra	Laxmi Narayan Abaitanik Primary School	Govt. tubewell	22°21'42.90" 88°32'14.90"	0.845	<3	0.363
8.	Canning-1	Bansra	Laxmi Narayan Abaitanik Primary School	Govt. tubewell	22°21'42.90" 88°32'14.90"	< 0.1	<3	0.44
9.	Canning-1	Bansra	Beside Road, Laxmi Narayan Abaitanik Primary School	Govt. tubewell	22°21'48.91" 88°32'18.13"	1.69	0.037	0.473
10.	Canning-1	Bansra	Beside Road, Laxmi Narayan Abaitanik Primary School	Govt. tubewell	22°21'04.42" 88°32'24.56"	0.025	1.3	0.418
11.	Canning-1	Bansra	Pather ses, Jibantala	Govt. tubewell	22°21'04.40" 88°32'23.49"	1.03	0.037	0.407
12.	Canning-1	Bansra	Beside Road, Pather ses	Govt. tubewell	22°21'06.80" 88°32'13.90"	0.865	1.587	0.484
13.	Canning-1	Bansra	Beside Road, Pather ses	Govt. tubewell	22°22'09.96" 88°32'67.19"	2.105	<3	0.561
14.	Canning-1	Bansra	Beside Road, Pather ses	Govt. tubewell	22°22'18.42" 88°32'03.77"	5.94	<3	0.495
15.	Canning-1	Gaurdaha	Gourdaha, Gochpur, Jibantala. Beside road	Govt. tubewell	22°22'35.87" 88°32'01.29"	3.775	<3	0.44
16.	Canning-1	Gaurdaha	Gourdaha, Jibantala. Beside road	Govt. tubewell	22°22'38.52" 88°32'51.08"	3.775	0.062	0.297
17.	Canning-1	Gaurdaha	Nakul chandra Das house	House tubewell	22°22'38.52" 88°32'51.08"	5.24	13.96	0.594
18.	Canning-1	Gaurdaha	Ratola Basu, Gourdaha, Biswaspara	House tubewell	22°22'37.27" 88°31'34.62"	0.04	<3	0.539
19.	Canning-1	Gaurdaha	Beside road, Supply line	Supply tap	22°22'35.08" 88°31'33.09"	<0.1	<3	0.495
20.	Canning-1	Gaurdaha	Beside road	Govt. tubewell	22°22'35.08" 88°31'33.09"	4.435	<3	0.451
21.	Canning-1	Gaurdaha	Joybrata Sen house, beside road	House tubewell	22°22'37.56" 88°31'27.75"	1.175	6.412	0.495
22.	Canning-1	Gaurdaha	Satinath Biswas	House tubewell	22°22'34.87" 88°32'27.23"	2.27	0.587	0.242

23.	Canning-1	Gaurdaha	Palang Chandra Mondal, Gochpur,Biswapara, Jibontala	House tubewell	22º22'28.92" 88º32'24.70"	2.7	25.51	0.484
24.	Canning-1	Gaurdaha	Tonmoy Chakraborty	House tubewell	22º22'26.58" 88º32'16.05"	1.565	13.63	0.451
25	Canning-1	Hatpukuria	Beside Road, Hatpukuria Gram Panchayat	Tubewell	22º18'41.68" 88º33'42.97"	2.1	76.7	0.484
26	Canning-1	Hatpukuria	Shib Nagar, Hatpukuria Gram Panchayat	Tubewell	22º18'10.53" 88º33'30.22"	6.96	4.737	0.286
27	Canning-1	Hatpukuria	Hatpukuria Bazar, In front of Bifla	Tubewell	22º18'03.47" 88º33'29.18"	1.075	<3	0.473
28	Canning-1	Hatpukuria	Beside Road, Hatpukuria Gram Panchayat	Tubewell	22º18'17.68" 88º33'19.15"	<0.1	0.062	0.517
29	Canning-1	Bhaleya	Beside Road, Bhaleya	Tubewell	22º18'54.45" 88º33'09.88"	1.565	1.075	0.539

BARUIPUR BLOCK, SOUTH 24 PARGANAS:

We have collected total 24 water samples from various tube wells from that area which have been used regularly wise for drinking purpose by the people.

We can easily see from the tables that maximum percentage of collected samples are within the permissible limit of arsenic and fluoride. Only 5 samples have crossed crossed the permissible limit of arsenic (> 10 ppb). While one sample have the arsenic concentration of greater than 50 ppb.

Almost 71% of samples have crossed the permissible limit of iron (i.e.0.3 ppm) in drinking water.

Almost every tubewells are in the permissible limit of fluoride (1-1.5 ppm). Even 84% samples have fluoride concentration below 0.5 ppm.

Table 12: BARUIPUR BLOCK, SOUTH 24 PARGANAS, WEST BENGAL SAMPLING DATA SHEET

DAY-2 **DATE - 09/09/2018**

SLNO	Block	Gram/ Gram Panchayate / Municipality	Place	Type	Coordinates	Iron [Fe] (mg/L)	Arsenic [As] (µg/L)	Fluoride [F] (mg/L)
1.	Baruipur	Kalabaru	Beside road, Kala Baru Bustand	Govt. tubewell	22°20'29.78" 88°32'01.62"	<0.1	0.65	0.462
2.	Baruipur	Tagarbaria	Tangaro Bajria, Beside Road	Govt. tubewell	22°20'56.06" 88°32'04.66"	2.69	0.075	0.429
3.	Canning-1	Piyali	Beside Road	Tubewell	22°22'16.48" 88°32'07.91"	0.91	3.68	0.451
4.	Baruipur	Begampur	Beside Road, Begumpur Colony	Tubewell	22°21'53.30" 88°31'16.82"	2.12	5.56	0.44
5.	Baruipur	Begampur	Beside Road, Begumpur Colony	Tubewell	22°21'55.17" 88°31'06.33"	3.41	1.23	0.396
6.	Baruipur	Begampur	Narayan Roy, Beside Road, Begumpur Colony	Tubewell	22°21'55.03" 88°32'06.32"	2.44	10.88	0.495
7.	Baruipur	Begampur	Beside Road	Tubewell	22°21'54.94" 88°31'06.30"	0.91	0.063	0.737
8.	Baruipur	Begampur	Biplab Sarkar	Tubewell	22°21'55.02" 88°31'06.30"	3.01	0.76	0.407
9.	Baruipur	Begampur	Sobuj Sangha Club	Tubewell	22°21'54.98" 88°31'06.45"	1.82	15.05	0.6
10.	Baruipur	Begampur	Sova Sarkar, Begampur , 200 Colony	Tubewell	22°21'54.51" 88°31'05.04"	0.35	0.075	0.55
11.	Baruipur	Begampur	Kartik Das	Tubewell	22°21'53.31" 88°31'06.74"	4.75	159.5	0.517

12.	Baruipur	Begampur	Sanjay Mistri, Beside Road	Tubewell	22°21'53.31" 88°31'06.74"	1.80	0.24	0.473
13.	Baruipur	Begampur	Beside Road	Tubewell	22°21'53.31" 88°31'06.74"	3.63	12.92	0.385
14.	Baruipur	Uttarbhag	Uttar bhag, Colony, In front of Buniyadi Vidyapith	Tubewell	22°21'41.43" 88°31'11.98"	0.25	1.94	0.55
15.	Baruipur	Uttarbhag	Beside Road	Tubewell	22°21'30.51" 88°31'07.03"	0.17	<3	0.594
16.	Baruipur	Uttarbhag	Laxman Baidya, Beside Road	Tubewell	22°21'21.43" 88°31'07.18"	4	1.325	0.462
17.	Baruipur	Uttarbhag	Beside Road	Tubewell	22°21'18.88" 88°31'06.40"	<0.1	<3	0.363
18.	Baruipur	Uttarbhag	Beside Road	Tubewell	22°20'59.00" 88°30'53.96"	51.35	<3	0.572
19.	Baruipur	Uttarbhag	Uttarvag, Dhosa Road	Tubewell	22°20'24.17" 88°31'06.53"	4.23	40.27	0.462
20.	Baruipur	Uttarbhag	Uttarvag, Dhosa Road, Beside Road	Tubewell	22°20'27.97" 88°32'43.20"	<0.1	0.95	0.275
21.	Baruipur	Uttarbhag	Uttarvag, Dhosa Road, Beside Road	Tubewell	22°20'27.90" 88°33'07.83"	<0.1	1.187	0.55
22.	Baruipur	Uttarbhag	J.N.Medical Hall, Ghola Bazar	Tubewell	22°20'22.26" 88°34'23.87"	<0.1	0.062	0.319
23.	Baruipur	Belagachi	Belagachi Gram Panchayat	Tubewell	22°19'11.57" 88°34'17.57"	1.39	0.162	0.396
24.	Baruipur	Belagachi	Ma Agarbati Centre	Tubewell	22°19'37.00" 88°34'01.14"	0.93	<3	0.253

Co-existence of Arsenic and Fluoride in Groundwater

Co-existence of arsenic (10 µg/L) and fluoride (1.5 mg/L) above the permissible limit has been found in two groundwater sample from **Ward No. – 6 and Ward No – 7** of Rajpur Sonarpur Municipality Area, South 24 Parganas District, West Bengal.

Table 13: Co-existance of arsenic and fluoride in study area

NAME	ADDRESS	TYPE	DEPTH	FLUORIDE CONC. (mg/L)	ARSENIC CONC. (µg/L)
Pranab Naskar	Boalia	Pump	250	1.31	10.73
Santu Kayal	Boalia	Pump	250	1.12	10.33
Asha Lata Mukherjee	Narendrapur	Pump	100	1.5	10.11

Table 14 : Concentration of arsenic, iron and fluoride Range in Study areas

STUDY AREA	NO. OF SAMPLES	NO. OF FLUORIDE SAMPLES HAVING CONC. (mg/L)				IRON CONC (mg/L)		NO. OF ARSENICSAMPLES HAVING CONC. (µG/L)		
		< 0.50	0.50 – 0.99	1.0 – 1.49	≥ 1.5	<0.3	>0.3	< 10	10.0 – 49.9	≥ 50.0
KALUPUR GP ,BONGAON, NORTH 24 PARGANAS (DAY 1)	25	25	-	-	-	2	23	10	7	8
KALUPUR GP ,BONGAON, NORTH 24 PARGANAS (DAY 2)	23	23	-	-	-	1	22	-	5	17
BOALIA (WORD NO 6), RAJPUR SONARPUR MUNICIPILATY ,SOUTH 24 PARGANAS	71	-	11	32	28	30	41	69	2	
NARENDRAPUR , KADARAT (WORD NO 7), RAJPUR SONARPUR MUNICIPILATY , SOUTH 24 PARGANAS	59	7	9	16	27	24	35	58	1	-
CANNING – I BLOCK, SOUTH 24 PARGANAS	29	24	5	-	-	6	23	25	3	1
BARUIPUR BLOCK, SOUTH 24 PARGANAS	24	20	4	-	-	7	17	19	4	1

SECTION - 2

REMEDIAL MEASUREMENTS OF GROUNDWATER ARSENIC AND FLUORIDE USING SUITABLE ADSORBENTS

CHAPTER - 10

LITERATURE REVIEW

- ## Adsorption

Adsorption is the adhesion of atoms, ions or molecules of gas, liquid, or dissolved solids to a surface but absorption is a process in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. Removal of excess fluoride from water by adsorption involves, physical, chemical or ion exchange within the adsorbent in which the fluoride is adsorbed on to a fixed bed packed with resin or other mineral particles. It is important to differentiate between adsorption of a single and of multiple compounds. In the latter case, the different adsorbate will compete for adsorption sites and the adsorption equilibrium as well as the isotherm can be significantly different than without competition. In a multi-component system, the initial concentration of the target adsorbate influences the resultant isotherm. The most important factors affecting adsorption are: surface area of adsorbent, particle size of adsorbent; particle sizes reduce internal diffusion and mass transfer limitation to the penetration of the adsorbate inside the adsorbent (i.e., equilibrium is more easily achieved and nearly full adsorption capability can be attained), affinity of the solute for the adsorbent, degree of ionization of the adsorbate molecule (more highly ionized molecules are adsorbed to a smaller degree than neutral molecules) and pH. Adsorption is still one of the most extensively used methods because of its simplicity and availability of wide range of adsorbent (Mahapatra et al., 2010). Adsorption is the adhesion of atoms, ions or moleculs from a gas, liquid or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. This process differs from absorption, in which a fluid (the absorbate) is dissolved by or permeates a liquid or solid (the absorbent), respectively. Adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It is important to distinguish between physical adsorption, involving only relatively weak intermolecular forces, and chemisorptions, which involves essentially the formation of chemical bond between the sorbet molecule and the surface of adsorbent. Douglas (1984) has compared the two techniques as shown in below table.

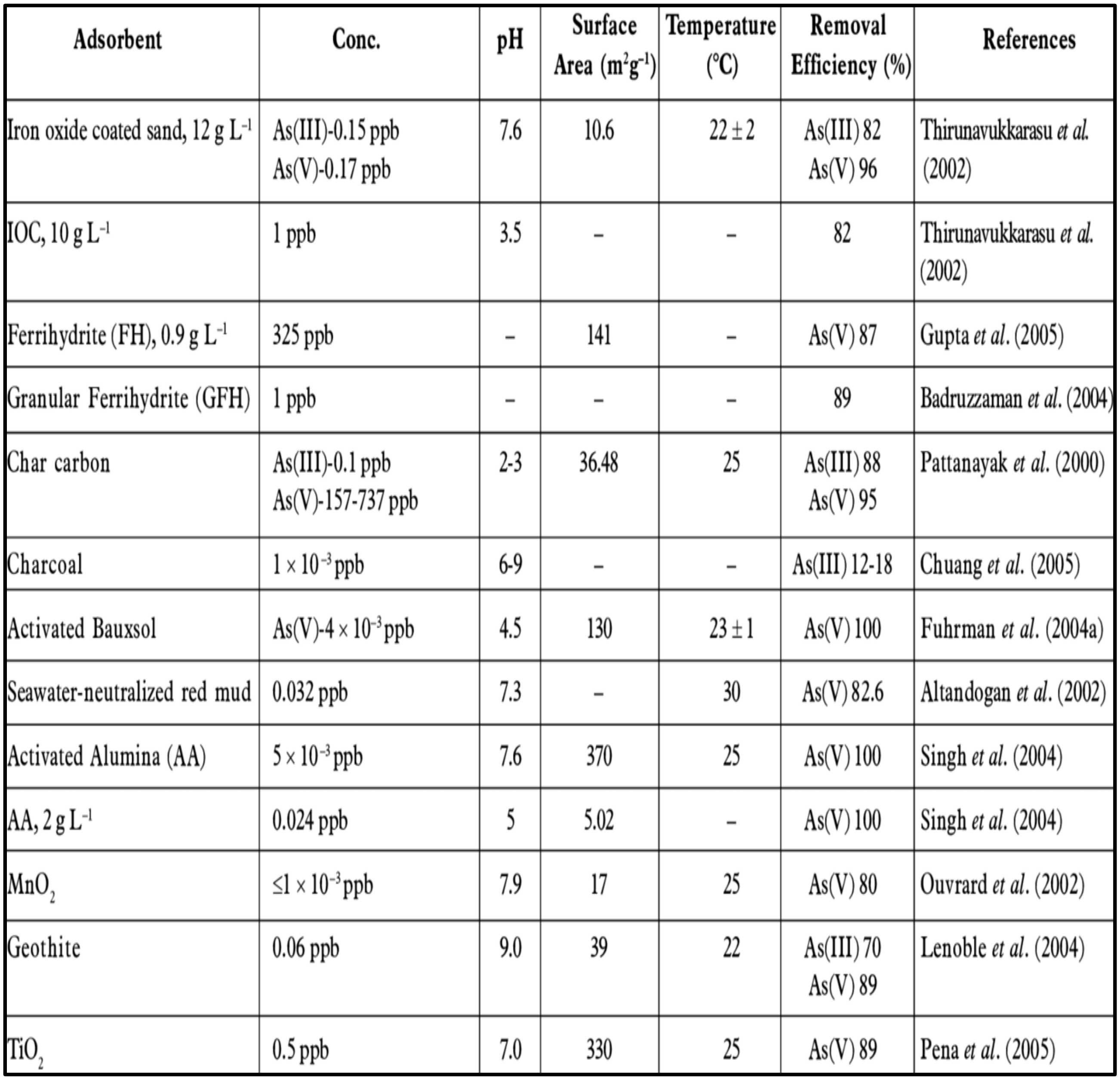
Table 15: Difference between Physical Adsorption and Chemisorption (source: Douglas &Ruthven, 1984)

Physical Adsorption	Chemisorption
The forces operating are weak Vander Waal's forces.	The forces is similar to a chemical bond.
Forms multi molecular layer and Non specific.	Forms unimolecular layer and Specific.
No dissociation of adsorbed species.	May involve dissociation.
The heat of adsorptions are low i.e. about 20 – 40 KJ mol^{-1}.	The heat of adsorptions are high i.e. about 40 – 400 KJ mol^{-1}.
The process is reversible.	The process is irreversible.
This type of adsorption decreases with increase of temperature.	This type of adsorption increases with increase of temperature.

- **Importance of adsorption**

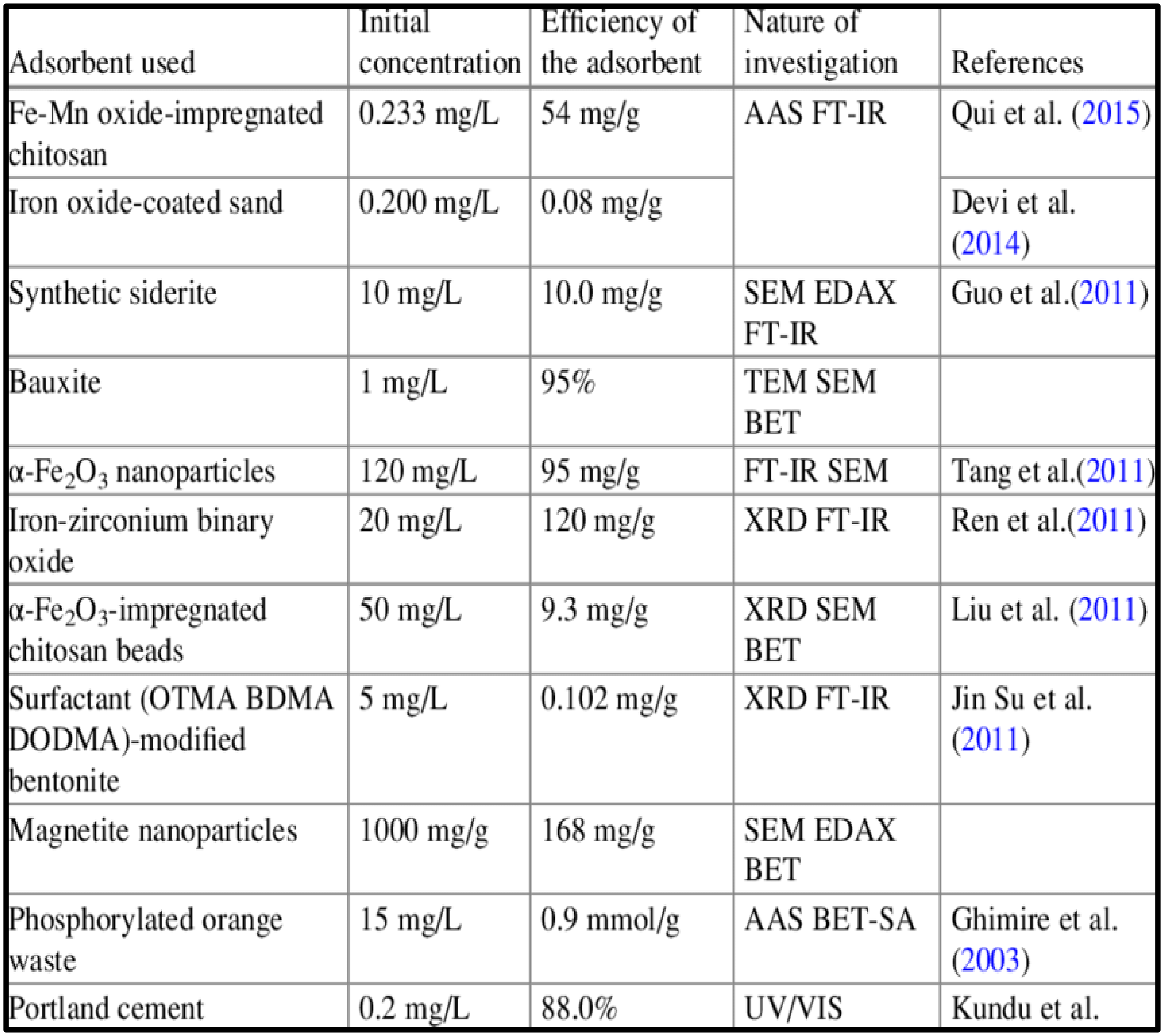
A. Low cost in installation and maintenance.
B. High efficiency, high productivity of fluoride removal (up to 90%).
C. Easy post-treatment after adsorption & High selectivity of adsorbents
D. Simple in the operation and design.
E. Eco-friendly nature & Lack of sludge production.
F. Removal of fluoride even at low concentration.
G. Wide range of availability of adsorbents.

Table 16: Various low cost adsorbents for removal of arsenic (source: Anjum et al., 2009)



Adsorbent	Conc.	pH	Surface Area (m^2g^{-1})	Temperature (°C)	Removal Efficiency (%)	References
Iron oxide coated sand, 12 g L^{-1}	As(III)-0.15 ppb As(V)-0.17 ppb	7.6	10.6	22 ± 2	As(III) 82 As(V) 96	Thirunavukkarasu *et al.* (2002)
IOC, 10 g L^{-1}	1 ppb	3.5	–	–	82	Thirunavukkarasu *et al.* (2002)
Ferrihydrite (FH), 0.9 g L^{-1}	325 ppb	–	141	–	As(V) 87	Gupta *et al.* (2005)
Granular Ferrihydrite (GFH)	1 ppb	–	–	–	89	Badruzzaman *et al.* (2004)
Char carbon	As(III)-0.1 ppb As(V)-157-737 ppb	2-3	36.48	25	As(III) 88 As(V) 95	Pattanayak *et al.* (2000)
Charcoal	1×10^{-3} ppb	6-9	–	–	As(III) 12-18	Chuang *et al.* (2005)
Activated Bauxsol	As(V)-4×10^{-3} ppb	4.5	130	23 ± 1	As(V) 100	Fuhrman *et al.* (2004a)
Seawater-neutralized red mud	0.032 ppb	7.3	–	30	As(V) 82.6	Altandogan *et al.* (2002)
Activated Alumina (AA)	5×10^{-3} ppb	7.6	370	25	As(V) 100	Singh *et al.* (2004)
AA, 2 g L^{-1}	0.024 ppb	5	5.02	–	As(V) 100	Singh *et al.* (2004)
MnO_2	$\leq 1 \times 10^{-3}$ ppb	7.9	17	25	As(V) 80	Ouvrard *et al.* (2002)
Geothite	0.06 ppb	9.0	39	22	As(III) 70 As(V) 89	Lenoble *et al.* (2004)
TiO_2	0.5 ppb	7.0	330	25	As(V) 89	Pena *et al.* (2005)

Table 17: Various synthesized modified adsorbents for removal of arsenic (Anjum and ansar, 2017)



Adsorbent used	Initial concentration	Efficiency of the adsorbent	Nature of investigation	References
Fe-Mn oxide-impregnated chitosan	0.233 mg/L	54 mg/g	AAS FT-IR	Qui et al. (2015)
Iron oxide-coated sand	0.200 mg/L	0.08 mg/g		Devi et al. (2014)
Synthetic siderite	10 mg/L	10.0 mg/g	SEM EDAX FT-IR	Guo et al.(2011)
Bauxite	1 mg/L	95%	TEM SEM BET	
α-Fe_2O_3 nanoparticles	120 mg/L	95 mg/g	FT-IR SEM	Tang et al.(2011)
Iron-zirconium binary oxide	20 mg/L	120 mg/g	XRD FT-IR	Ren et al.(2011)
α-Fe_2O_3-impregnated chitosan beads	50 mg/L	9.3 mg/g	XRD SEM BET	Liu et al. (2011)
Surfactant (OTMA BDMA DODMA)-modified bentonite	5 mg/L	0.102 mg/g	XRD FT-IR	Jin Su et al. (2011)
Magnetite nanoparticles	1000 mg/g	168 mg/g	SEM EDAX BET	
Phosphorylated orange waste	15 mg/L	0.9 mmol/g	AAS BET-SA	Ghimire et al. (2003)
Portland cement	0.2 mg/L	88.0%	UV/VIS	Kundu et al.

Table 18: Various low cost adsorbents for removal of fluoride

Name of adsorbent	pH	Dosage (g/L)	Contact time (hr)	Removal Percentage (%)	Reference
Clay material	2	5-10	3	40-50	Ravikumar and Nazeebkhan (2015)
Granular activated carbon & sewage sludge	neutral	GAC-4 SS-3	3	60-70	Poundyl and Sandhya (2015)
Tea Ash	6	0.8	1	51.3-77.6	Mondal.et.al.(2011)
Pumic	7	20	3	74.64	Malakootianet.al.,(2011)
Neem leaves	2	10	1	90	Goswami et al.,(2015)
Rice Husk	2-10	10	2	75	Deshmukh et.al., (2009)
Eggshell powder	2-6	5	2	94	R. Bhavnik & N.K. Mondal,2015
Neem stem charcoal	5	0.1 - 0.6	3	94	Chakrabarty &Sharma(2012)
Citrus limonum (lem on)leaf	2-8	1-10	2.4	70	V.Jomae.et.al (2014)
Devadaru leaf powder	7	7-8	3	77	Bharali and Bhattachary (2011)
Banana peel and coffee husk	2	72	12	80-84	Getechew et al.,2014
Wheat straw and sawdust	6	4	1	42 & 50	Yadav et al., 2013
Dolomite					

CHAPTER - 11

AIM AND OBJECTIVE

We have seen that arsenic and fluoride contaminated groundwater has become the major source of drinking water for the majority of people in our country especially in rural areas. Dearsenification and defluoridation of water is the only practicable option to get rid of excess arsenic and fluoride. The available technologies may be used for mitigating the contamination,but cost effective and fast techniques for the reduction of arsenic and fluoride concentration is very important as discussed earlier.

The main objective of the proposed study is to develop an integrated treatment for the drinking water containing arsenic and fluoride by carrying out experimental investigation on removal of arsenic and fluoride from aqueous solution using suitable adsorbents. The specific objectives are as follows:

1. To identify effective technique for removal of arsenic and fluoride from groundwater
2. Adsorbent characterization.
3. Batch study of the adsorbent in lab scale i.e. Percentage removal of arsenic and fluoride with variation of
    a) Effective pH
    b) Effective contact time
    c) Effective contact speed
    d) Effective adsorbents dose
    e) Effective activated adsorbent Temperature
    f) Effective initial arsenic or fluoride concentration
4. Kinetic study
5. Isotherm study

CHAPTER – 12

METHODOLOGY

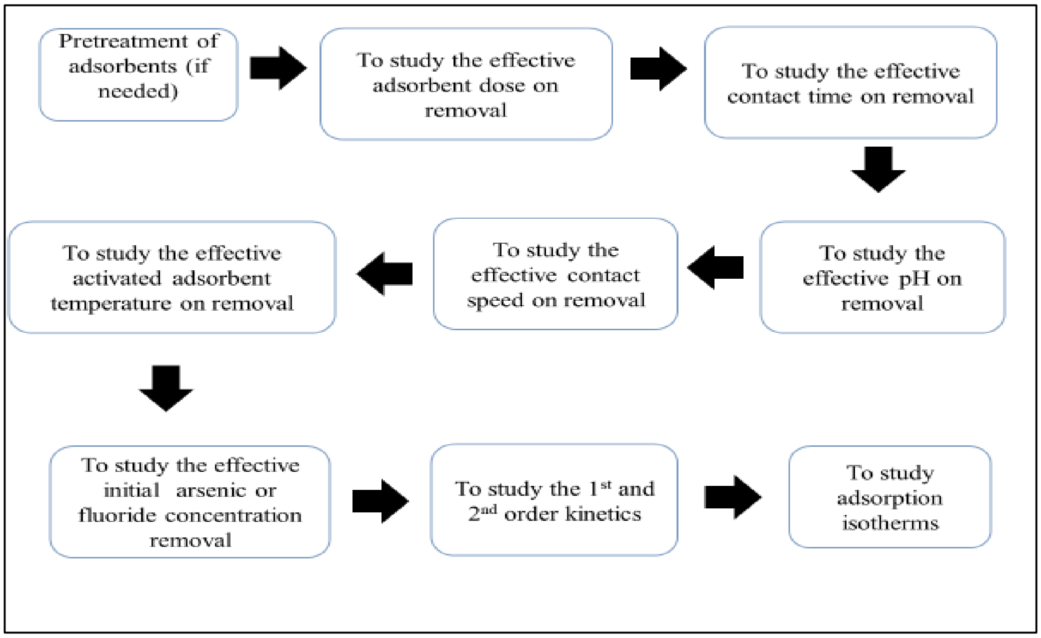


Fig 43: Methodology Scheme of Adsorption

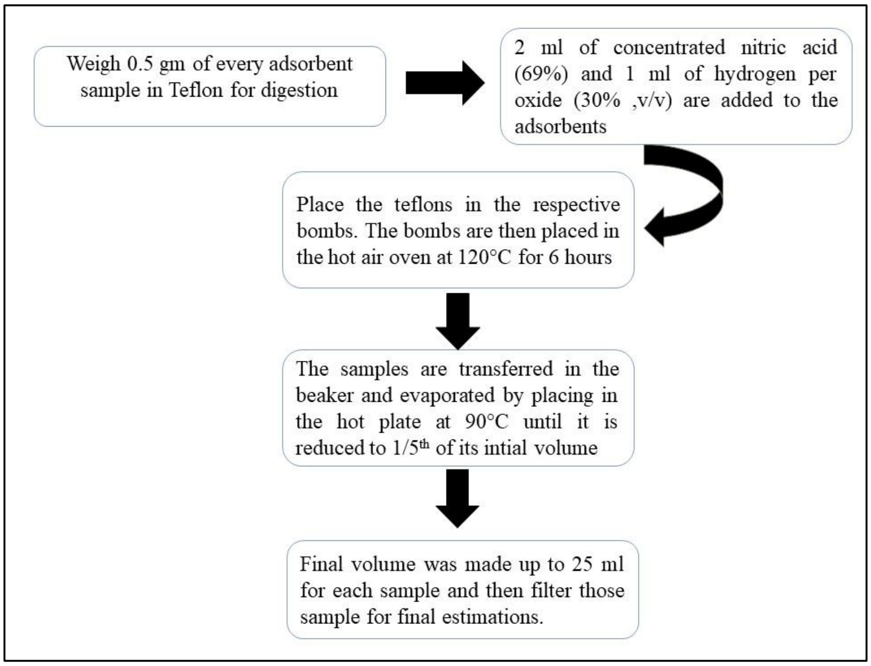


Fig 44: Methodology of Acid Digestion

Fig 45: Setup of teflon bomb acid digestion

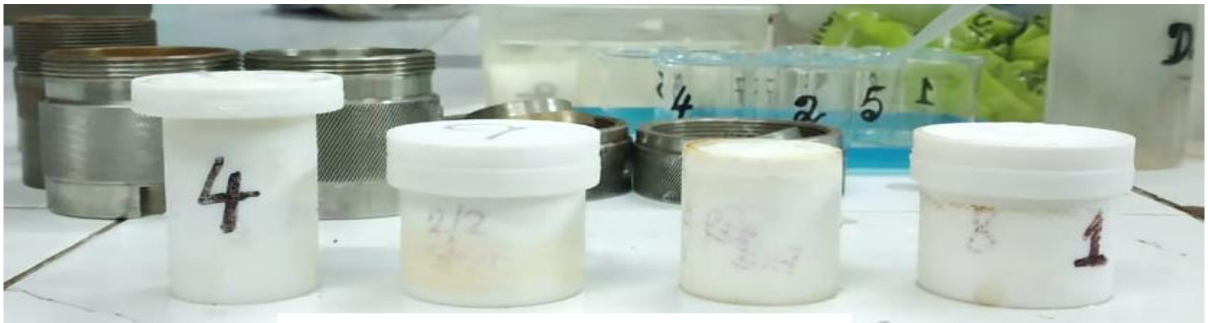


Fig 46: Teflon bomb

Adsorbents used

Dolomoite

It is an anhydrous carbonate mineral composed of calcium magnesium carbonate, ideally CaMg(CO3)2. The term is also used for a sedimentary carbonate rock composed mostly of the mineral dolomite.

Fig 45: Dolomite (source: Google images)

Sea Shell

A seashell is usually the exoskeleton of an invertebrate (an animal without a backbone), and is typically composed of calcium carbonate or chitin. Most shells that are found on beaches are the shells of marine mollusks, partly because these shells are usually made of calcium carbonate, and endure better than shells made of chitin.

Fig 46: Sea shell (source: Google images)

Mixture of Dolomite And Sea Shell

It is basically the mixture of both dolomite and mixture by equal quantities.

We have collected the homogenous powder form with particle size of 100 mesh (i.e. diameter of 149 µm) adsorbents (dolomite sea shell and their mixture) from **DISHA AGROTECH (PINGLA, PASCHIM MEDINIPUR).**

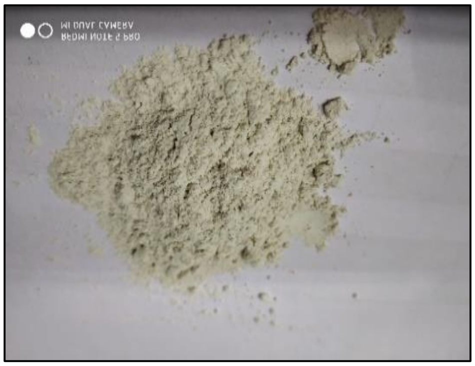


Fig 47: Dolomite

Fig 48: Sea Shell

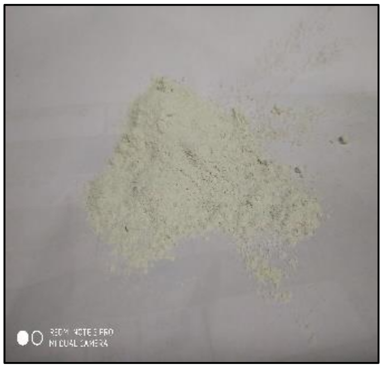


Fig 49: Mixture

X-RAY DIFFRACTION (XRD)

X-ray powder diffraction (XRD) is a fast analytical method that mainly used for phase identification and unit cell dimensions of a crystalline material. The analyzed material should be finely ground, homogenized so that average bulk composition can be determined (Dutrow et al.,1997)

This technique is mainly based on the Bragg's theory. The Bragg equation is in the followings.

It states that

$n\lambda = 2d\sin\theta$, where,

n is an integer,

λ is the characteristic wavelength of the X-rays that imparts crystallize sample

d is the interplanar spacing between rows of atoms

θ is the angle of the X-ray beam with respect to these planes.

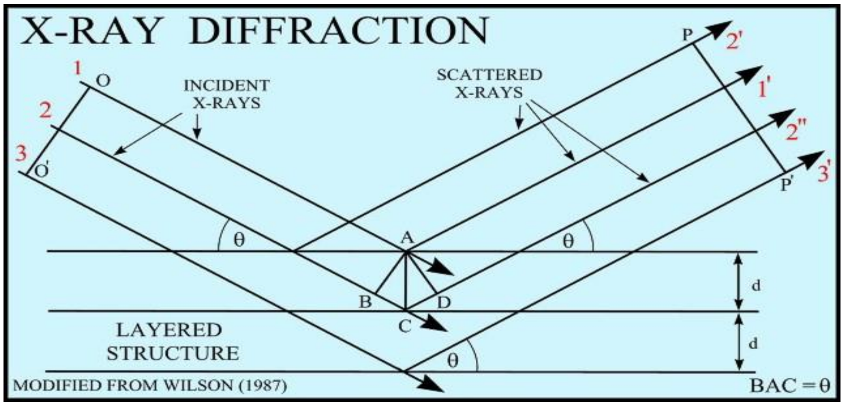


Fig 50: Incident X-Rays are diffracted by the layers of atoms in a crystalline material

CHAPTER - 13

BATCH STUDY

13.1 Batch study for removal of arsenic

- Dilution of arsenic conc. made: 200,100,70,50,20 ppb
- pH varied 3 to 12 by using NaOH and HNO_3
- Adsorbent dosage 5 gm/L to 34 gm/L
- Contact time 10 to 60 min
- Performed at temp RT, 70°C,100°C,200°C and 600°C
- Contact speed 0,30,40,50 and 60 RPM
- At the end of contact time, filtrate examined for residual arsenic conc.

Removal of arsenic (%) = $(C_0-C_t)/C_0 \times 100\%$

Where, C_0 = arsenic conc. initially (µg/L),C_t = arsenic conc. at any time (µg/L)

Again, $q_t = (C_0-C_t) / m_s$

q_t =arsenic adsorbed (µg) per gm of dolomite or sea shell

m_s = amount of dolomite or sea shell (gm/L)

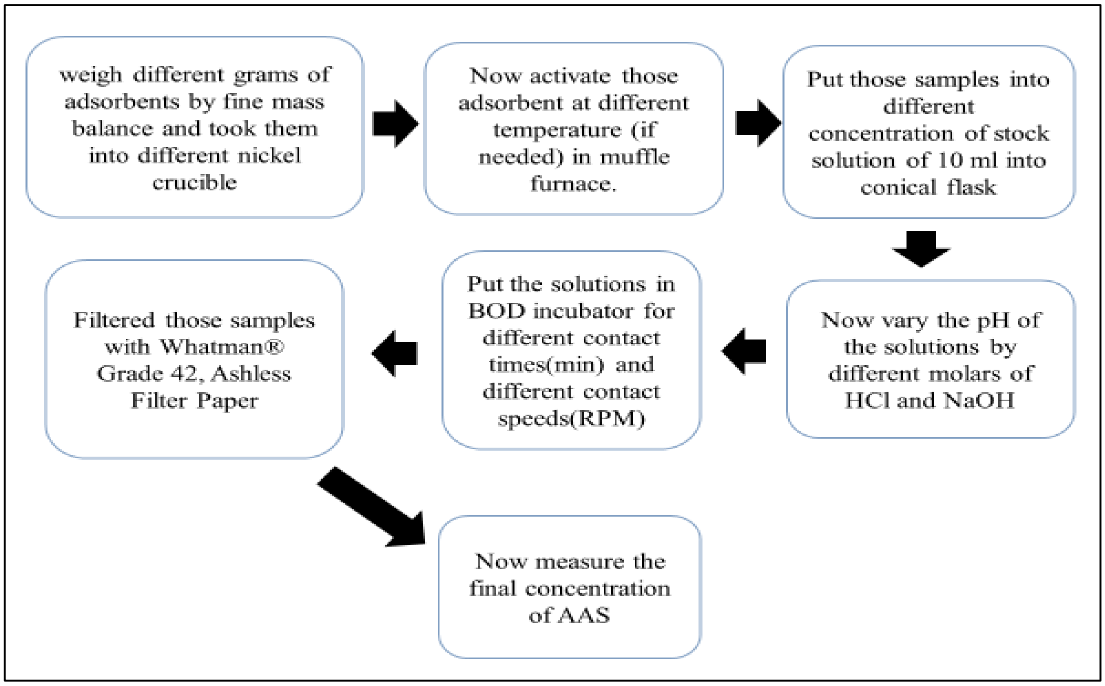


Fig 51: Batch study procedure for arsenic

13.2 Batch study for removal of fluoride

• Dilution of fluoride conc. made:	10,5,4,2 ppm
• pH varied	3 to 11 by using NaOH and HNO_3
• Adsorbent dosage	5 gm/L to 50 gm/L
• Contact time	10 to 60 min

At the end of contact time, filtrate examined for residual fluoride conc.

Removal of fluoride (%) = $(C_0-C_t)/C_0 \times 100\%$

Where, C_0 = Fluoride conc. initially (μg/L), Ct = fluoride conc. at any time (μg/L)

Again, $q_t = (C_0-C_t) / m_s$

q_t = Fluoride adsorbed (μg) per gm of dolomite or sea shell

m_s = Amount of adsorbents (gm/L)

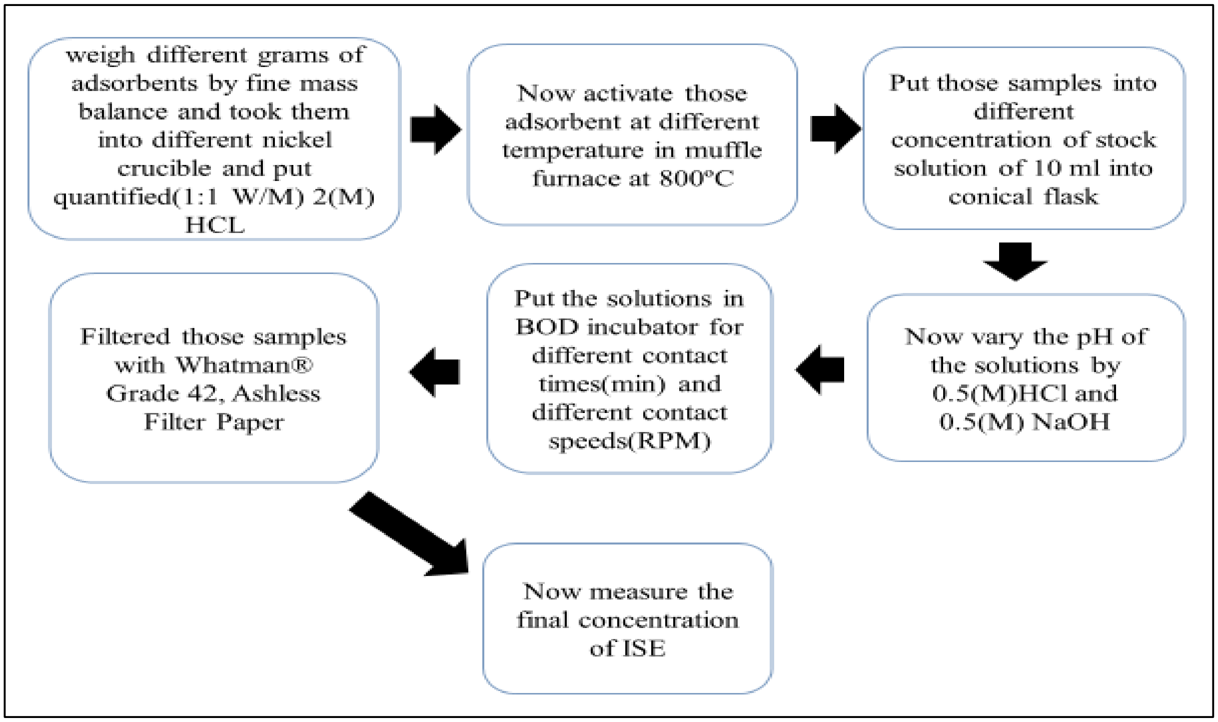


Fig 52: Batch study procedure for fluoride

CHAPTER – 14

ADSORPTION ISOTHERM

There are different types of the adsorption equilibrium models exist, which are differing in complexity and in the number of parameters necessary. An equation that relates the amount of a substance attached to a surface to its concentration in the gas phase or in solution, at a fixed temperature, is known as an adsorption isotherm. The two models that use frequently are the Langmuir (1918) and Freundlich, (1906) isotherms.

14.1 Langmuir Adsorption isotherm:

The theoretical of Langmuir isotherm is the equilibrium distribution of sorbate ions between the solid and liquid phases (Kumar et al., 2011). It is assumed that the surface of the adsorbents is uniform so that all the adsorption site are equal, adsorbed molecules will not interact, all adsorption occurs through the same mechanism and at the maximum adsorption only a monolayer is formed. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without interaction of adsorbate in the plane of the surface where adsorbate molecules can be chemically bound.

It is also assumed that the reaction is in a constant free-energy change for all sites and a maximum of one adsorbate molecule can be bound to each site (monolayer coverage). The Langmuir equation which is in most cases only applicable for small concentration ranges since the Langmuir equation assumes that homogeneous structure of the adsorbent surface, i.e. it is assumed as all sites of adsorption energetically equal (Langmuir, 1918).

The Langmuir in its nonlinear equation is commonly expressed as follows (Kumar et al., 2011):

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \quad \text{……………….. (1)}$$

The linear Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir isotherm in its linear form is represented by:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad \text{………….……… (2)}$$

Where the Qo is the amount of adsorbate at complete monolayer coverage (mg/g) and gives the maximum sorption capacity of sorbent, Ce is the equilibrium concentration of fluoride (mg/L) and b (L/mg) is Langmuir isotherm constant that relates to the energy of adsorption and qe is an adsorption capacity. The Langmuir constants Qo and b can be calculated from the slope and intercept of the plot Ce/qe versus Ce respectively. The feasibility of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, RL (Weber et al., 1974), which is expressed as:

$$R_L = \frac{1}{1 + bC_o} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

Where b is the Langmuir isotherm constant and Co is the initial concentration of fluoride (mg/L). The RL values lying between 0 and 1 indicate the conditions are favorable for adsorption.

Table 19: Favorability of Langmuir isotherm model (source: Weber et al., 1974)

RL	**Type of Isotherm**
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

14.2 Freundlich Adsorption isotherm:

Freundlich isotherm is an empirical equation which encompasses the heterogeneity of sites and the exponential distribution of sites and their energy. It is empirical expression that encompasses the heterogeneity of the surface and the exponential distribution of sites and their energies. The Freundlich isotherm can be derived assuming a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites. The Freundlich isotherm is generally better suited to describe adsorption in aqueous solutions than the Langmuir isotherm. It has been shown that the Freundlich equation can be derived from the Langmuir equation if a logarithmic decrease of the differential adsorption enthalpy with increasing solid-phase concentration is assumed, corresponding to the behaviour of a heterogeneous adsorbent surface. It is important to note that the Freundlich equation can only be used to describe experimental data within a limited concentration range where the constants are valid. To describe adsorption outside of this range, other isotherms have to be derived in experiments within other concentration ranges.

The Freundlich model is commonly given by the non-linear equation (Freundlich, 1906):

$$q_e = K_f C_e^{1/n} \quad \text{………………} (4)$$

The Freundlich isotherm in its linear form is represented by:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Where qe is the amount of fluoride adsorbed per unit weight of the sorbent (mg/g), Ce is the equilibrium concentration of fluoride in solution (mg/L), Kf is a measure of adsorption capacity and 1/n is the adsorption intensity. The Freundlich isotherm constants 1/n and Kf can be calculated from the slope and intercept of the plot log qe vs log Ce. The values of 1/n lying between 0 and 1 and the n values lying in between 1 and 10 indicate the conditions favorable for adsorption. The intercept of the line, Kf is roughly indicator of the adsorption capacity and the slope is an indication of adsorption effectiveness (Cooney, 1998).

CHAPTER - 15

ADSORPTION KINETICS

When adsorption is concerned, thermodynamic and kinetic aspects should be involved to know more details about its performance and mechanisms. Except for adsorption capacity, kinetic performance of a given adsor- bent is also of great significance for the pilot application. From the kinetic analysis, the solute uptake rate, which determines the residence time, required for completion of adsorption reaction, may be established (Qiu et al., 2009). Also, one can know the scale of an adsorption apparatus based on the kinetic information. Generally speaking, adsorption kinetics is the base to determine the performance of fixed-bed or any other flow-through systems. In the past decades, several mathematical models have been proposed to describe adsorption data, which can generally be classified as adsorption reaction models and adsorption diffusion models. Both models are applied to describe the kinetic process of adsorption. However, they are quite different in nature (Mohammed et al., 2011).

At present, adsorption reaction models have been widely developed or employed to describe the adsorption kinetics (Banat et al.,2003). To develop sorption kinetics, knowledge of the rate law describing the sorption system, is required. The rate law is determined by experimentation and it cannot be inferred by more examination of the overall chemical reaction equation.

Numerous sorption systems have been investigated particularly during the past fifteen years. From the kinetic analysis, the solute uptake rate, which determines the equilibrium time, required for completion of adsorption reaction, may be established. Three well known kinetic models, pseudo-first order, pseudo-second order model and intraparticle diffusion models, were employed to describe the adsorption process (Agarwal et al., 2015).

15.1 Pseudo-first order kinetic:

In 1898, Lagergren presented a first-order rate equation to describe the kinetics of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model, pertaining to the adsorption rate, based on the adsorption capacity (Agarwal et al., 2015). This model is designed by Lagergren (1898) and is expressed as

$$\log\left(q_e - q_t\right) = \log q_e - \frac{K_{ad} t}{2.303}$$

where,

q_e = quantity for arsenic adsorbed (μg/gm) during equilibrium
q_t = quantity for arsenic adsorbed (μg/gm) at any specific time t
K_{ad} = pseudo-first-order kinetic constant (min^{-1})

To distinguish kinetic equations, based on adsorption capacity from solution concentration, Lagergren’s first order rate equation has been called pseudo-first order . In recent years, it has been widely used to describe the adsorption of pollutants from wastewater in different fields.

15.2 Pseudo-Second order kinetic:

In 1995, Ho described the adsorption kinetics of divalent metal ions onto peat, in which the chemical bonding among divalent metal ions and polar functional groups on peat, such as aldehydes, ketones, acids, and phenolics, are responsible for the cation-exchange capacity of the peat.

The main assumptions for the above were that the adsorption may be second-order, and the rate limiting step, may be chemical adsorption, involving valent forces through sharing or the exchange of electrons between the peat and divalent metal ions. In addition, the adsorption follows the Langmuir equation. Therefore, the rate expression, i.e. pseudo-second order equation is:

$$\frac{t}{q_t} = \frac{1}{K' q_e^2} + \frac{1}{q_e} t$$

Where,

q_e = quantity for arsenic adsorbed (µg/gm) during equilibrium

q_t = quantity for arsenic adsorbed (µg/gm) at any specific time t

K' = pseudo-second-order kinetic constant (gm/mg min)

CHAPTER – 16

RESULTS AND DISCUSSION

16.1 Adsorption characterization:

We have already seen the various removal technologies of arsenic and fluoride from groundwater and their corresponding advantages and disadvantages. Out of them adsorption is quite safe, simple and effective and it is preferred due to low-cost, Abundance, Easy availability, Effectivity & efficiency, Easy disposal methods.

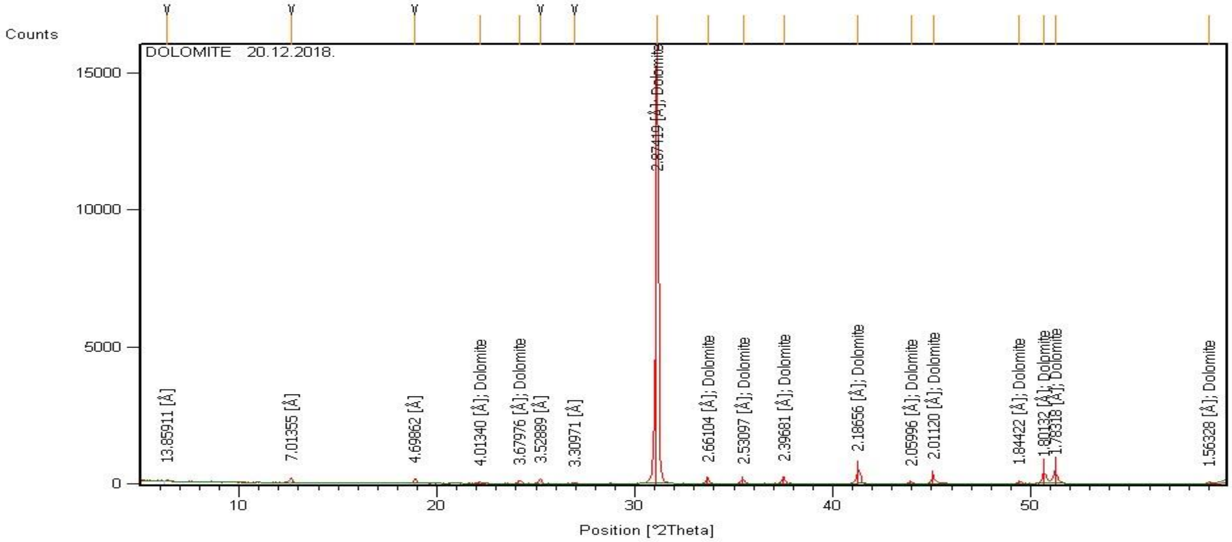


Fig 53 : X-ray diffraction (XRD) of dolomite

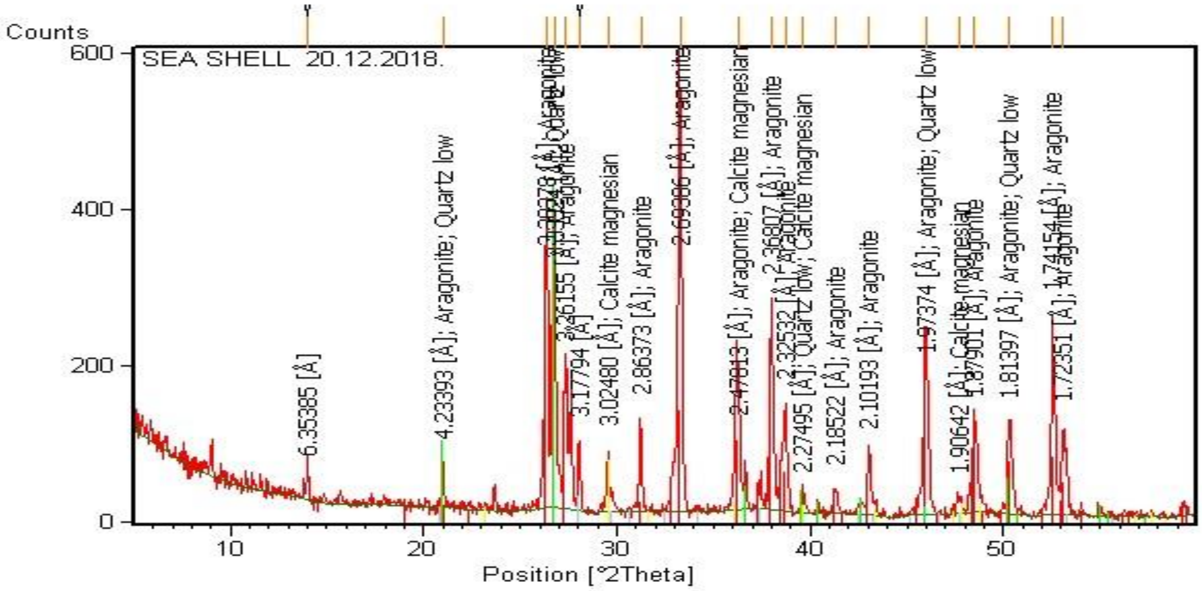


Fig 54: X-ray diffraction (XRD) of sea shell

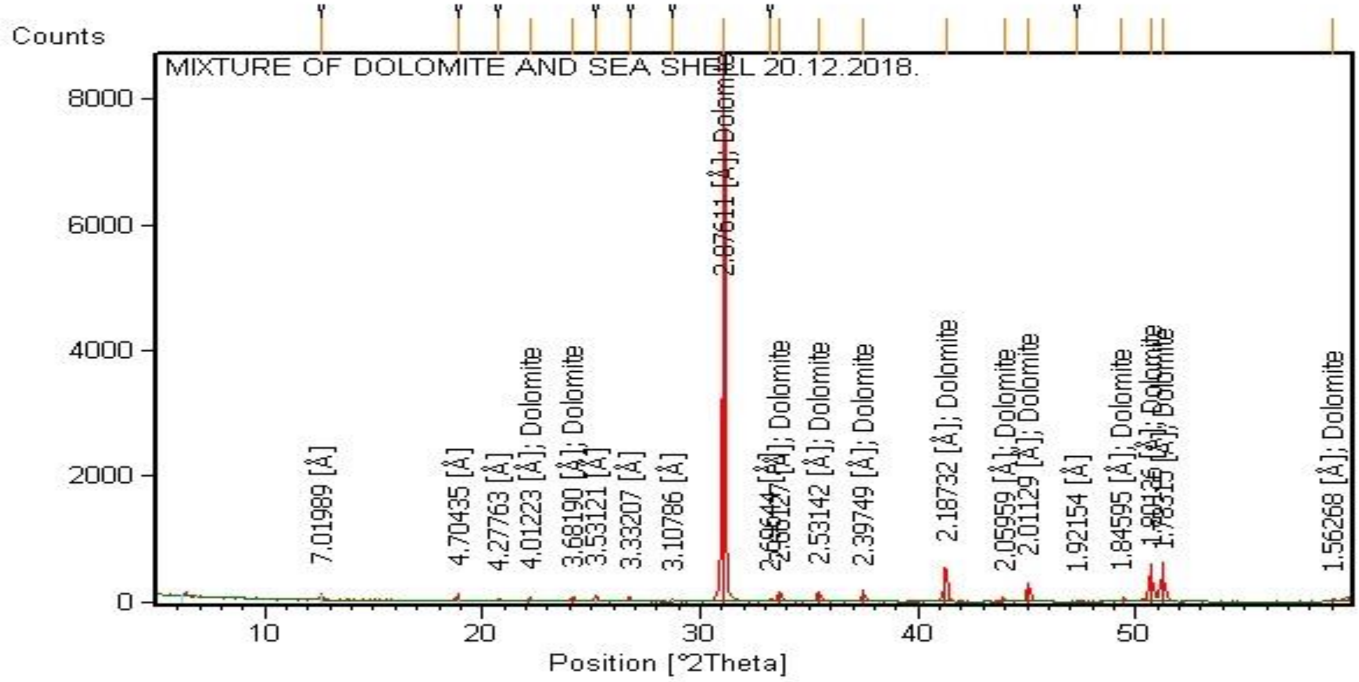


Fig 55: x-ray diffraction (XRD) of mixture

Table 20: Result of elemental distribution of adsorbents by acid digestion

Sample Name	As (ppb)	Fe (ppm)	Ca^{2+} (ppm)
Dolomite	457.83	2033.43	142
Sea shell	7481.5	7145.89	259.5
Mixture of Dolomite & Sea shell	1268.5	3201.43	167.5

Dolomite is mainly a common sedimentary rock -forming mineral. It basically consists the layers of carbonate ions (CO_3^{2-} , calcium ions (Ca^{2+}) and magnesium ions (Mg^{2+}). Thermally activated and treated dolomite at higher temperature (600Cor 800ºC) leads to change its original chemical composition and formed calcium oxide. magnesium oxide and calcite as shown in the below equation (Staszczuk et al.,1997).

$$2CaCO_3\ MgCaCO_3 \longrightarrow 2MgO + CaCO_3 + CaO + 3CO_2$$

This change of chemical composition increased in the BET surface area of the dolomite (Staszczuk et al.,1997). Again it is also reported that many fold increase in the surface area of the dolomite after thermal treatment at

800C enhances its adsorption properties (Walker et al.,2003). From the XRD and elemental distribution it is also clear that this adsorbent are highly calcium and iron enriched and calcite is in the maximum and dominating proportion which also increases the adsorption.

Seashell usually consists of an outer layer of protein followed by an intermediate layer of calcite and a smooth inner layer of platy calcium carbonate crystal. (Narayanan et al. 2006). It have important fuctional groups like -CH_2,-OH,-CO_2 and -PO_4 which make its more effective adsorbent for removal both organic and inorganic pollutants.(Chowdhury & Saha 2010).Temperature plays a vital role on the calcination process of seashell. It has been reported that thermally activated seashell (mainly at 800ºC) has the higher amount of CaO and this calcination process also increased the amount of Ca and oxygen and reduced the carbon content (Nordin et al.2015).

Hence thermally activated (at higher temperature like 600C or 800ºC) adsorbents are found most appropriate for its rapid increasing of BET surface area, pore size distribution and pore volume. (Chaudhary and Prasad).

16.2 Adsorption of Arsenic using Dolomite

16.2.1 Effect of Various parameters on adsorption of arsenic using dolomite

Effect of pH on removal of arsenic

Experiment

Initial pH: 3-12
Arsenic conc.: 100 µg/L
Dolomite dose: 10 gm/L
Contact time: 20 min
Temperature: 30C (RT)
Contact speed: 40 RPM

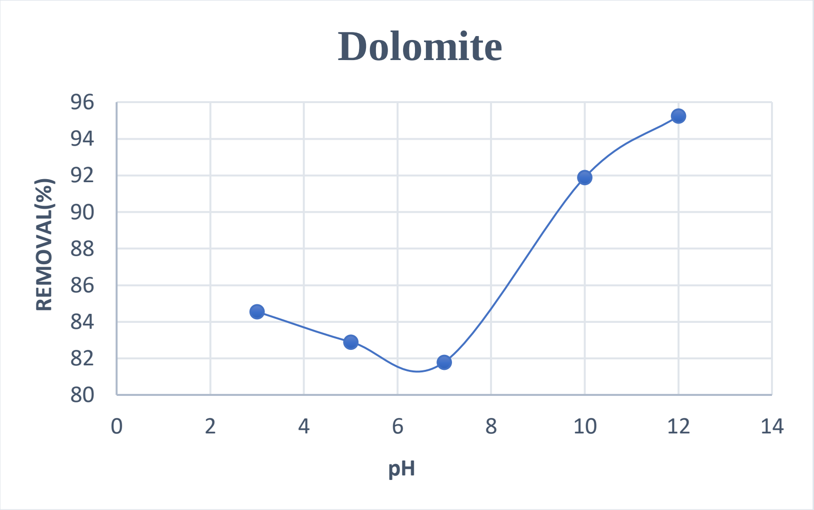


Fig 56: Removal (%) vs pH Graph

Effect of Adsorption Dose on removal of arsenic

Experiment

Initial pH : 5

Arsenic conc. : 100 µg/L

Dolomite dose: 5-34 gm/L

Contact time : 20 min

Temperature : 30C (RT)

Contact speed: 40 RPM

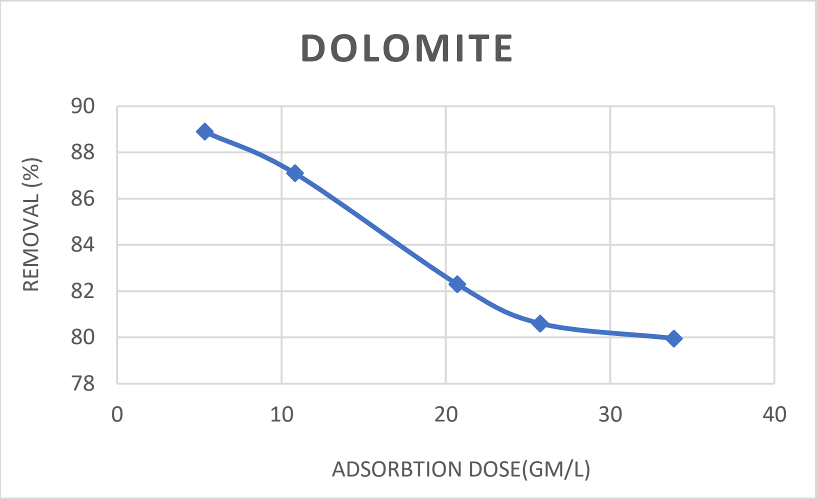


Fig 5: Removal (%) vs adsorbent dose graph

Effect of Contact speed on removal of arsenic

Experiment

Initial pH : 5-6

Arsenic conc. : 100 µg/L

Dolomite dose: 10 gm/L

Contact time : 20 min

Temperature : 30C (RT)

Contact speed: 30-60 RPM

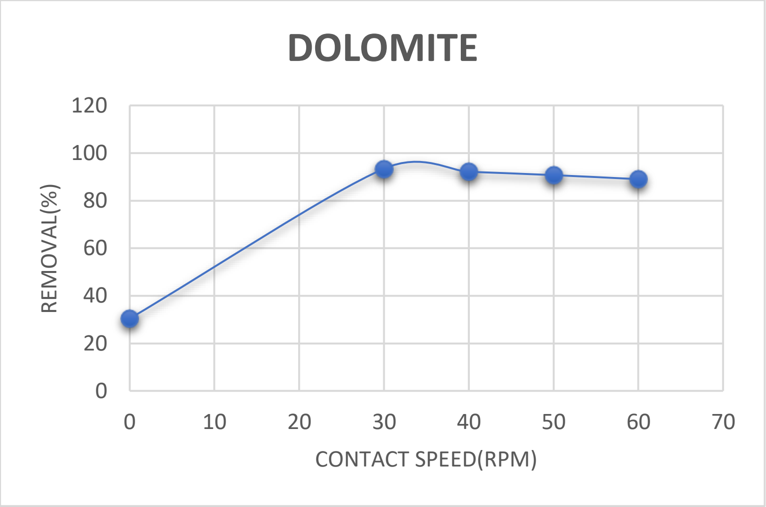


Fig 58: Removal (%) vs contact speed graph

Effect of Arsenic Concentration on removal of arsenic

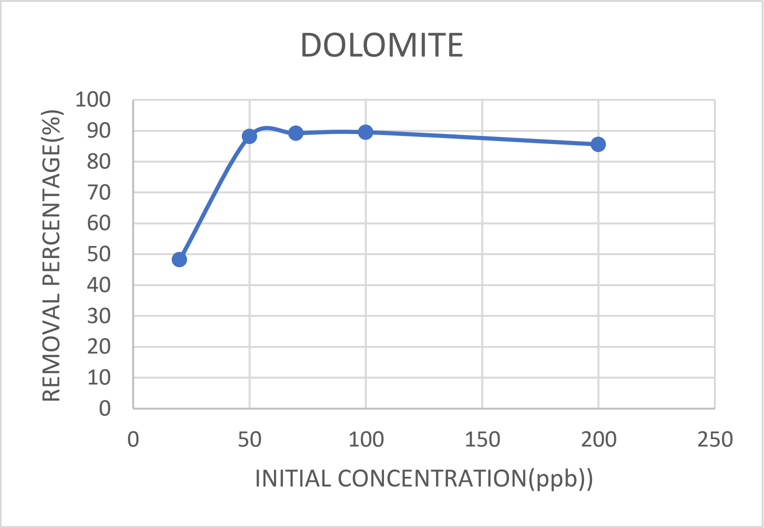


Fig 59: Removal (%) vs initial arsenic concentration(ppb) graph

Experiment

Initial pH : 5

Arsenic conc : 20,50,70,100 and 200 µg/L

Dolomite dose: 10 gm/L

Contact time : 20 min

Temperature : 30C (RT)

Contact speed 40 RPM

Effect of Contact time on removal of arsenic

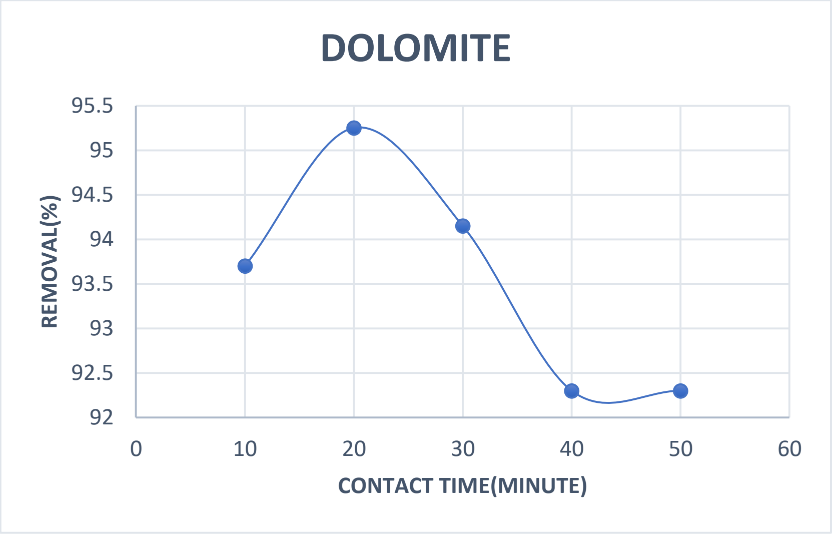


Fig 60: Removal (%) vs contact time graph

Experiment

Initial pH : 5-6

Arsenic conc. : 100 µg/L

Dolomite dose : 10 gm/L

Contact time : 10-50 min

Temperature : 30C (RT)

Contact speed : 40 RPM

Effect of activated temperature of adsorbent for removal of arsenic

Experiment

Initial pH : 5-6

Arsenic conc : 100 ppb

Dolomite dose : 10 gm/L

Contact time : 20 min

Temperature : RT,70,100,200 & 600°C

Contact speed: 40 RPM

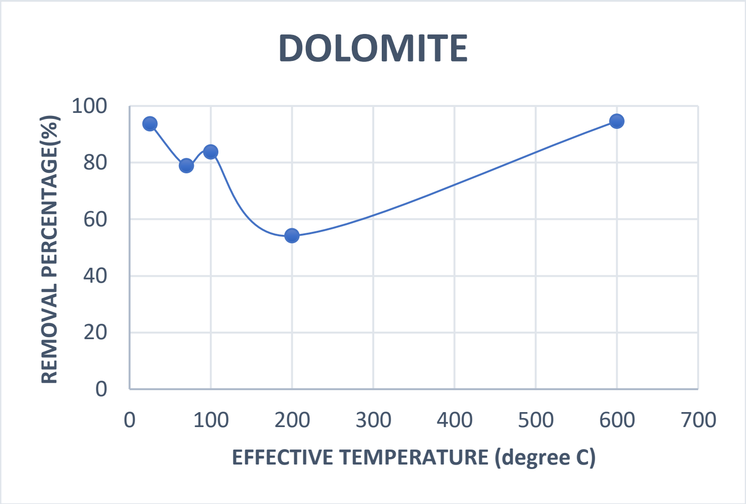


Fig 61: Removal (%) vs activated temperature of Dolomite graph

16.2.2 Adsorption Isotherms on removal of arsenic using dolomite

Langmuir model

This model given in Equation

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}}$$

C_e = arsenic concentration during equilibrium (mg/L)

q_e = quantity of adsorbate (µg) adsorbed per adsorbent (gm) at the equilibrium

q_{max} = Langmuir constant linked to max adsorption (µg of adsorbate / gm of adsorbent)

b = free energy during adsorption (L/mg)

The important characteristic of Langmuir isotherm is that it is used to evaluate R_L, the constant separation factor (dimensionless) as

$$R_L = \frac{1}{1 + bC_0}$$

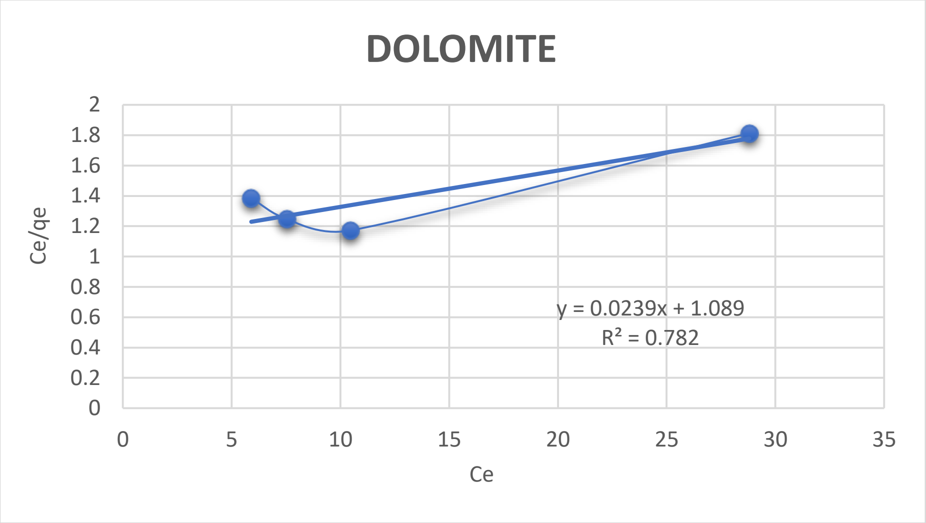


Fig 62: C_e/q_e vs C_e of Dolomite graph

$$\begin{array}{lccccc} R_L = & 0.476 & 0.393 & 0.312 & 0.185 & \\ C_0 = & 50 & 70 & 100 & 200 & \mu g/L \end{array}$$

Since R_L lies within 0 and 1, the Langmuir isotherm is favourable within experimental range.

Freundlich model

This model is given in Equation

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

C_e = Arsenic concentration during equilibrium (μg/L)

q_e = quantity of adsorbate (μg) adsorbed per adsorbent (gm) at the equilibrium

K_f = Freundlich constant linked to capacity of adsorption

n = Freundlich constant linked to strength of the adsorption

The magnitude of K_f represents easy removal of arsenic from the groundwater.The value of n represents intensity of adsorption follows the limit

$$(0 < \frac{1}{n} < 1)$$

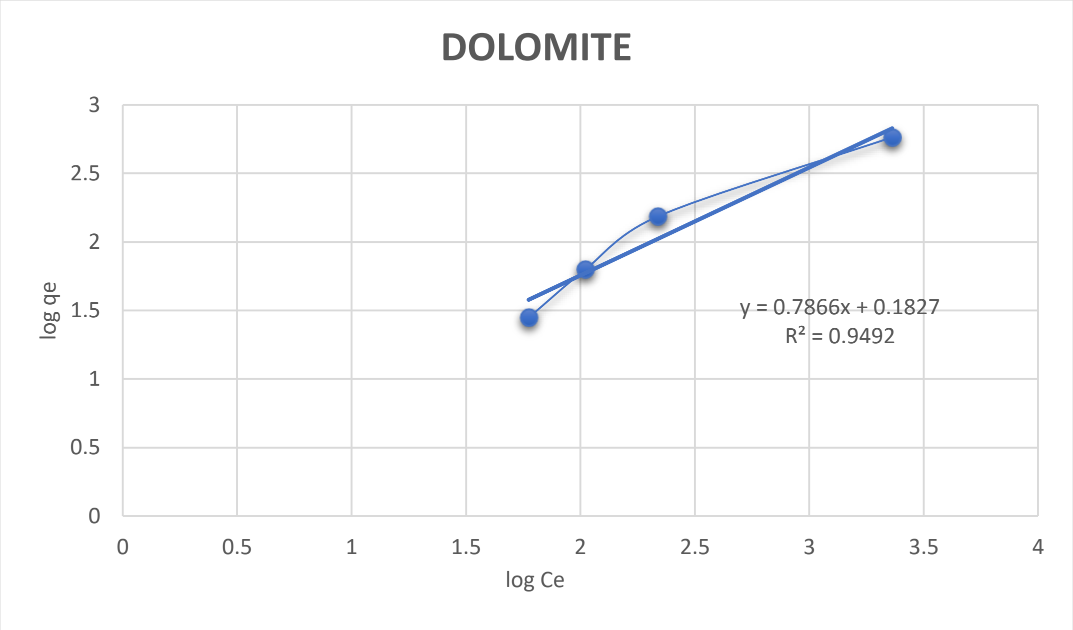


Fig 63: log q_e vs log C_e graph

Table 21: Adsorption isotherm datasheet for dolomite

Langmuir isotherm			*Freundlich isotherm*		
q_{max} **(µg/gm)**	***b* (L/mg)**	r^2	K_f	***n***	r^2
41.84	**0.022**	**0.782**	**1.197**	**1.268**	**0.9494**

The Table infers that all three isotherm models are applicable because of the high correlation coefficients (r^2), however the Freundlich is the best supportive and the monolayer adsorption capacity is found to be 41.84 µg/gm.

16.2.3 Adsorption kinetics on removal of arsenic using dolomite

The present study was undertaken to evaluate the effectiveness of the dolomite, sea shell and their mixture for the removal of arsenic by adsorption. Laboratory batch kinetic studies were con- ducted to determine the adsorption behavior of the adsorbents. The pH of the solution was maintained in the range of 5.5 - 9.0 (pH limits for effluents as recommended by Central Pollution control Board, India).

Pseudo 1st order kinetic model

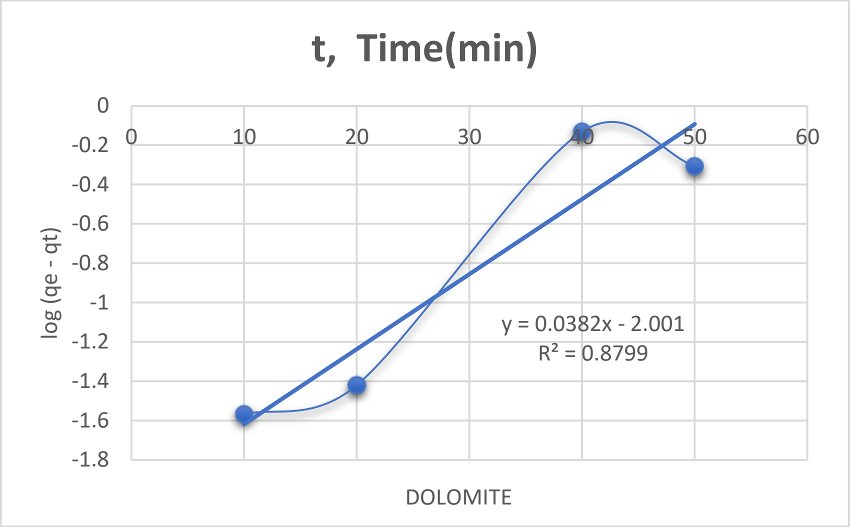


Fig 64: The graph of log(q_e-q_t) vs t (pseudo 1st order kinetic model)

Pseudo 2nd order kinetic model

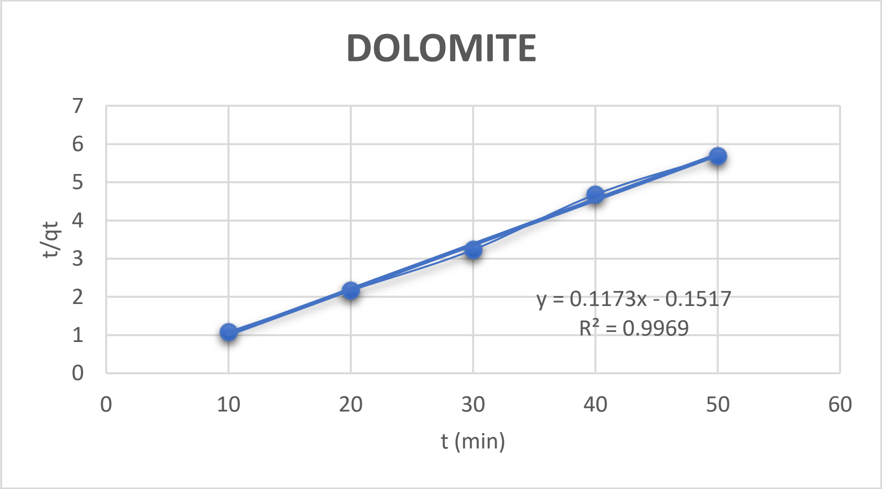


Fig 65: The graph of t/q_t vs t (pseudo 2nd order kinetic model)

Table 23: Adsorption kinetics datasheet for dolomite

C_o (µg/L)	$q_{e,\ exp}$ (µg/gm)	*Pseudo first order*			*Pseudo second order*		
		K_{ad} (1/min)	$q_{e,\ cal}$ (µg/gm)	r^2	K' (gm/µg min)	$q_{e,\ cal}$ (µg/gm)	r^2
100	9.285	0.0879	100.23	0.8790	0.0907	8.525	0.9969

16.3 Adsorption of Arsenic using Seashell

16.3.1 Effect of Various parameters on adsorption of arsenic using seashell

Effect of pH on removal of arsenic

Experiment

Initial pH: 3-12

Arsenic conc.: 100 µg/L

Sea shell dose: 10 gm/L

Contact time: 20 min

Temperature: 30C (RT)

Contact speed: 40 RPM

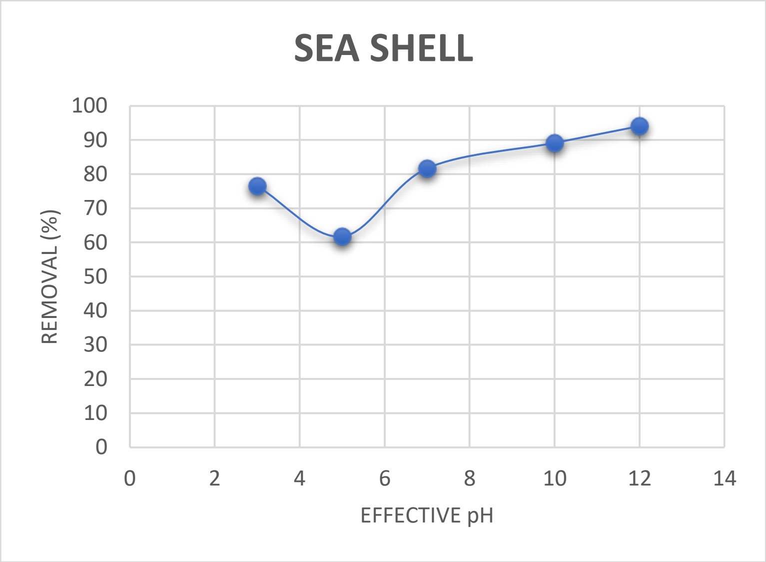


Fig 66: Removal (%) vs pH Graph

Effect of Adsorption Dose on removal of arsenic

Experiment

Initial pH : 5

Arsenic conc. : 100 µg/L

Sea shell dose: 5-34 gm/L

Contact time : 20 min

Temperature : 30C (RT)

Contact speed: 40 RPM

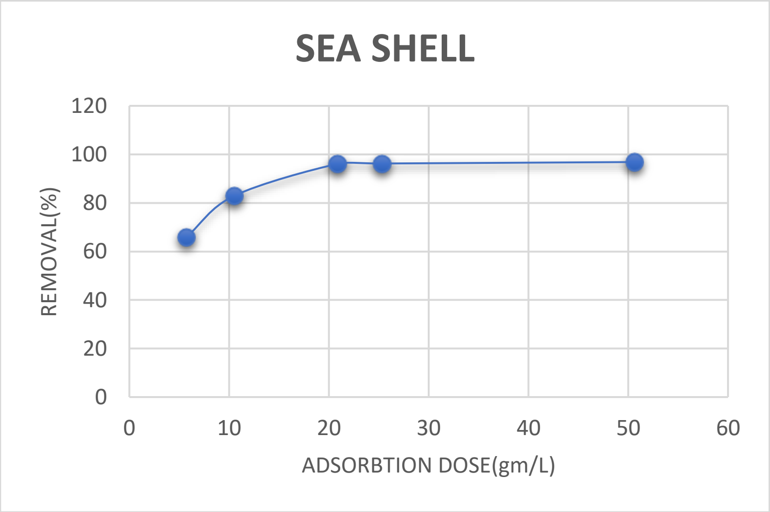


Fig 67: Removal (%) vs adsorbent dose graph

Effect of Contact speed on removal of arsenic

Experiment

Initial pH : 5-6

Arsenic conc. : 100 µg/L

Sea shell dose: 10 gm/L

Contact time : 20 min

Temperature : 30C (RT)

Contact speed: 30-60 RPM

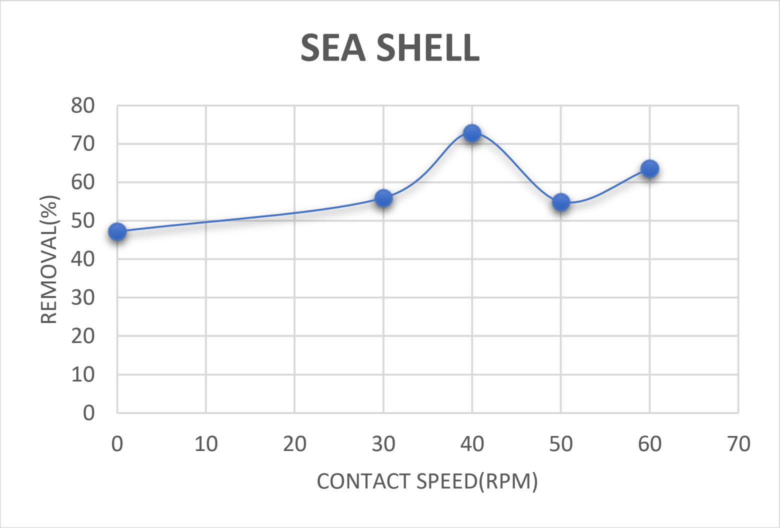


Fig 68: Removal (%) vs contact speed graph

Effect of Arsenic Concentration on removal of arsenic

Experiment

Initial pH : 5

Arsenic conc : 20,50,70,100 and 200 µg/L

Sea shell dose: 5-34 gm/L

Contact time : 20 min

Temperature : 30C (RT)

Contact speed 40 RPM

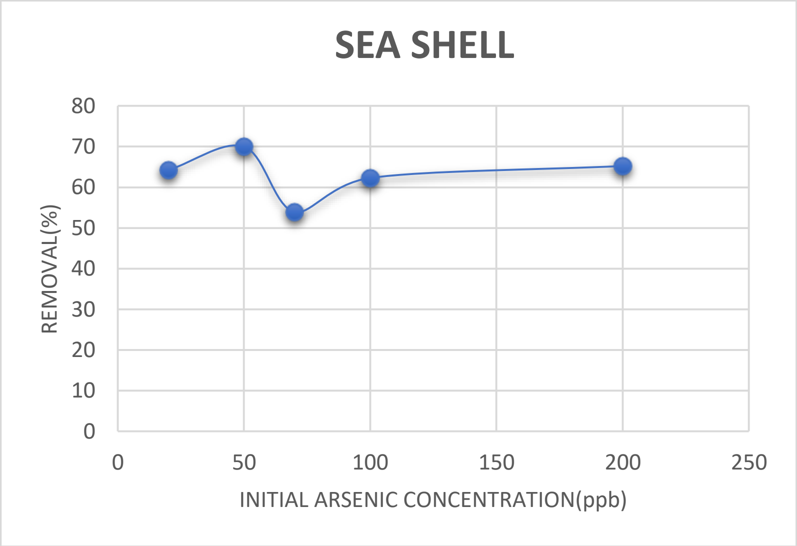
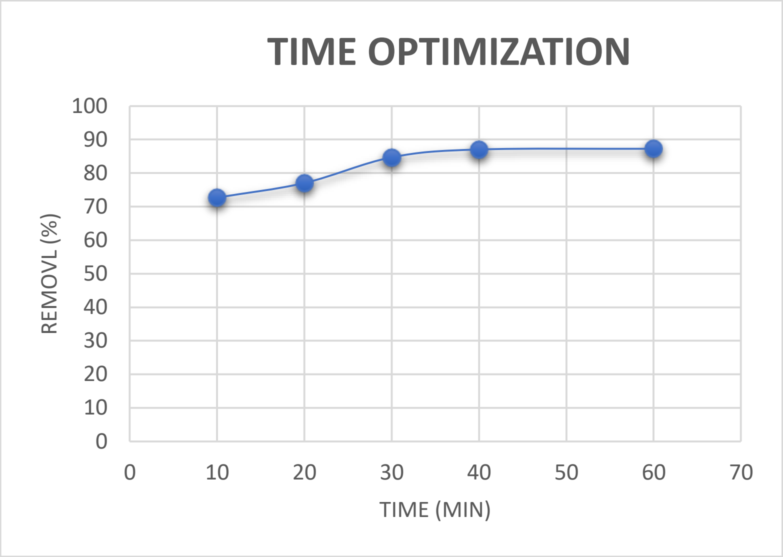


Fig 69: Removal (%) vs initial arsenic concentration(ppb) graph

Effect of Contact time on removal of arsenic



Experiment

Initial pH : 5-6

Arsenic conc. : 100 µg/L

Sea shell dose : 10 gm/L

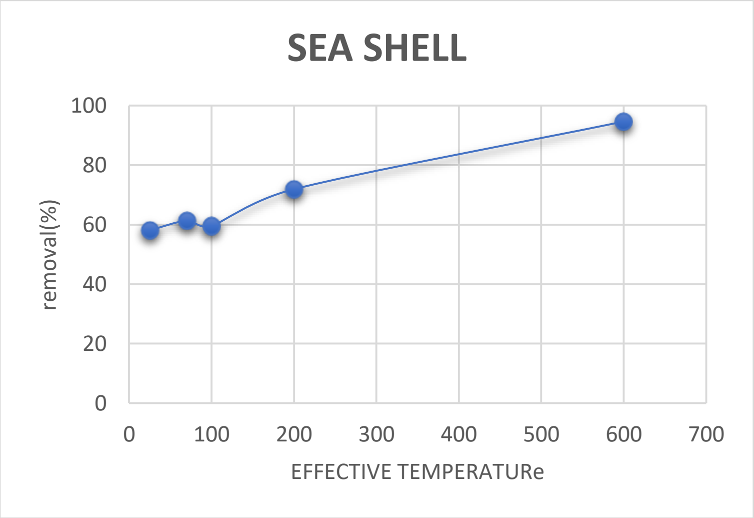
Contact time : 10-50 min

Temperature : 30C (RT)

Contact speed : 40 RPM

Fig 70: Removal (%) vs contact time graph

Effect of activated temperature of adsorbent for removal of arsenic



Experiment

Initial pH : 5-6

Arsenic conc : 100 ppb

Sea shell dose : 10 gm/L

Contact time : 20 min

Temperature : RT, 70,100,200 & 600°C

Contact speed: 40 RPM

Fig 71 : Removal (%) vs activated temperature graph

16.3.2 Adsorption Isotherms on removal of arsenic using seashell

Langmuir model

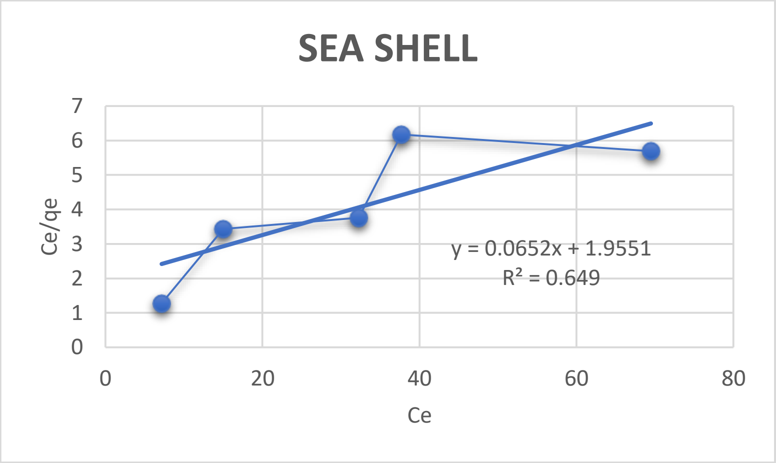


Fig 72: C_e/q_e vs C_e graph

R_L = 0.476 0.393 0.312 0.185

C_0 = 50 70 100 200 μg/L

Since RL lies within 0 and 1, the Langmuir isotherm is favourable within experimental range

Freundlich model

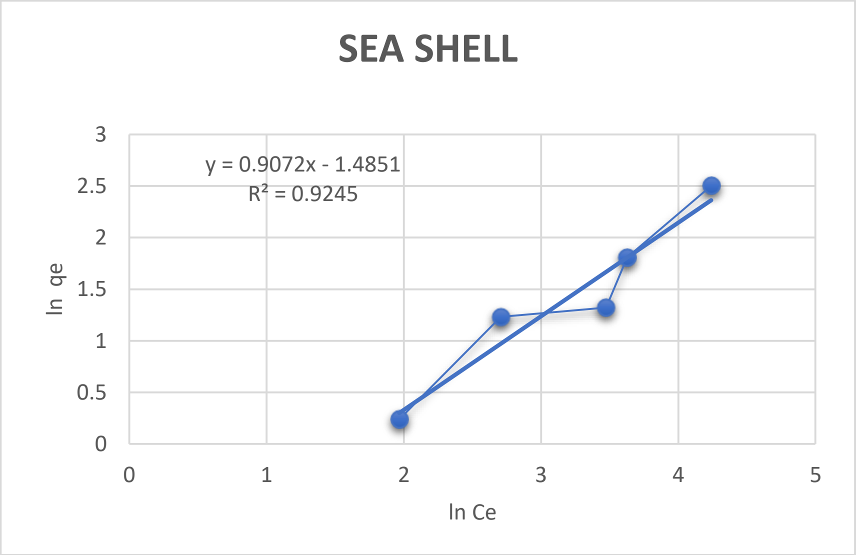


Fig 73: log q_e vs log C_e graph

Table 24: Adsorption isotherm datasheet for Sea shell

Langmuir isotherm			*Freundlich isotherm*		
q_{max} (µg/gm)	*b* (L/mg)	r^2	K_f	*n*	r^2
15.34	**0.0333**	**0.64**	**0.2264**	**1.10**	**0.9245**

The Table infers that all three isotherm models are applicable because of the high correlation coefficients (r^2), however the Freundlich is the best supportive and the monolayer adsorption capacity is found to be 15.34 µg/gm.

16.3.3 Adsorption kinetics on removal of arsenic using seashell

<u>Adsorption Kinetic study of arsenic by Sea Shell</u>

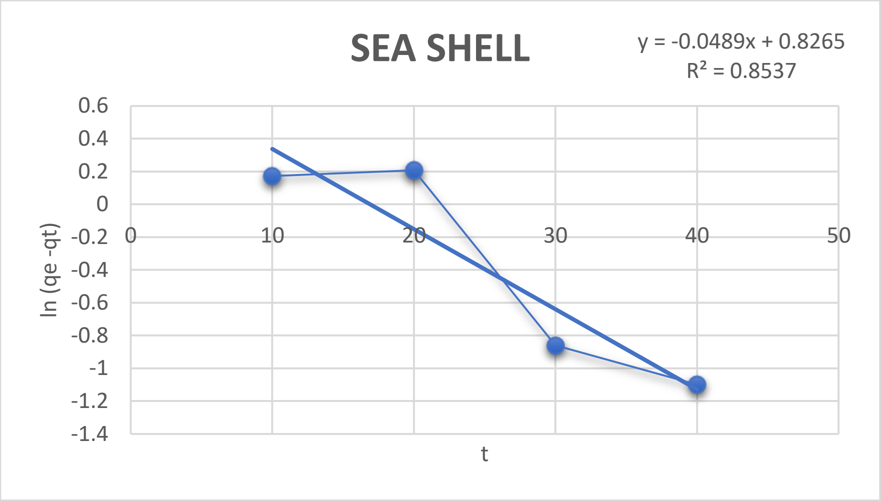


Fig 74: The graph of log(q_e-q_t) vs t (pseudo 1st order kinetic model)

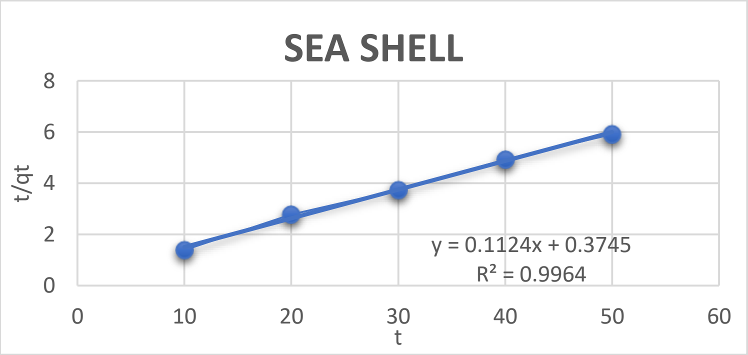


Fig 75: The graph of t/q_t vs t (pseudo 2nd order kinetic model)

Table 25: Adsorption kinetics datasheet for sea shell

C_o (µg/L)	$q_{e,\,exp}$ (µg/gm)	Pseudo first order			Pseudo second order		
		K_{ad} (1/min)	$q_{e,\,cal}$ (µg/gm)	r^2	K' (gm/µg min)	$q_{e,\,cal}$ (µg/gm)	r^2
100	8.450	0.0489	2.285	0.854	0.034	8.896	0.9964

16.4 Adsorption of Arsenic using mixture

16.4.1 Effect of Various parameters on adsorption of arsenic using mixture

<u>Effect of pH on removal of arsenic</u>

<u>Experiment</u>

Initial pH: 3-12

Arsenic conc.: 100 µg/L

Mixture dose: 10 gm/L

Contact time: 20 min

Temperature: 30C (RT)

Contact speed: 40 RPM

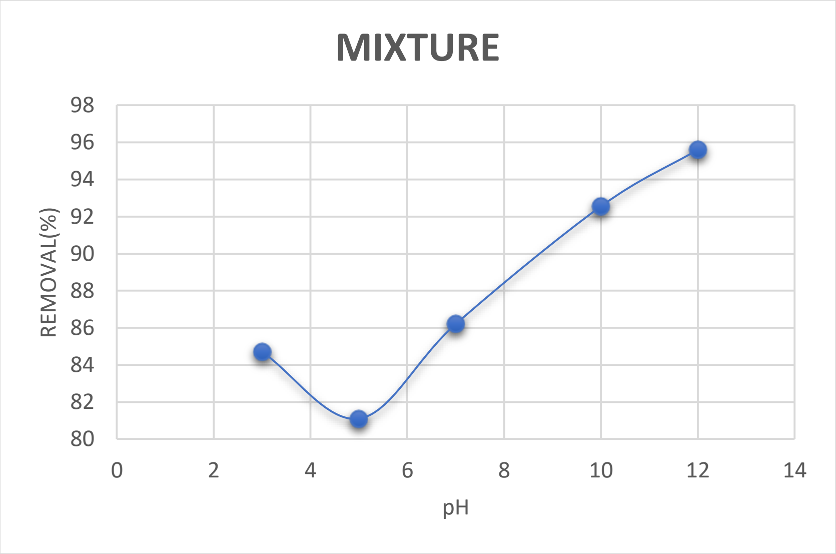
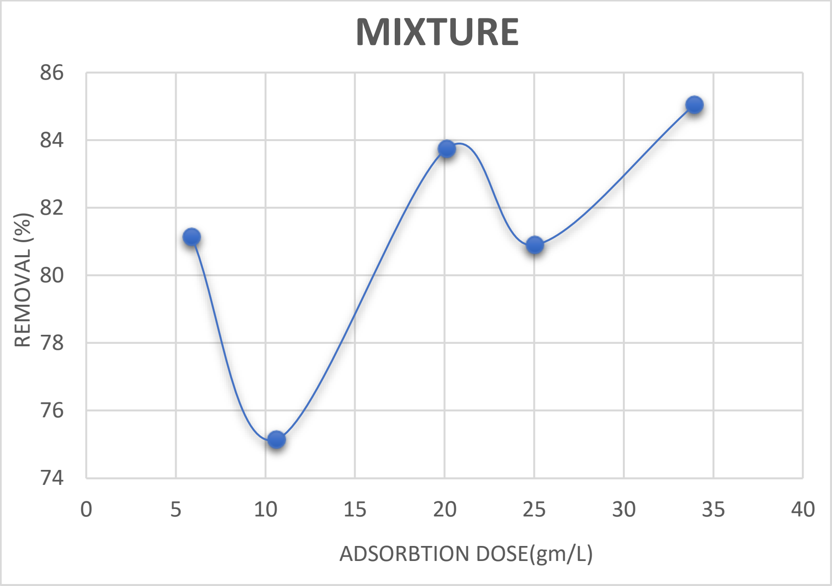


Fig 76: Removal (%) vs pH Graph

Effect of Adsorption Dose on removal of arsenic



Experiment

Initial pH : 5

Arsenic conc. : 100 µg/L

Mixture dose: 5-34 gm/L

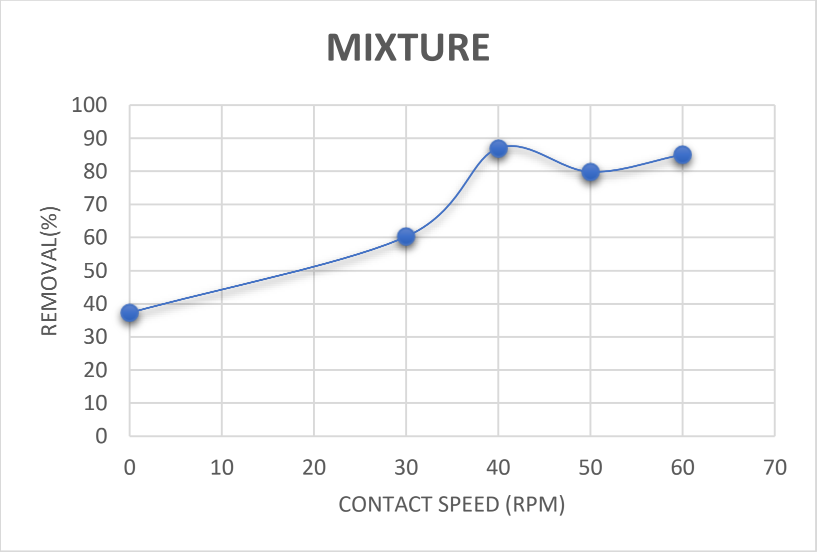
Contact time : 20 min

Temperature : 30C (RT)

Contact speed: 40 RPM

Fig 77: Removal (%) vs adsorbent dose graph

Effect of Contact speed on removal of arsenic



Experiment

Initial pH : 5-6

Arsenic conc. : 100 µg/L

Mixture dose: 10 gm/L

Contact time : 20 min

Temperature : 30C (RT)

Contact speed: 30-60 RPM

Fig 78: Removal (%) vs contact speed graph

Effect of Arsenic Concentration on removal of arsenic

Experiment

Initial pH : 5

Arsenic conc : 20,50,70,100 and 200 µg/L

Mixture dose: 5-34 gm/L

Contact time : 20 min

Temperature : 30C (RT)

Contact speed 40 RPM

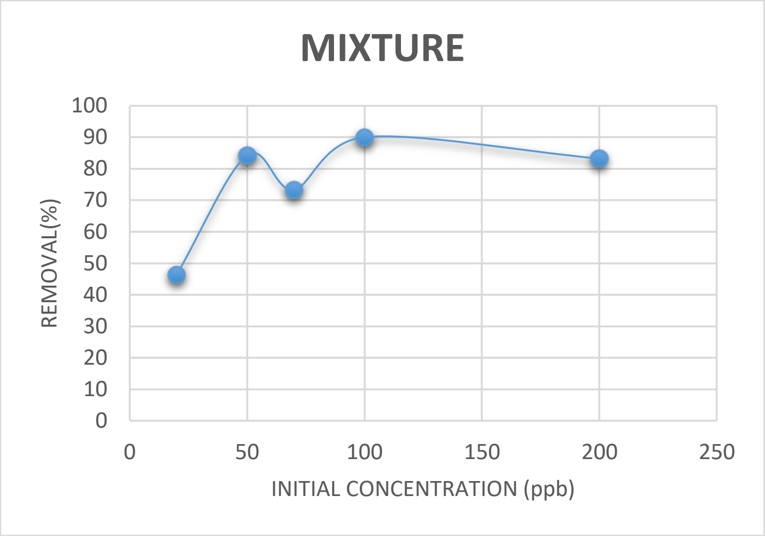


Fig 79: Removal (%) vs initial arsenic Concentration (ppb) graph

Effect of Contact time on removal of arsenic

Experiment

Initial pH : 5-6

Arsenic conc. : 100 µg/L

Mixture dose : 10 gm/L

Contact time : 10-50 min

Temperature : 30C (RT)

Contact speed : 40 RPM

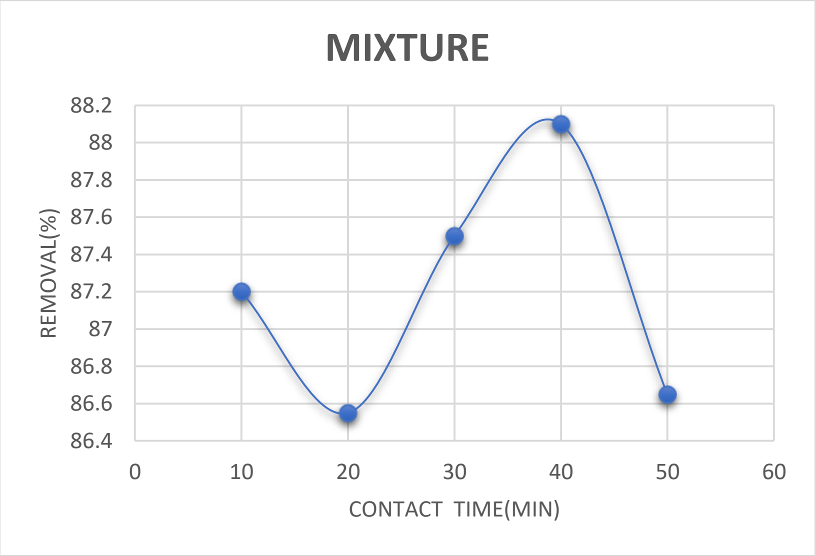
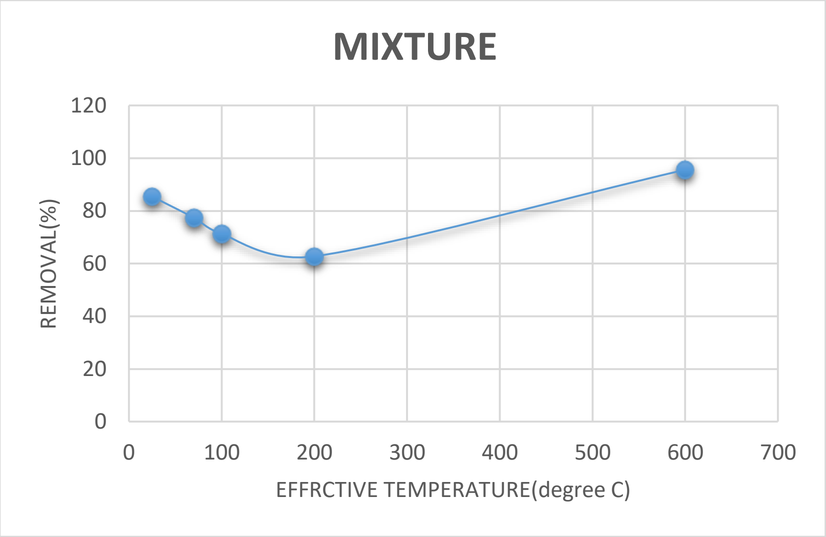


Fig 80: Removal (%) vs contact time graph

Effect of activated temperature of adsorbent for removal of arsenic



Experiment

Initial pH : **5-6**

Arsenic conc : **100 ppb**

Mixture dose : **10 gm/L**

Contact time : **20 min**

Temperature : **RT, 70,100,200 & 600°C**

Contact speed: **40 RPM**

Fig 81: Removal (%) vs activated temperature graph

16.4.2. Adsorption Isotherms on removal of arsenic using mixture

Langmuir model

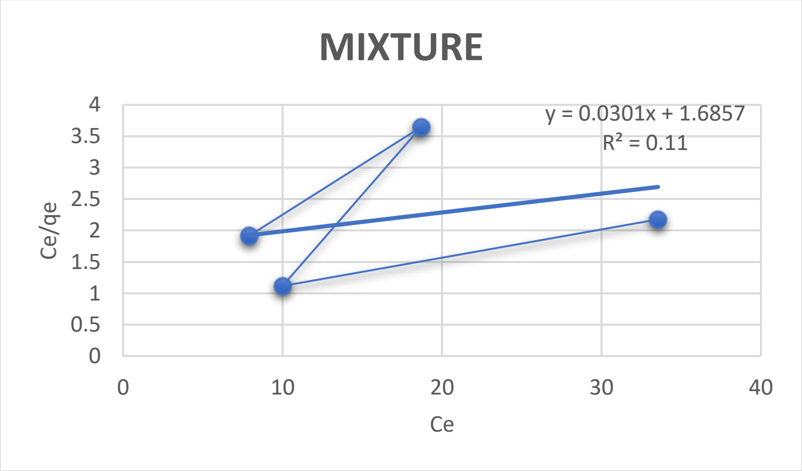


Fig 82: C_e/q_e vs C_e graph

$$R_L = \frac{1}{1 + bC_0}$$

R_L = 0.529 0.445 0.350 0.219
C_0 = 50 70 100 200 µg/L

Since RL lies within 0 and 1, the Langmuir isotherm is favourable within experimental range

Freundlich model

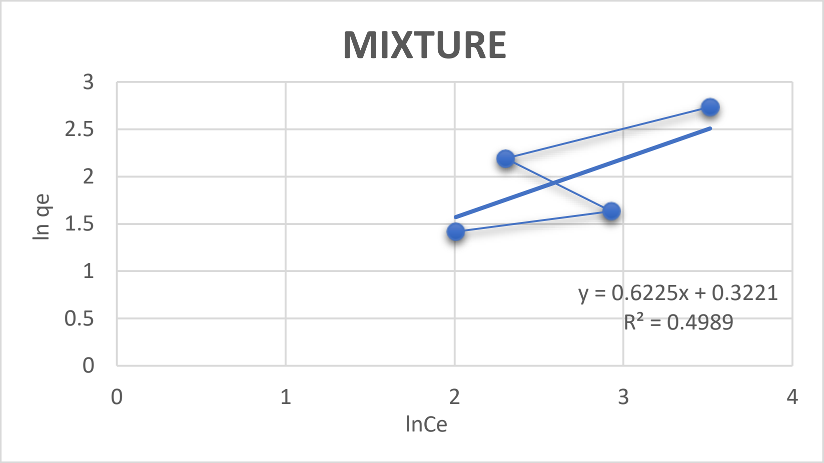


Fig 83: log qe vs log Ce graph

Table 26: Adsorption isotherm datasheet for mixture

Langmuir isotherm			*Freundlich isotherm*		
q_{max} (µg/gm)	***b (L/mg)***	***r^2***	***K_f***	***n***	***r^2***
33.22	**0.0178**	**0.11**	**1.38**	**1.606**	**0.498**

The Table infers that all isotherm models are applicable because of the high correlation coefficients (r^2), however the Freundlich is the best supportive and the monolayer adsorption capacity is found to be 33.22 µg/gm.

16.4.3 Adsorption kinetics on removal of arsenic using mixture

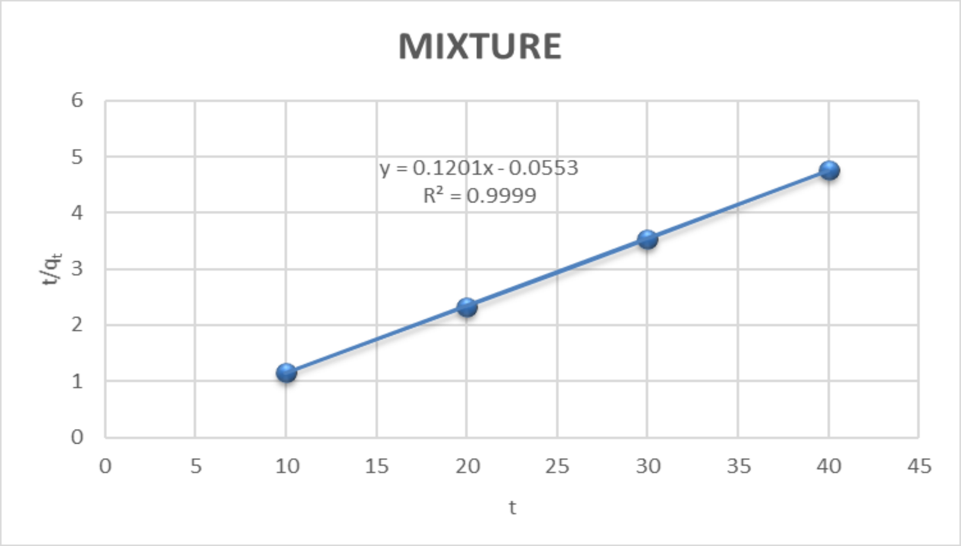


Fig 84: The graph of log(qe-qt) vs t (pseudo 1st order kinetic model)

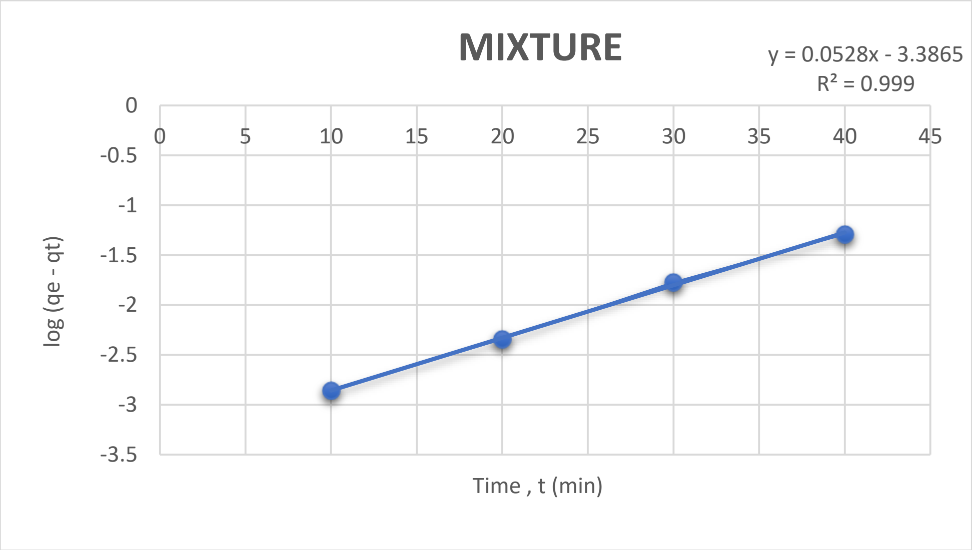


Fig 85: The graph of t/q_t vs t (pseudo 2nd order kinetic model)

Table 27: Adsorption kinetics datasheet for mixture

C_o (µg/L)	$q_{e,\,exp}$ (µg/gm)	Pseudo first order			Pseudo second order		
		K_{ad} (1/min)	$q_{e,\,cal}$ (µg/gm)	r^2	K' (gm/µg min)	$q_{e,\,cal}$ (µg/gm)	r^2
100	9.285	0.0528	0.033	0.999	0.261	8.326	0.9969

16.5 Adsorption of fluoride using dolomite

16.5.1 Effect of Various parameters on adsorption of fluoride using dolomite

Effect of pH on removal of fluoride

Experiment

Initial pH: 3-11
Fluoride conc.: 5 mg/L
Dolomite dose: 50 gm/L
Contact time: 60 min
Temperature: 800ºC
Contact speed: 40 RPM

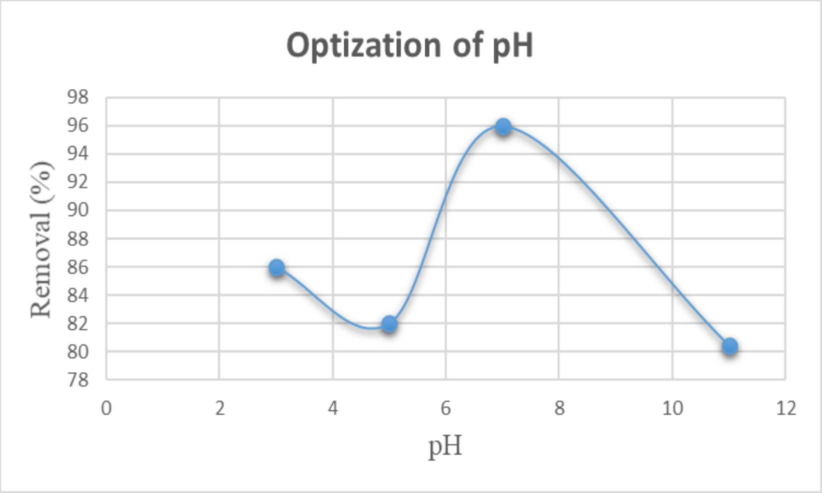
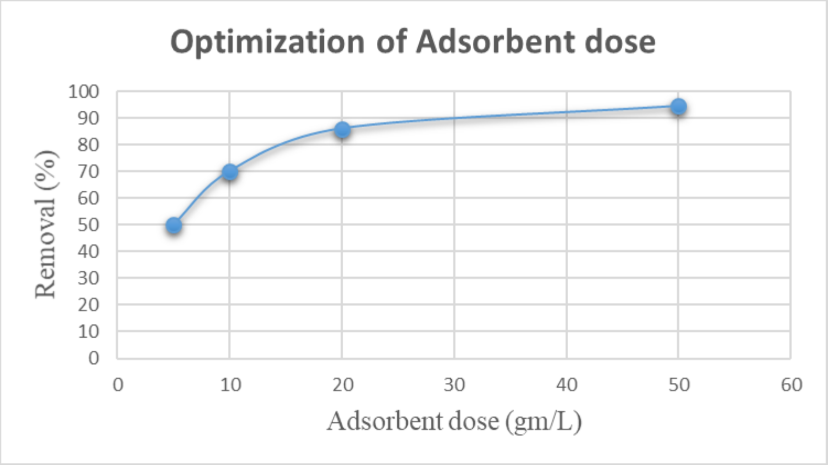


Fig 86: Removal (%) vs pH Graph

Effect of Adsorption Dose on removal of fluoride



Experiment

Initial pH: 7

Fluoride conc.: 5 mg/L

Dolomite dose: 5-50 gm/L

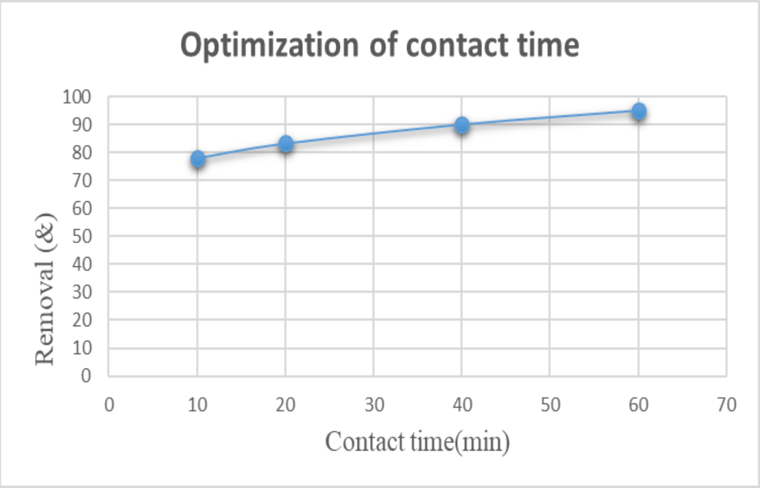
Contact time: 60 min

Temperature: 800ºC

Contact speed: 40 RPM

Fig 87: Removal (%) vs adsorbent dose graph

Effect of Contact time on removal of fluoride



Experiment

Initial pH: 7

Fluoride conc.: 5 mg/L

Dolomite dose: 50 gm/L

Contact time: 10-60 min

Temperature: 800ºC

Contact speed: 40 RPM

Fig 88: Removal (%) vs contact time graph

Effect of initial fluoride Concentration on removal of fluoride

Experiment

Initial pH: 7

Fluoride conc.: 2-10 mg/L

Dolomite dose: 50 gm/L

Contact time: 60 min

Temperature: 800°C

Contact speed: 40 RPM

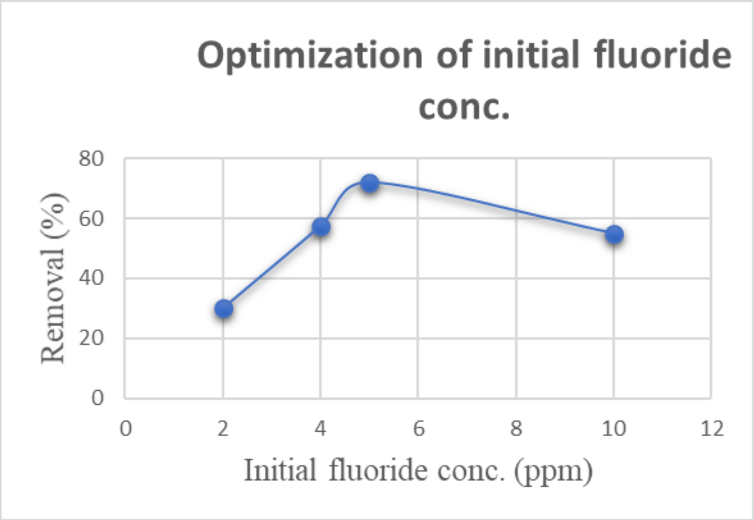


Fig 89: Removal (%) vs initial fluoride concentration(ppm) graph

16.5.2 Adsorption isotherm on removal of fluoride using dolomite

Langmuir model

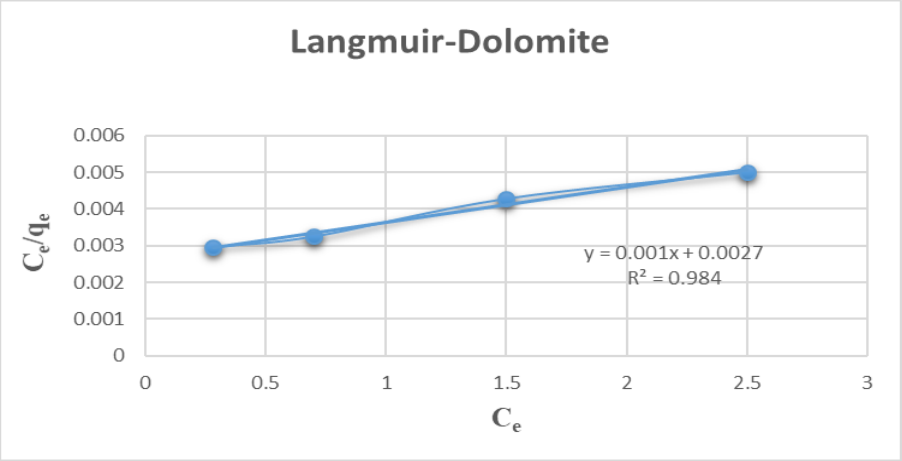


Fig 90: C_e/q_e vs C_e graph

Again from the Graph ,we can have the R_L values

$$R_L = 0.351$$

Since R_L lies within 0 and 1, the Langmuir isotherm is favourable within experimental range

Freundlich model

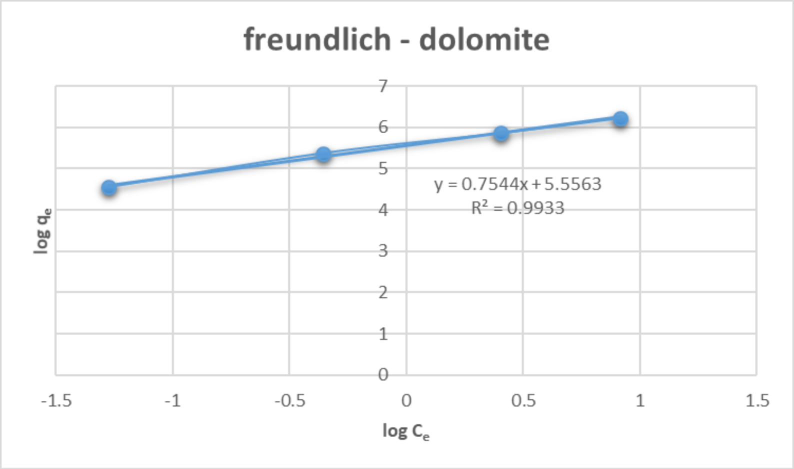


Fig 91: log q_e vs log C_e graph

Table 28: Adsorption isotherm datasheet for dolomite:

Langmuir isotherm			***Freundlich isotherm***		
q_{max} (µg/gm)	***b (L/mg)***	***r^2***	***K_f***	***n***	***r^2***
1000	**0.37**	**0.984**	**258.86**	**1.32**	**0.9933**

16.5.3 Adsorption kinetics on removal of fluoride using dolomite

Adsorption Kinetic study of fluoride by dolomite

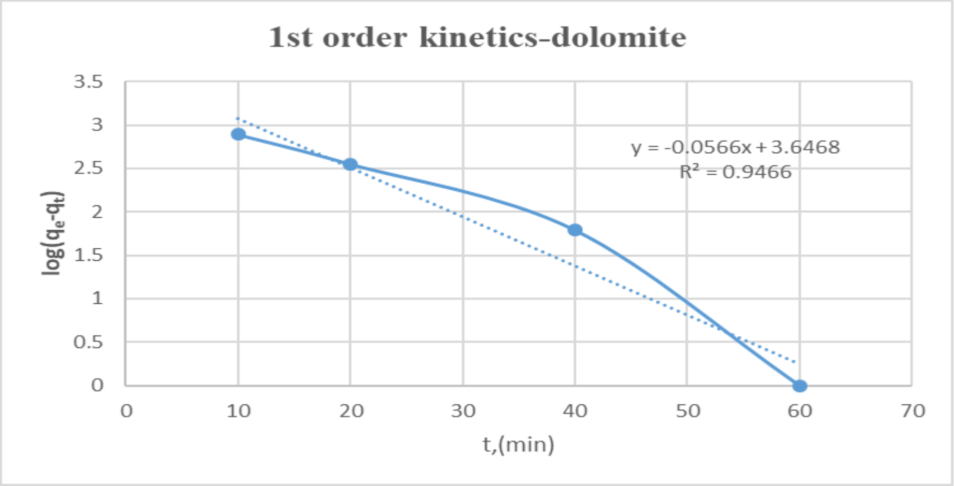


Fig 92: The graph of log(q_e-q_t) vs t (pseudo 1st order kinetic model)

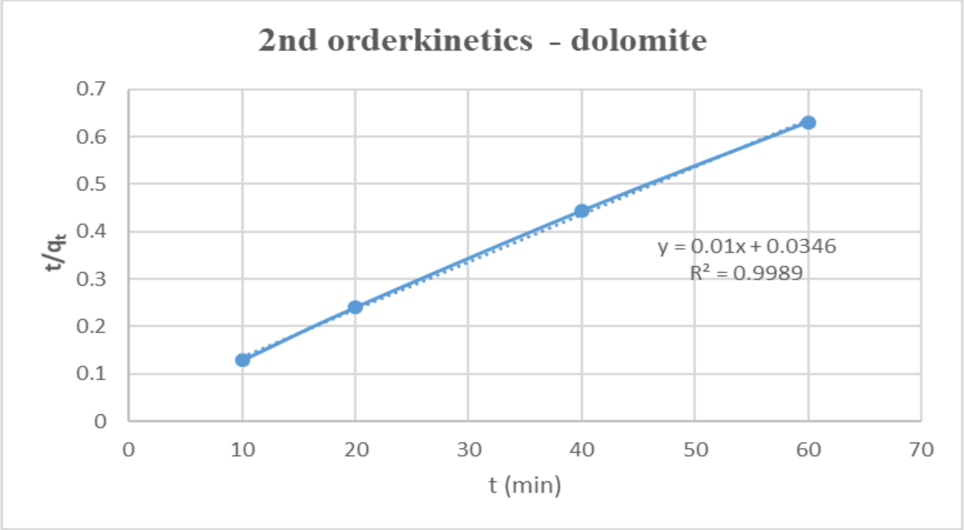


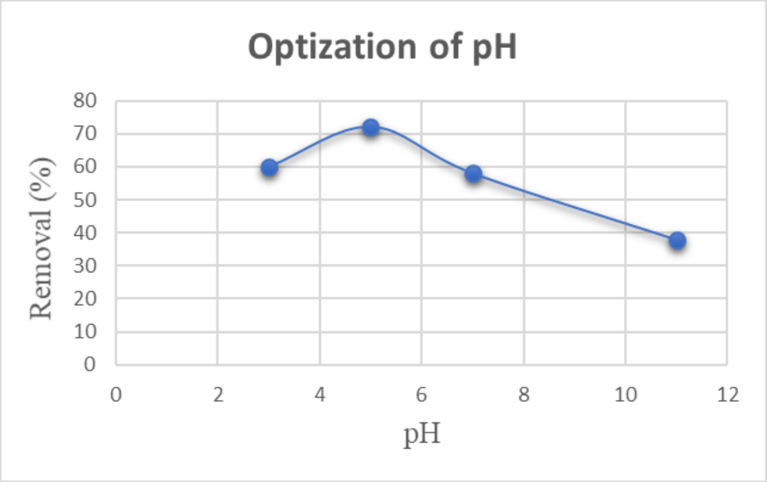
Fig 93: The graph of t/q_t vs t (pseudo 2nd order kinetic model)

Table 29: Adsorption kinetics datasheet for dolomite

C_o (mg/L)	$q_{e,\,exp}$ (µg/gm)	*Pseudo first order*			*Pseudo second order*		
		K_{ad} (1/min)	$q_{e,\,cal}$ (µg/gm)	r^2	K' (gm/µg min)	$q_{e,\,cal}$ (µg/gm)	r^2
5	**90**	**0.057**	**38.55**	**0.9466**	**0.0028**	**100**	**0.9989**

16.6 Adsorption of fluoride using sea shell

16.6.1 Effect of pH on removal of fluoride



Experiment

Initial pH: 3-11

Fluoride conc.: 5 mg/L

Sea shell dose: 50 gm/L

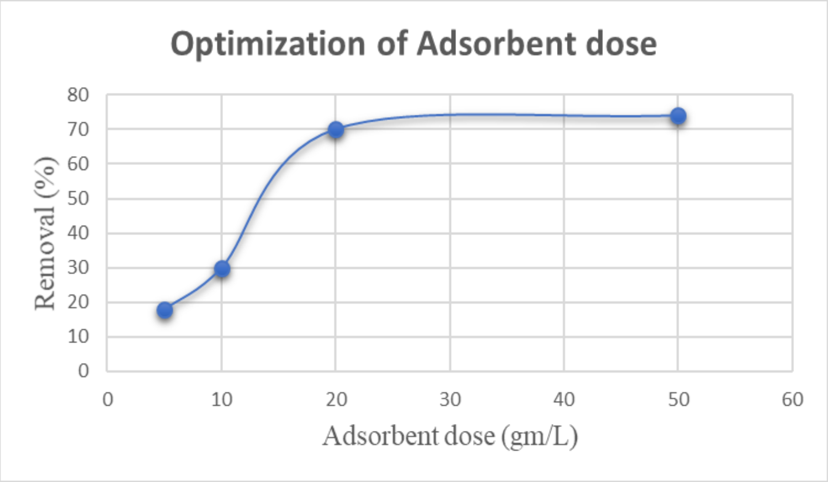
Contact time: 60 min

Temperature: 800ºC

Contact speed: 40 RPM

Fig 94: Removal (%) vs pH Graph

Effect of Adsorption Dose on removal of fluoride



Experiment

Initial pH: 5

Fluoride conc.: 5 mg/L

Sea shell dose: 5-50 gm/L

Contact time: 60 min

Temperature: 800ºC

Contact speed: 40 RPM

Fig 95: Removal (%) vs adsorbent dose graph

Effect of Contact time on removal of fluoride

Experiment

Initial pH: 5

Fluoride conc.: 5 mg/L

Sea shell dose: 50 gm/L

Contact time: 10-60 min

Temperature: 800°C

Contact speed: 40 RPM

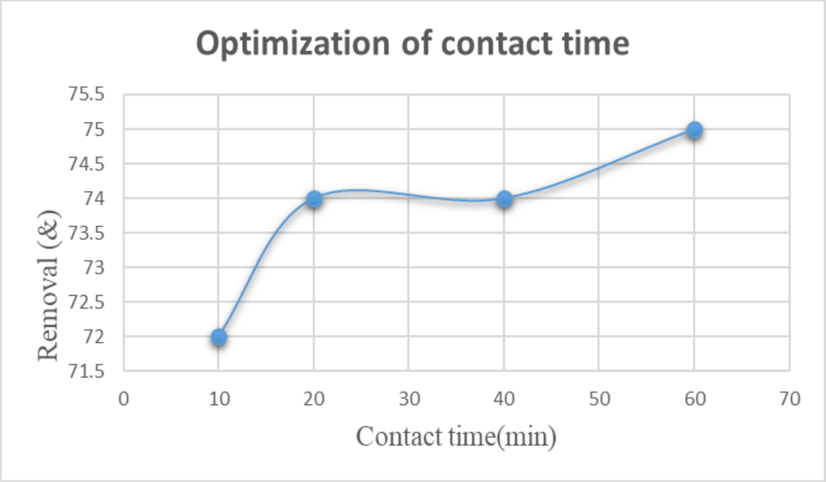


Fig 96: Removal (%) vs contact time graph

Effect of initial fluoride Concentration on removal of fluoride

Experiment

Initial pH: 5

Fluoride conc.: 2-10 mg/L

Sea shell dose: 50 gm/L

Contact time: 60 min

Temperature: 800°C

Contact speed: 40 RPM

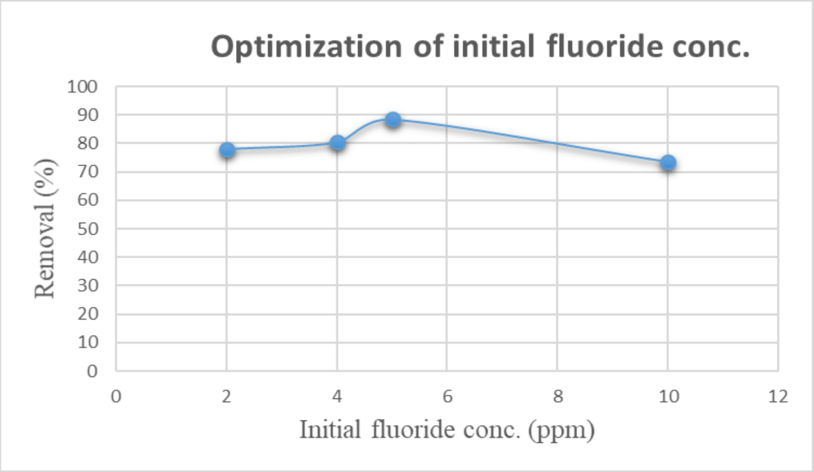


Fig 97: Removal (%) vs initial fluoride Concentration (ppm) graph

16.6.2 Adsorption Isotherm Models of fluoride by sea shell

Langmuir model

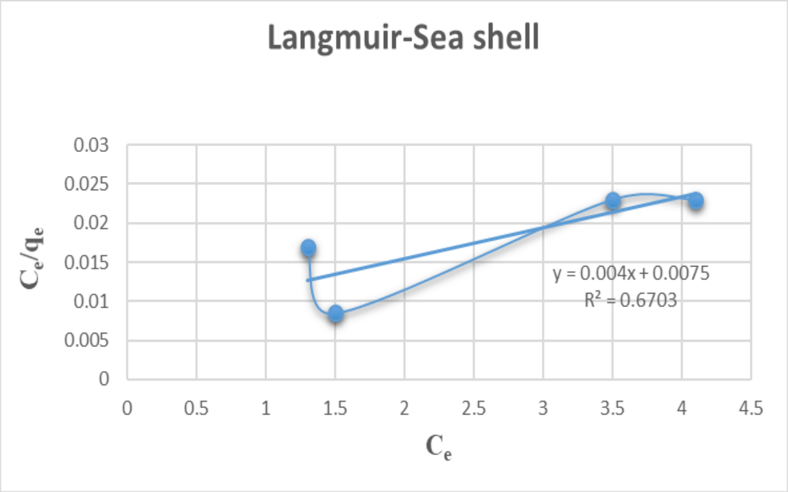


Fig 98: C_e/q_e vs C_e graph

Again from the Graph ,we can have the R_L values

$R_L = 0.274$

Since R_L lies within 0 and 1, the Langmuir isotherm is favourable within experimental range

Freundlich model

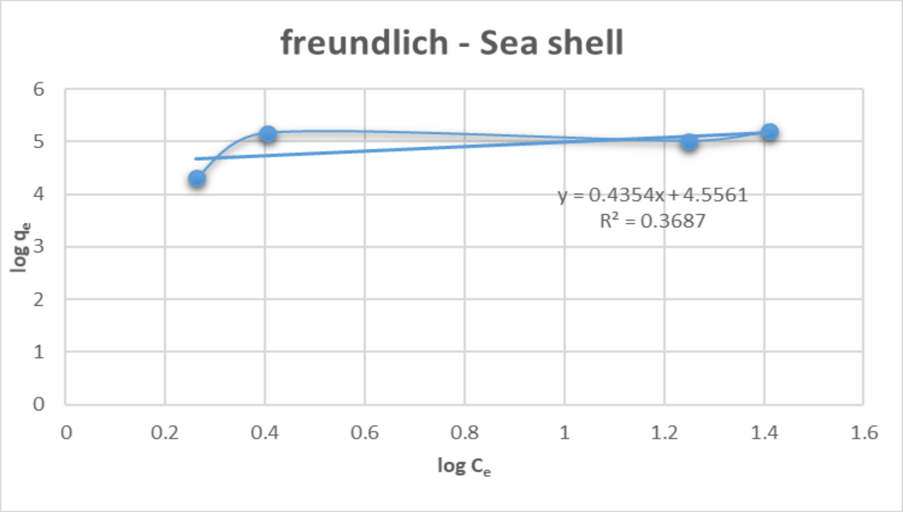


Fig 99: log q_e vs log C_e graph

Table 30: Adsorption isotherm datasheet for dolomite:

Langmuir isotherm			*Freundlich isotherm*		
q_{max} (μg/gm)	*b (L/mg)*	*r^2*	*K_f*	*n*	*r^2*
250	**0.53**	**0.67**	**95.21**	**2.29**	**0.3687**

16.6.3 Adsorption Kinetic study of fluoride by Sea Shell

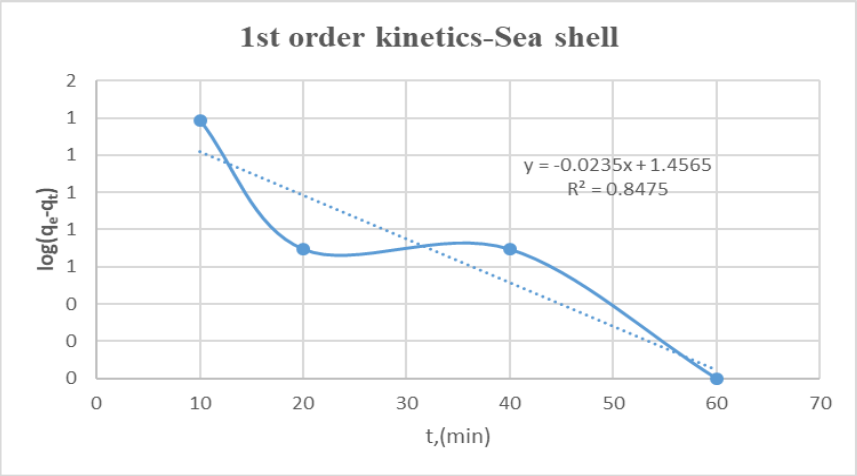


Fig 100: The graph of log(q_e-q_t) vs t (pseudo 1st order kinetic model)

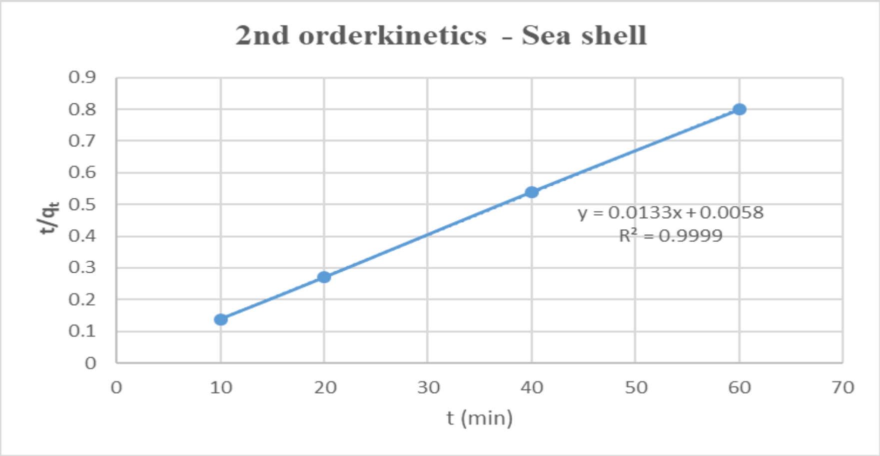


Fig 101: The graph of t/q_t vs t (pseudo 2nd order kinetic model)

Table 31: Adsorption kinetics datasheet for sea shell

C_o (mg/L)	$q_{e,\,exp}$ (µg/gm)	*Pseudo first order*			*Pseudo second order*		
		K_{ad} (1/min)	$q_{e,\,cal}$ (µg/gm)	r^2	K′ (gm/µg min)	$q_{e,\,cal}$ (µg/gm)	r^2
5	75	0.024	4.3	0.8475	0.03	76.92	0.999

16.7 Adsorption of fluoride using Mixture

16.7.1 Effect of Various parameters on adsorption of fluoride using mixture

Effect of pH on removal of fluoride

Experiment

Initial pH: 3-11

Fluoride conc.: 5 mg/L

Mixture dose: 50 gm/L

Contact time: 60 min

Temperature: 800ºC

Contact speed: 40 RPM

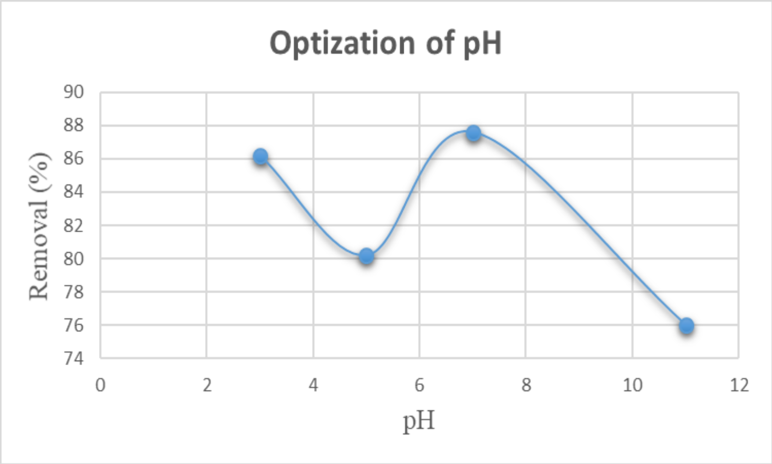


Fig 102: Removal (%) vs pH Graph

Effect of Adsorption Dose on removal of fluoride

Experiment

Initial pH: 7

Fluoride conc.: 5 mg/L

Mixture dose: 5-50 gm/L

Contact time: 60 min

Temperature: 800ºC

Contact speed: 40 RPM

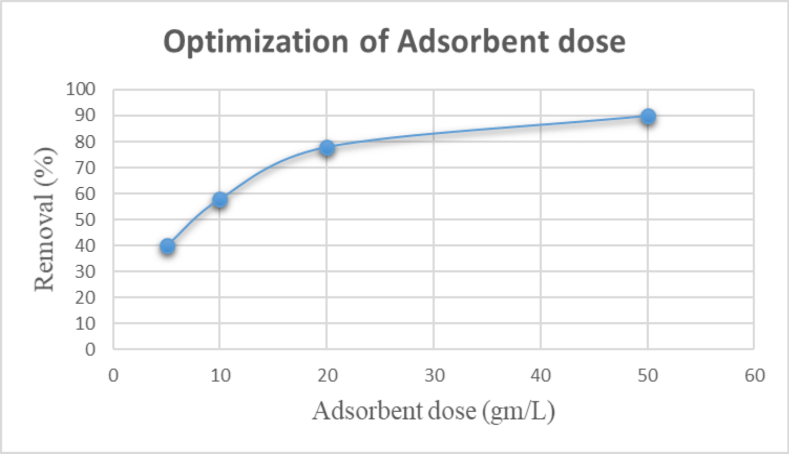


Fig 103: Removal (%) vs adsorbent dose graph

Effect of Contact time on removal of fluoride

Experiment

Initial pH: 7

Fluoride conc.: 5 mg/L

Mixture dose: 50 gm/L

Contact time: 10-60 min

Temperature: 800ºC

Contact speed: 40 RPM

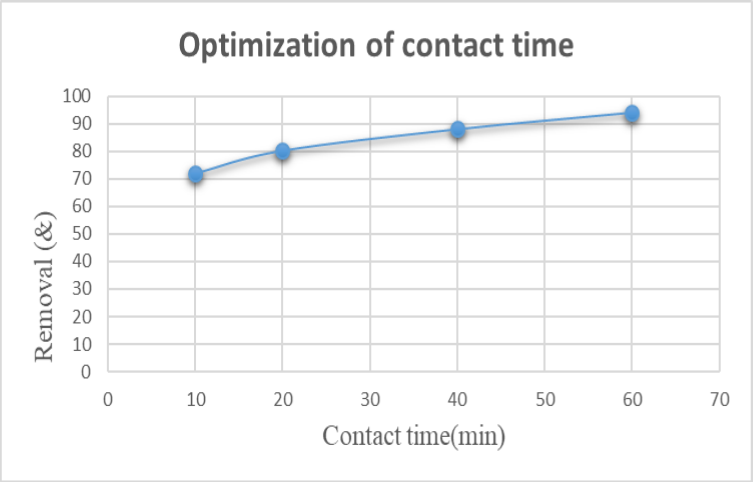


Fig 104: Removal (%) vs contact time graph

Effect of initial fluoride Concentration on removal of fluoride

Experiment

Initial pH: 7

Fluoride conc.: 2-10 mg/L

Mixture dose: 50 gm/L

Contact time: 60 min

Temperature: 800°C

Contact speed: 40 RPM

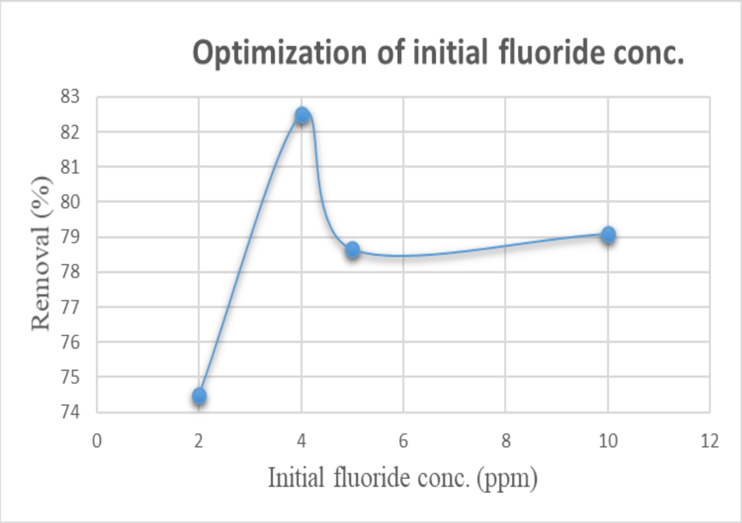


Fig 105: Removal (%) vs initial fluoride concentration (ppm) graph

16.7.2 Adsorption Isotherm Models of fluoride by mixture

Langmuir model

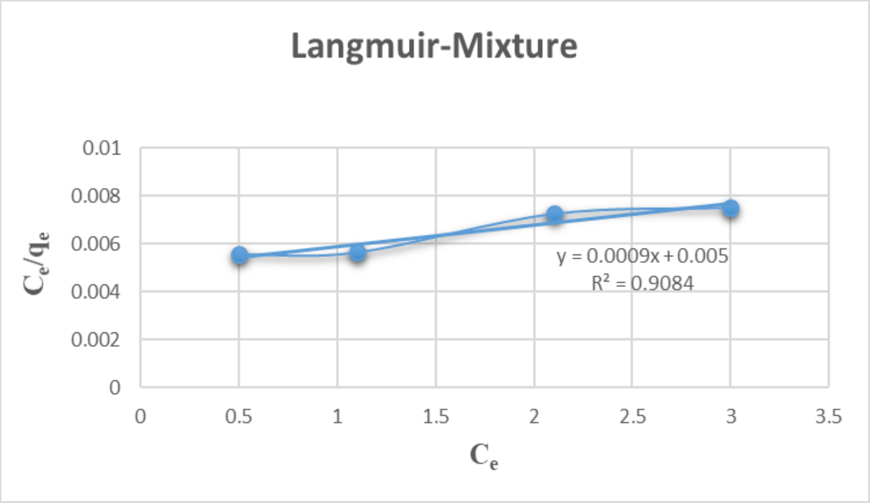


Fig 106: C_e/q_e vs C_e graph

Again from the Graph ,we can have the R_L values

$R_L = 0.529$

Since R_L lies within 0 and 1, the Langmuir isotherm is favourable within experimental range

Freundlich model

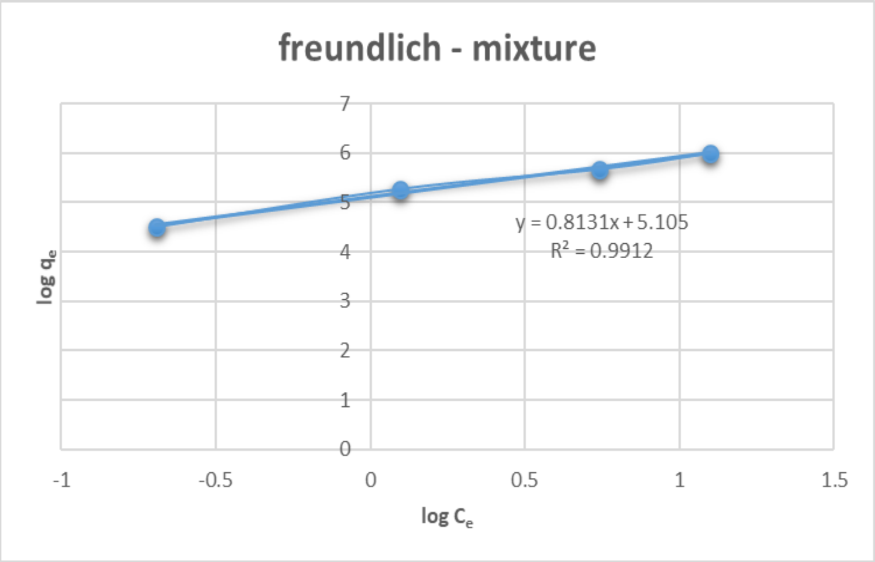


Fig 107: log q_e vs log C_e graph

Table 32: Adsorption isotherm datasheet for mixture:

Langmuir isotherm			***Freundlich isotherm***		
q_{max} (µg/gm)	***b (L/mg)***	***r^2***	***K_f***	***n***	***r^2***
1111.11	**0.18**	**0.9084**	**164.84**	**1.23**	**0.9912**

16.7.3 Adsorption Kinetic study of fluoride by mixture

Adsorption Kinetic study of fluoride by Mixture

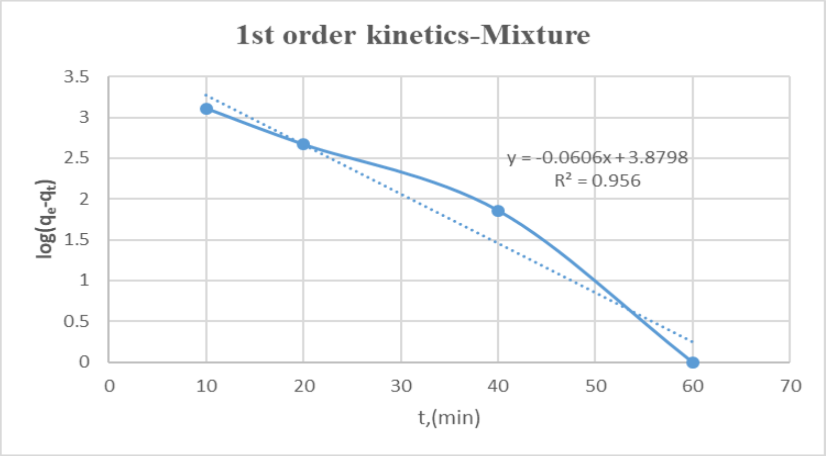


Fig 108: The graph of log(qe-qt) vs t (pseudo 1st order kinetic model)

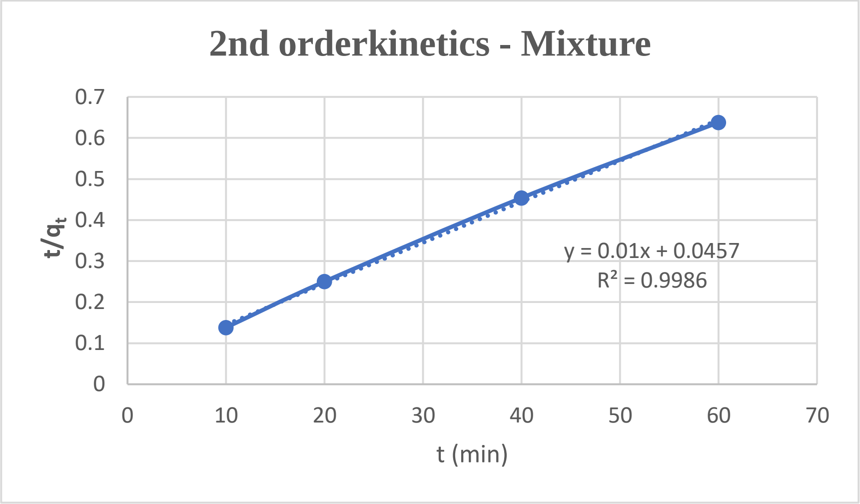


Fig 109: The graph of t/q_t vs t (pseudo 2^{nd} order kinetic model)

Table 33: Adsorption kinetics datasheet for mixture

C_o (mg/L)	$q_{e, exp}$ (µg/gm)	*Pseudo first order*			*Pseudo second order*		
		K_{ad} (1/min)	$q_{e, cal}$ (µg/gm)	r^2	K' (gm/µg min)	$q_{e, cal}$ (µg/gm)	r^2
5	**94**	**0.061**	**48.41**	**0.956**	**0.0022**	**100**	**0.9986**

Table 34: Various optimum parameters of adsorbents used in this study for removal of arsenic

Name of the adsorbent	**Optimum pH**	**Optimum Adsorbent Dose (gm/L)**	**Optimum Initial arsenic concentration (µg/L)**	**Optimum Contact time (minute)**	**Optimum Contact speed (RPM)**	**Optimum Activated temperature (ºC)**	**Maximum removal percentage (%)**
Dolomite	**12**	**5.33**	**100**	**20**	**30**	**600**	**95**
Sea shell	**12**	**20.88**	**50**	**60**	**40**	**600**	**91**
mixture	**12**	**34**	**100**	**60**	**40**	**600**	**93**

Table 35: Isotherms and Kinetic models of adsorbents used in this study for removal of arsenic

Name of the adsorbent	**Adsorption Isotherm suited**	**Adsorption Kinetics suited**	**Remarks**
Dolomite	**Freundlich**	**Pseudo 2nd order**	**This isotherm signifies that surface of dolomite dust is monolayer and heterogeneous in nature.** **This kinetics supports that the adsorbent particles are heterogeneous and the adsorption process is chemical.**
Sea shell	**Freundlich**	**Pseudo 2nd order**	**This isotherm signifies that surface of sea shell dust is monolayer and heterogeneous in nature.** **This kinetics supports that the adsorbent particles are heterogeneous and the adsorption process is chemical.**
mixture	**Freundlich**	**Pseudo 2nd order**	**This isotherm signifies that surface of mixture dust is monolayer and heterogeneous in nature.** **This kinetics supports that the adsorbent particles are heterogeneous and the adsorption process is chemical.**

Table 36: Various optimum parameters of adsorbents used in this study for removal of fluoride

Name of the adsorbent	**Optimum pH**	**Optimum Adsorbent Dose (gm/L)**	**Optimum Initial fluoride concentration (mg/L)**	**Optimum Contact time (minute)**	**Maximum removal percentage (%)**
Dolomite	**7**	**50**	**5**	**60**	**95**
Sea shell	**5**	**50**	**4**	**60**	**94**
mixture	**7**	**50**	**4**	**60**	**88**

Table 37: Isotherms and Kinetic models of adsorbents used in this study for removal of fluoride

Name of the adsorbent	**Adsorption Isotherm suited**	**Adsorption Kinetics suited**	**Remarks**
Dolomite	**Freundlich**	**Pseudo 2nd order**	**This isotherm signifies that surface of dolomite dust is monolayer and heterogeneous in nature.** **This kinetics supports that the adsorbent particles are heterogeneous and the adsorption process is chemical.**
Sea shell	**Freundlich**	**Pseudo 2nd order**	**This isotherm signifies that surface of sea shell dust is monolayer and heterogeneous in nature.** **This kinetics supports that the adsorbent particles are heterogeneous and the adsorption process is chemical.**
mixture	**Freundlich**	**Pseudo 2nd order**	**This isotherm signifies that surface of mixture dust is monolayer and heterogeneous in nature.** **This kinetics supports that the adsorbent particles are heterogeneous and the adsorption process is chemical.**

The pH is an important factor in adsorption process as well as removal of arsenic and fluoride .For removal of fluoride it has been observed the effective pH is 7 for dolomite and mixture whereas it was pH of 5 for sea shell.therefore it has been cleared that at both high and low pH the removal percentage decreased.The slow rateof removal at higher pH may be caused due to hydroxide ion competition with fluoride ion for surface adsorption whereas solubility of dolomite in high acidic media is the reason for its less fluoride efficiency at lower pH Chaudhary and Prasad. similarly , the maximum fluoride removal has been reported ay pH using calcite.Turner et al.,2005.the pH at neutral condition will be beneficial for the practical implementation.

Again for removal of arsenic the effective pH is 12.this is basically due to the dissolution of high concentration calcium ions.(Kanel et al.,)

Conclusion

The positive results of the present field study work it is very much obvious that if extensive sampling could be done on the above Study. Areas mainly focusing like Kalupur Gram Panchayat and other GPs of Bongaon Block, North 24 Parganas , Rajpur-Sonarpur Municipilaty of South 24 Parganas are very interesting and unreported facts about the groundwater status can be highlighted, promoting the awareness of the future adverse health effects on the exposed population.

The present study has proven that thermally activated adsorbents like dolomite, sea shell and their mixture has the excellent removal efficiency for both arsenic and fluoride. The highest adsorption capacity of dolomite on removal of arsenic if found 16.68 µg/gm with adsorbent dose of 5.33 gm/L, initial arsenic concentration of 100 µg/L in 20 minutes whereas highest adsorption capacity of dolomite on removal of fluoride is found 426.62 µg/gm with adsorbent dose 20.08 gm/L, initial fluoride concentration of 10 mg/L in 40 minutes. The highest adsorption capacity of sea shell on removal of arsenic if found 11.53 µg/gm with adsorbent dose of 5.72 gm/L, initial arsenic concentration of 100 µg/L in 20 minutes whereas highest adsorption capacity of dolomite on removal of fluoride is found 387.29 µg/gm with adsorbent dose 20.14 gm/L, initial fluoride concentration of 10 mg/L in 40 minutes. The highest adsorption capacity of dolomite on removal of arsenic if found 13.80 µg/gm with adsorbent dose of 5.88 gm/L, initial arsenic concentration of 100 µg/L in 20 minutes whereas highest adsorption capacity of dolomite on removal of fluoride is found 391.27 µg/gm with adsorbent dose 20.14 gm/L, initial fluoride concentration of 10 mg/L in 40 minutes. The maximum removal of both arsenic and fluoride by all the adsorbents followed pseudo 2nd order kinetics as well as freundlich adsorption. The proposed method is simple, safe. the most cost effective and quick for both dearsenification and defluoridation of drinking water. From the results of this study concludes that the dolomite, sea shell and their mixure is a low-cost and proper adsorbent for arsenic and fluoride removal from groundwater. The present study also shows us that mixing of geoadsorbent (i.e. dolomite) and bioadsorbent (i.e. sea shell) can be a effective adsorbent and could be the solution to save the future adverse health effects on the exposed population to arsenic and fluoride Contamination. Many unreported areas having groundwater contaminated with fluoride or arsenic have been identified during the course of this project. Co-existence of Arsenic and Fluoride contamination above the permissible limits in the groundwater at the same time is very rarely found at global scale but samples of these type have been found and areas identified during the project work.

FUTURE SCOPE

Arsenic and fluoride both are the priority pollutant due to its toxicity and affects both human and environment. These become the major concern by worldwide as groundwater becomes the major source for drinking water.Adsorption efficiency of dolomite, sea shell and their mixure to remove arsenic and fluoride from groundwater is assessed in this research.

This study has enabled us to approach the adsorption process to be a solution for the treatment of arsenic and fluoride contamination groundwater. Through this study we were able to identify and characterize the adsorbents which were most effective for removal of those pollutants.

The novelty of the research is that the study has covered elaborated testing of several models for the removal of arsenic and fluoride with typical arsenic and fluoride concentration. Thus this research work is suitably applicable in groundwater treatment plant or for the water filters and many other industries(where groundwater is main ingredient)

As the batch study has become effective for removal both arsenic and fluoride, we can go for the column bed study for contaminated arsenic and fluoride water which will provide us more details for the construction of an efficient filtering unit for removal of arsenic and fluoride.

The present study mainly deals with the lab based synthetic samples. Therefore we can go for the removal characteristics of the adsorbent for the field based real samples .

The disposal of the sludge generated after adsorption is one of the main concern. A safe disposal technique can be established to make the study more efficient and effective.

This proposed study has mainly focused on the removal of arsenic and fluoride. So the influence and effect of other water quality paramerts like hardness,alkalinity, conductance,iron content should be also investigated.

This present study also can be implemented to remove other contaminants of drinking water like lead ,mercury, cadmium and other heavy metal.

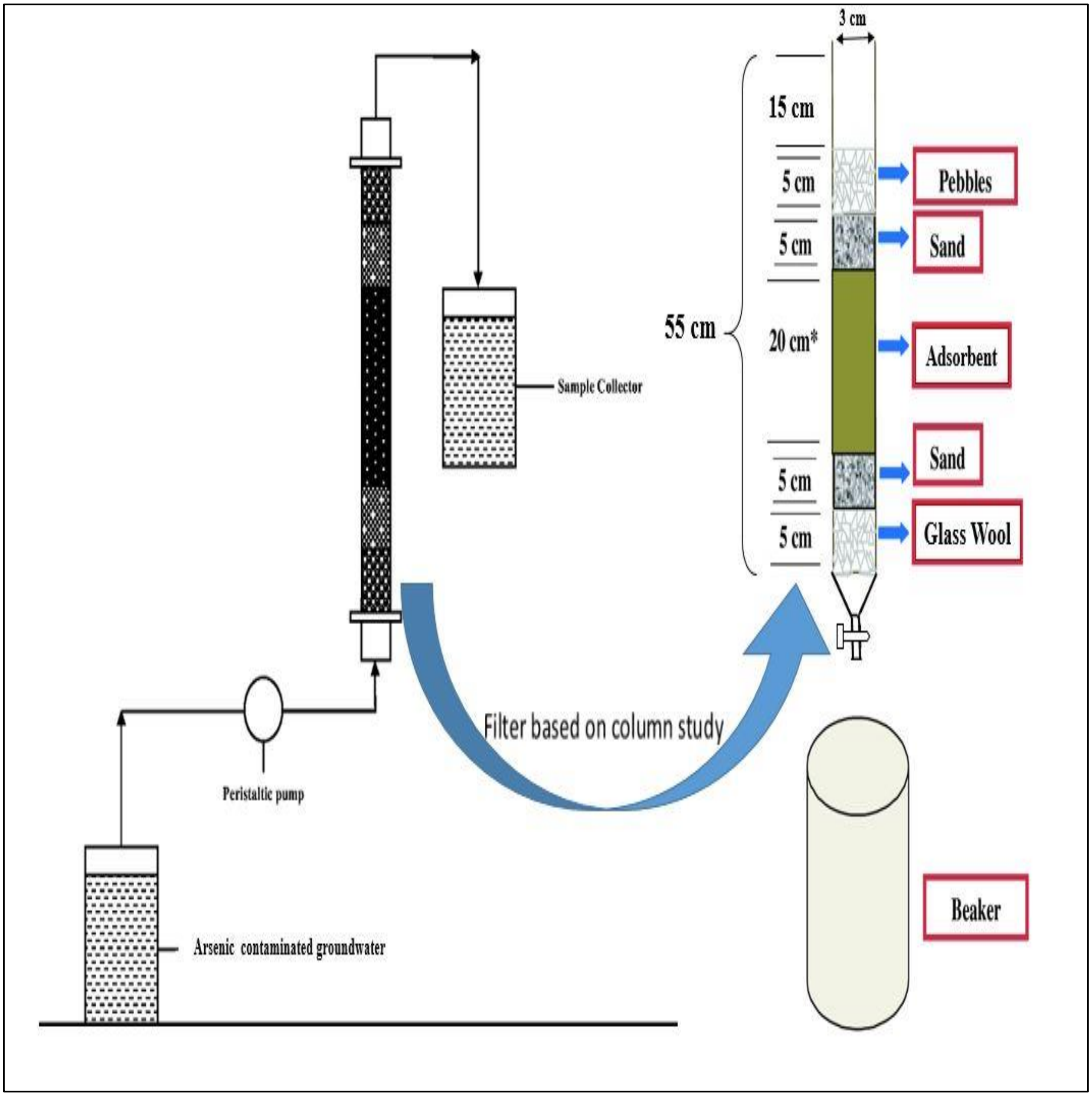


Fig 110: An approach of Column Study and Groundwater Treatment Technology by adsorption

PUBLICATIONS

Groundwater arsenic contamination with special reference to its entry in rice grain post-harvest in Bengal delta. T. Roychowdhury, N. Roy Chowdhury, M. Joardar, S. Swain, A. Das, M. Mukherjee, A. De, S. Ghosh, D. Saha, **B. Ghosh**, S. S. Das, S. Majumder. Proceedings in Twentieth National Symposium on Environment (NSE-20), Focal Theme: Challenges in energy resource management & climate change. Eds. R. M. Tripathi, M. Kumar, S. K. Jha, V. Jain, A. v. Kumar, V. Pulhani, I. V. Saradhi, A. C. Patra, M. K. Mishra, S. K. Sahoo. Health, Safety & Environment Group, Bhabha Atomic Research Centre, Mumbai and Indian Institute of Technology, Ganghinagar, Board of Research in Nuclear Sciences, Department of Atomic Energy, Govt. of India, pp. 101-102.

Removal of arsenic from groundwater using suitable adsorbent: Dolomite. A. De, **B. Ghosh**, S. S. Das, S. Majumder, D. Saha, T. Roychowdhury. National Seminar on ‘Groundwater arsenic contamination problem in Ganga-Meghna-Brahmaputra (GMB) plain: Its health effects, socio-economic implications and mitigation strategies. Department of Economics, Vijaygarh Jyotish Ray College, Jadavpur in collaboration with School of Environmental Studies, Jadavpur University, Vijaygarh Jyotish Ray College, 25th March, 2019.

An insight of arsenic contamination in groundwater and food chain with special reference to health effects on domestic animals. A. Das, M. Joardar, N. Roy Chowdhury, S. Swain, A. De, M. Mukherjee, **B. Ghosh**, S. S. Das, S. Majumder, T. Roychowdhury. National Seminar on ‘Groundwater arsenic contamination problem in Ganga-Meghna-Brahmaputra (GMB) plain: Its health effects, socio-economic implications and mitigation strategies. Department of Economics, Vijaygarh Jyotish Ray College, Jadavpur in collaboration with School of Environmental Studies, Jadavpur University, Vijaygarh Jyotish Ray College, 25th March, 2019.

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