Development of carbonaceous and polymeric material grafted composites for remediation of pollutants from wastewater

Synopsis submitted by

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Aim and objectives

Pure water accessibility is one of the crucial and basic needs in the world. With advancement of technology and industrial activity, demand for uncontaminated water for daily use is increasing. Untreated industrial effluent contains an extensive variety of harmful carcinogenic chemical products such as heavy metals, dyes, radioactive pollutants, toxic chemicals, fluoride. Dye is used in several sectors like textile, cosmetic, plastic, paper, leather, and pigment industries. The effluent of those industries heavily pollutes the surface and groundwater, thereby, making it unhealthy for consumption and also for agricultural purposes. The toxicity of dyes can range from irritants for eyes and skin, to having carcinogenic and mutagenic effects if allowed to remain in the body at high doses for a long time. Additionally, the color water obstructs the penetration of sunlight on water bodies. This prevents the growth of marine lives by preventing photosynthesis and reducing the concentration of dissolved oxygen. Malachite Green (MG) is the most popular cationic dye used for dyeing cotton, wool, leather, nylon, and silk. It is also used in significant quantities in the aquaculture industries where it is illegally used as low-cost topical antifungal and parasiticide. According to the U.S. FDA (Food & Drug Administration) sample testing protocols, MG dye residue must be below 1 mg/g (USA Today, 2017).

Manmade sources of Fluoride contamination are effluent discharged from various industrial activities such as coal-burning stations, steel production, aluminum, phosphorus, production of bricks, glass, plastic, cement, and HF production plant. Another source of fluoride pollution in potable water and surface water is the excessive use of fertilizers (superphosphate, NPK, potash etc.). WHO (world health organization) recommended permissible limit of fluoride as 1.5 mg/L. Almost 19 states of India, including Rajasthan, Andhra Pradesh, Uttar Pradesh, Maharashtra, West Bengal, and Gujarat are suffering from high fluoride concentrations in groundwater as well as surface water (Ayoob and Gupta 2006; Amalraj and Pius 2013). Fluoride affects the ecosystem and living beings by contaminating water, air, soil, crops and vegetables. Intake of fluoride lead to the fluorosis syndrome, reproductive decline, skeletal tissues damages, and damage to the thyroid.

Several advanced physicochemical techniques such as electrodialysis, precipitation, reverse osmosis, ion exchange process, and adsorption have been investigated to remove dye and flouride pollutant from their aqueous solution. The limitations of many of these procedures are complex, highly expensive, and produce poisonous carcinogenic secondary pollutant. Of late, researchers are focusing on environmental-friendly, economical, and low energy-consuming treatment technology. Adsorption is accepted as the most efficient process for decolorization and defluoridation process due to advantages such as ease of operation, low operating cost, insensitivity to toxic substances, viability etc.

India is one of the agricultural countries in the world. A large number of agro-based industries, such as jute, cotton, and sugar produce large quantities of agro-waste which require proper waste disposal management to prevent damage to environmental ecosystem. According to the Press Information Bureau, India generates 62 million tons of waste (mixed waste containing both recyclable and non-recyclable waste) every year, with an average annual growth rate of 4%. In recent years, researchers are paying attention to efficient use of agricultural residues to minimize the accumulation of waste. Agricultural wastes are affluent in organic substances due to presence of various functional groups which help to bind the electro-positive ions and electro-negative ions. Despite having many appreciable properties, commercial adsorbents (such as activated carbon) that are most used on industries are very expensive and non-biodegradable. Researchers are therefore investigating agro-waste and their derivatives as an efficient and eco-friendly adsorbent for treatment of industrial effluent water due to its favorable properties, including abundance, biocompatibility, biodegradability, cost-effectivity, and non-toxicity. Agro-waste derived biosorbent material can offer an alternate purification process to substitute the commercial adsorbent (Matei et al., 2001).

The uptake rate of pollutants by adsorbents depends on the intraparticle and continuous phase mass transfer resistances. Decreasing the particle size enhances the removal rate of pollutants leading to reduced equipment size and more efficient use of the adsorbents. However, limitations of application of fine, granular adsorbent include reactor cleaning, difficulty in separation of adsorbent from treated solution and clogging. They could be easily released in effluent discharge resulting in underutilization of their removal capacity as they could be reused by regeneration. The complexity involved in recovering the powdery adsorbents from treated solutions post adsorption also makes these undesirable for the large-scale application. Beads or hydrogel film form of those granular adsorbents reduce these drawbacks. Composite production by inserting agro-waste derived activated biochar and biopolymer within an inflexible polymer has become a new appreciated technique.

Research Gap: Feasible application of agro-waste derived adsorbents in the wastewater treatment process was explored in many research papers (Chowdhury et al., 2011; Sing et al., 2011; Madhusudana Rao et al., 2013;). However, the application of the proposed agro-waste derived carbonaceous and bio polymeric materials grafted composite beads and hydrogel films for dye and fluoride removal process is still a not much researched area. Biodegradation of pollutant loaded adsorbent is essential before disposing/discarding to reduce its adverse effect on the environment (Wagner et al., 1996; Premraj and Doble, 2005). Though there is huge volume of work on the biodegradation of pollutants from wastewater (such as Bacillus sp. used to biodegrade 2, 4, 6-TNT (Lin et al., 2013), Pseudomonas sp used for bioremediation of Reactive Red 2 (Kalyani et al., 2009; Banerjee et al., 2017)), there has been only limited research on use of micro-organism for degradation of pollutant loaded adsorbent.

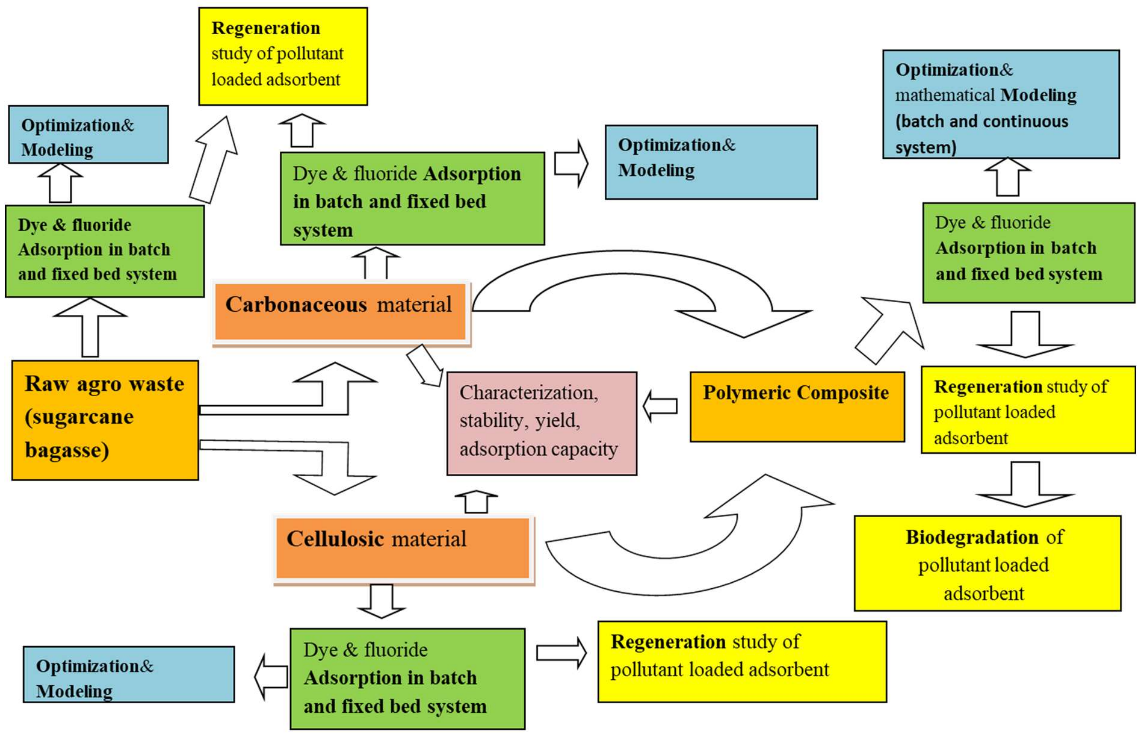
Sugarcane is widely cultivated in tropical and subtropical countries such as India, Sri Lanka, Pakistan, Bangladesh, Malaysia, Philippines Hawaii, Australia, and Indonesia. Bagasse is the by-product obtained after crushing the sugar cane stalks and is fibrous in nature. Burning as fuel and landfilling are extensively used method in many states of India to discard the crop residue. Landfilling of the waste sugarcane bagasse produces a large amount of leachate which causes hazardous contamination to the open water body as well as groundwater. The recycling of the sugarcane bagasse into biosorbent is an efficient alternative to the conventional process for minimizing the solid-waste handling problems and produce inexpensive, ecofriendly biodegradable adsorbent for wastewater treatment. Sugarcane bagasse contains about 40–55% of cellulose, hemicellulose as much as 26–35% (Wulandari et al. 2016; Mandal and Chakrabarty 2011). Hence, it is also a potential resource of readily available low-cost raw material for cellulose extraction, activated biochar production and surface modified biosorbent preparation for wastewater treatment process.

The objective of this research work is to synthesis carbonaceous and polymeric material grafted biodegradable composites derived from abundantly available low-cost agro-waste sugar cane bagasse and to investigate the application of these biodegradable adsorbents for decolorization of MG dye contaminated wastewater and defluoridation of water. The focus has also been on reutilization of dye and fluoride-loaded adsorbents obtained post-adsorption and biodegradation of pollutant loaded adsorbents by isolated microorganism before final disposal of the biosorbents into the environment.

The following was done within the framework of the present research work

- Preparation of activated charcoal and extraction of cellulose from sugarcane bagasse
- Synthesis of different types of carbonaceous material and biopolymer-based composites (raw sugarcane bagasse (SB), SB activated biochar (SBAC), Cellulose, Alginate-bentonite/SBAC beads, Nanocellulose/PVA hydrogel film, Alginate-Nanocellulose beads).
- Physiochemical characteristics of prepared adsorbents were analyzed using FTIR, SEM, TGA, and BET. FTIR was conducted to analyze the characteristic functional groups on the surface of adsorbents. Surface morphology of adsorbent was evaluated by SEM characterization. The estimate of adsorbent surface area which is important for fixed bed was obtained using BET analysis.
- Investigation on the adsorption efficiency of synthesized biosorbent for removal of MG dye and Fluoride separately both in batch process and continuous removal in fixed bed.
- Investigation of the effects of various operational parameters (factors) on removal efficiency of the prepared adsorbents.
- Estimation of adsorption isotherms, kinetic and thermodynamic parameters from experimental data. The adsorption capacity under equilibrium condition and the rate constants of contact time-dependent adsorption process were estimated by applying kinetic model. Batch kinetic study was performed to understand the mass transfer mechanism dictating uptake rate required for designing suitable contactors. Thermodynamic study was conducted to describe the thermodynamic behavior of adsorption process.
- Evaluation of the dynamic behavior and performance of the fixed bed adsorbent column in terms of the breakthrough curve at various investigational conditions (such as feed flow rate, feed concentration, adsorbent-bed height, solution pH). The feasibility to use Yoon-Nelson model and Thomas model to predict the experimental data was also examined.
- Investigation on the Recycle potential (Regeneration study) and Biodegradation study of the pollutant-loaded composites. Pollutant elimination by biosorption process becomes less expensive and beneficial if the pollutant-loaded biosorbent can be regenerated.

Complete Work Flow



Results:

- Kinetic and equilibrium batch study was performed for removal of Malachite Green dye and Fluoride Removal using SB powder, SBC, SBAC, Alginate-Bentonite/SBAC beads, Cellulose, NanoCellulose/PVA, Alginate-Nanocellulose beads as adsorbents. Sugarcane bagasse (SB) collected from local markets in Kolkata, India and washing was followed by drying process. For preparing activated biochar (SBAC), crushed and sieved SB was pyrolyzed in a muffle oven for 2 hr at a temperature of 800˚C in an inert atmosphere (N_2 air purging). Alginate-bentonite/SBAC composite beads were prepared by adding Sugarcane bagasse activated biochar (SBAC) and bentonite clay to the Sodium alginate solution. Beads of different diameter was prepared by allowing the suspension to flow into the calcium chloride solution from openings of different diameter. Cellulose was extracted from SB by removing hemicellulose and lignin. NaClO solution was used to bleach Sugarcane bagasse powder. Hemicellulose and lignin was eliminated from the dried mass by treating with NaOH and $NaHSO_3$ solution. Synthesized cellulose was used to prepare nano-cellulose using H_2SO_4 by acid hydrolyzation technique. For aking Nnaocellulose/PVA composite film nano-cellulose was added to Poly vinyl alcohol (PVA) and the mixture was stirred until it was dissolved completely. Final polymeric suspensions were poured into a petri-dish and left to dry at 40 °C. After drying, the composite films were cut into designated small sizes (~ 40 mm and 30mg weight). Alginate-nanocellulose composite beads were prepared by adding extracted cellulose to the sodium-alginate solution Beads of different diameter was prepared by allowing the suspension to flow into the calcium chloride solution from openings of different diameter.

- It was noted that the adsorption efficiency depends on the parameters such as: adsorbate concentration, adsorbent dosage, contact time, pH and temperature.
  - With increasing pH dye efficiency increased and at basic media dye adsorption efficiency decreased. At basic conditions, due to the presence of a large amount of OH^- ions protonation decreases which enhanced the adsorption of positively charged dye molecule to the adsorbent surface. On the other hand, at lower pH, higher biosorption efficiency for anionic fluoride removal was noted as the adsorbent surface become electropositive at acidic condition due to presence of H^+ ions. At higher pH adsorbent surface become predominantly negative charged resulting in low adsorption efficiency.
  - With increasing dosage of prepared adsorbents, dye adsorption efficiency increased. This is because initially, when we increase the amount of adsorbent, for the same solution concentration, the number of active sites available per unit molecule of adsorbate increases, resulting in a higher rate of adsorption.
  - With increasing adsorbate concentration, competition for active adsorptive sites increased which reduces the removal efficiency due to the unchanged number of active adsorptive sites. With an increase in initial concentration (keeping all other parameters constant), the number of competing molecules for each vacant site is more. Hence the adsorption efficiency is lower.
  - the mobility of adsorbate molecules is enhanced on increasing the system temperature. While the active sites on the adsorbent surface is reduces. High temperature facilitates the desorption process which reduces the adsorption efficiency and demote the interaction between the adsorbate and the binding sites at the bio-adsorbent surface.
- The estimated value of monolayer adsorption capacity obtained on fitting of equilibrium MG dye experimental data with adsorption Langmuir model is shown in Table 9.1 and Table 9.2 for dye and fluoride respectively

Table 9.1: Dye adsorption capacity results for different type of prepared adsorbents

Prepared adsorbents	% Removal	Initial dye concentration (mg/L)	Adsorbent dosage (g/L)	Adsorption capacity (mg/g)	Chemical used in composites
Sugar cane bagasse (SB) powder	83.04	20.0	1.0	169.49	-
SB Biochar (SBC)	90.	20	1.0	172.414	-
NaOH Activated Biochar (SBAC)	93.42	20	1.0	185.185	SBC:NaOH (15%)=1:10
Sodium alginate-Bentonite/SBAC beads	98.2	20.0	1.0	196.1	1g SBC, 2% (w/v) of sodium alginate 2% (w/v) bentonite clay
Cellulose	94.78	20.0	1.0	188.68	0.75%$NaClO_2$, 2%$NaHSO_3$, 17%NaOH
NanoCellulose/PVA	99.2	20.0	1.0	212.76	0.5g cellulose, 4% (w/v)PVA
Alginate-Nanocellulose beads	99.6	20.0	1.0	263.158	0.5g cellulose, 2% (w/v) of sodium alginate

Table 9.2: Fluoride adsorption capacity results for different type of prepared adsorbents

Prepared adsorbents	% Removal	Initial fluoride concentration (mg/L)	Adsorbent dosage	Fluoride Adsorption capacity (mg/g)	Chemical used in composites
Sugar cane bagasse (SB) powder	54.63	6.0	2g/L	19.88	-
SB Biochar (SBC)	57.68	6.0	2g/L	20.53	-
NaOH Activated Biochar (SBAC)	60.72	6.0	2g/L	22.22	SBC:NaOH (15%)=1:10

Sodium alginate-Bentonite/SBAC beads	76.65	6.0	2g/L	23.06	1g SBC, 2%(w/v) of sodium alginate , 2% (w/v) bentonite clay
Cellulose	75.96	6.0	2g/L	14.75	0.75% $NaClO_2$, 2%$NaHSO_3$, 17% NaOH
NanoCellulose/PVA	83.44	6.0	2g/L	28.41	0.5g cellulose , 4% (w/v) PVA
Alginate-Nanocellulose beads	83.23%	6 mg/L	2g/L	23.809 mg/g	0.5g cellulose, 2% (w/v) of sodium alginate

- Adsorption kinetic study indicated that the removal of both the pollutants using composite beads would better describe by Pseudo-second-order kinetic model. From the Weber-Morris model it was noted that plot (q_t vs. $t^{0.5}$ graph) didn't pass through the origin and was not straight line which indicated that the intra-particle-diffusion process was not the solely rate controlling step for the adsorption process.
- Negative value of Gibbs free energy and negative Enthalpy value indicated the spontaneous nature of the reaction and that the adsorption process was exothermic
- RSM modelling showed that optimization was effectively correlated with batch experimental data. The optimized conditions for MG dye removal study using raw SB was observed as pH: 6.81, dose: 1.06 g/L and contact time: 114.93 min and at this condition removal efficiency was found as 83.71%. The maximum adsorption efficiency was obtained as 93.833% at a pH value of 7.08 after 77.95 min contact time in case of SBAC. The optimized condition for Alginate-nanocellulose beads was pH-6.46, dose 0.98 g/L and time 64.42 min and maximum removal efficiency was 99.52%.
- The optimized condition for Fluoride adsorption experiment was observed from RSM model using SB as adsorbent, was 57% at a dose of 1.96 g/L at pH 5.0 for contact time of 114.44 min. using Alginate-bentonite/SBAC composite beads maximum removal efficiency was found as 77.32 at pH-5.84, dose 1.82 g/L and time 80.63 min. Using nanocellulose/PVA as adsorbent optimized condition was pH value of 5.41 dose of 1.93 g/L at 92.80 min and maximum removal efficiency was 84.89 %.
- The breakthrough in fixed bed study was achieved faster at a higher influent flow rate. With increasing inlet dye concentration breakthrough time decreased. On the other hand, with rising bed height and pH the breakthrough time increased. With increasing adsorbent loading the interaction time between adsorbate molecules and the surface of

adsorbent increased as well as the number of vacant active sites. The increase in adsorption capacity of adsorbent bed at constant column bed height with decreasing feed flow rate may be attributed to the longer contact time between MG dye molecules and adsorbent which facilitated the enhancement of amount of solute transfer to the adsorbent bed thereby increasing biosorption efficiency.

With increasing feed flow rate, adsorption rate in fluidized bed increased but with increasing bed weight the adsorption rate decreased.

- With increasing feed flow rate, adsorption rate in fluidized bed increased but with increasing bed weight the adsorption rate decreased. The adsorption efficiency reduced by rising initial feed concentrations. With increasing weight of biosorbent mass, movement/suspension of particles in fluidized media of the column reduced which leads to the decreased in adsorbent-adsorbate interaction (or contact in between adsorbate and adsorbent) and reduce the removal proficiency. The reduced adsorption efficiency on increasing feed concentrations of dye solution could be associated with the competition between large amount of adsorbate molecules for active sites on composite beads surface Removal proficiency is improved by using smaller size of solid particle because of higher adsorbent surface area for better interaction with adsorbate molecule at the same adsorbent mass.

- After five cycles, the average adsorption efficiency for MG dye removal reduced to 70 %. The adsorption efficiency for Fluoride removal study was just over 40%.
- The regenerability or recyclability of adsorbents were better with dye as compared with fluoride.
  - Isolated Bacteria was Gram positive bacteria and showed better growth rate at pH 5-8 and at 35 °C temperature
  - Bio-degradation of dye loaded exhausted adsorbents using isolated bacteria showed appreciated results

The present study demonstrated that proposed composites (Alginate-Bentonite/SBAC beads, NanoCellulose/PVA, Alginate-Nanocellulose composite polymeric beads) are efficient, high-potential biodegradable biosorbent and could be used as potential alternatives for decolorization and defluoridation of wastewater.