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Adsorption of hazardous azo dye from aqueous solution onto Parthenium flower activated carbon: Approach to the batch and regeneration studies

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Abstract — In the current article, an azo dye adsorbent was prepared by using Parthenium flowers activated carbon (PFAC). Sulphuric acid (H_2SO_4) was utilized as an activator for the preparation of activated carbon from a biomass solid waste, parthenium flowers. The sulphuric acid-treated activated carbon (PFAC) was used as low-cost adsorbent for the removal of Eriochrom black-T (EBT) azo dye from aqueous solution. The prepared activated carbon was characterized by Fourier transform infrared spectroscopy (FT-IR) before and after the adsorption process and scanning electron microscopy (SEM). A FT-IR spectrum the various functional groups present in the PFAC. SEM micrographs show the rough and irregular along with heterogeneous cavities that well distributed across the PFAC surface. Morphology of the product which is irregular shape and uniformly distributed. Adsorption property of PFAC against EBT was examined by considering the dosage effect, effect of pH, stirring time and varying concentration. At neutral pH, 10 ppm EBT azo dye aqueous solution adsorbed on PFAC (92%). Batch adsorption and regeneration studies were studied.

Keywords - Activated Carbon, Azo dye, Adsorption, Parthenium flowers.

I. INTRODUCTION

Textile sector is one of the foremost economical sources for a country, but the effluents produced from dyeing, and finishing processes of textile industries are reported to afflict public health, and biodiversity as they contain various hazardous materials [1]. Through some complex series of physical, chemical, and biological phenomena, these dyes consume dissolved oxygen in aquatic system and reduce the transmitted sunlight into water streams, finally interrupt many regular processes such as photosynthesis, respiration, and other metabolic processes of aquatic species [2]. Use of activated carbon as adsorbent has been found to be effective, but it is too expensive and the spent activated carbon can be regenerated with some mass lost. Thus, there is a demand for other adsorbents, such as inexpensive material from agricultural byproducts and industry waste with simple pre-treatment steps [3]. Adsorption technique is quite popular due to its simplicity as well as the availability of a wide range of adsorbents and it is proved to be an effective and attractive process for removal of refractory pollutants (including dyes, heavy metal ions, etc.) from wastewater [4]. Environmental contamination by dyes has gained widespread public attention as a pervasive problem [5,6]. The removal of dyes from wastewaters is an important environmental issue. There are several strategies for the treatment of dye wastewater, such as advanced oxidation processes [7, 8]. Then, due to such an extensive use, they may be later dispersed in the environment as contaminants, which occur through a large variety of ways. One of the most common dispersion way is through the water, solubilized in some liquid media and then dumped into water bodies that carry them for long distances from its sources, or yet infiltrating the soil and attaining the ground water [9]. Another dispersion way is through the atmosphere, adsorbed onto solid particles arising from the burning of materials/substances that contain such elements [10].

Among various water purification and recycling technologies, adsorption is a fast, less expensive and universal method. The industrial application of the conventional methods is frequently restricted by their high cost and disadvantages like slow process, incomplete removal, low selectivity, high-energy consumption, and generation of toxic sludge, which is difficult to be eliminated [11]. The spent adsorbent goes to hazardous waste landfill and is a long term liability for the society. The development of low-cost adsorbents has led to the rapid growth of research interests in this field [13]. The present protocol describes salient features of adsorption and detailed experimental methodologies for the development and characterization of low-cost adsorbents, water treatment and recycling using adsorption technology including batch operations.

Here in, we report PFAC as a highly potential adsorbent with excellent separation properties. EBT was selected as model pollutant to evaluate the adsorption performance under laboratory conditions. The main objectives are (i) to identify the key process controlling the rate of dye adsorption by PFAC, (ii) to provide direct evidence regarding the relative importance of multiple mechanisms for the adsorption of dyes, and (iii) to evaluate the performance for dye removal from wastewaters [7]. The present study focused on the adsorption of EBT azo dye by using low cost PFAC in batch adsorption experiment under various conditions (i.e., pH, contact time, variation of adsorbent and different dye concentration), the adsorption mechanism is discussed comprehensively based on the results. Further, commonly used dyes with opposite charge, EBT were examined and the adsorption mechanism of EBT dye molecules onto PFAC was investigated [15].

II. MATERIAL AND METHODS

a. Chemicals

Eriochrome Black-T (EBT) was used as an organic pollutant, sodium bicarbonate, sodium hydroxide, hydrochloric acid and sulfuric acid purchased from E-Merck and SD fine Companies. Double-distilled water was used throughout the experiments. Stock solution of dye of 10 ppm was prepared by dissolving 10 mg of EBT in 1000 ml distilled water. The structure and UV spectrum of EBT are given in Fig.1. (a) and (b).

b. Preparation of PFAC

White colour Parthenium flowers on the plants were collected in and around local areas of Kerehalli Chamarajanagar district, dried in hot air oven 2-3 days at the dried Parthenium flowers were ground into powder. Then it was soaked with concentrated sulfuric acid and kept at 200 °C for 24 hours.

The carbonized material was then washed with sodium bicarbonate ($NaHCO_3$) solution for several times to remove the acid medium and soaked in 0.1N sodium bicarbonate solution for 6 hours to remove any residual acids. The product was then washed with double distilled water and dried at 110^{o}C in a hot air oven for 24 hours and it was ground till to get fine powder.

c. Adsorbent characterization of PFAC

Scanning Electron Microscope (SEM), micrograph of the charcoal revealed that the surface rough and irregular along with heterogeneous cavities that well distributed across the PFAC surface. The irregular size of fresh activated charcoal was larger space than the dye loaded raw charcoal as show in the Fig 2. After the activation process, surface images of activated carbon obtained from scanning electron microscope (SEM) showed change in carbon morphology with large surface area, so it is good adsorbent particle.

To analyze the composition change of adsorbent by the adsorption, a comparison between the FT-IR spectra before and after adsorption of EBT was done. The FT-IR spectrum of the adsorbent before and after adsorption is given in Fig. 3. The absorption peaks at 3430 cm^{-1} (the O-H stretching vibration), around 1590 cm^{-1}, 1385 cm^{-1} (the O-H bending vibration), can be clearly seen, indicating that the adsorbent possessed some oxygen-containing functional groups and the O-H stretching vibration occurred at 3430 cm^{-1} also can indicate the presence of “free” hydroxyl groups. Besides, the small peak around 615 cm^{-1} was assigned to the vibration of Fe-O bonds. It can be seen that the intensity of O-H bending vibrations showed a little decrease and shift after the adsorption, indicating that EBT binding mostly at OH groups on the adsorbent [33]. Furthermore, it can be seen from the plot c (used sample) that there is a new peak around 1635 cm^{-1}, which is in good agreement with the plot of pure EBT (plot a). These results indicated that MB has been adsorbed on the PFAC [15].

d. Preparation of Eriochrome Black-T aqueous solution

The EBT dye is consider as azo dye, Eriochrome Black-T, nature- basic blue, wavelength maximum is 623 nm and chemical formula ($C_{20}H_{12}N_3O_7SNa$) has been used in this studies. The accurately weighed 10 mg quantity of the Eriochrome Black-T dye was dissolved in 1000 cm^3 double distilled water to prepare stock solution (10 mg/L). The percentage purity of the dye was taken into consideration while preparing the stock solutions. Experimental solution of desired concentration was obtained by successive dilution.

e. Batch experiment

Batch adsorption studies were carried out by agitating the adsorbent with 100 ml of dye solution of desired concentration and pH at room temperature in a magnetic stirrer at constant rpm. After agitation, samples were withdrawn from the stirrer and dye solutions were separated from the adsorbent by centrifugation. The residual dye concentration was estimated in supernatant spectrophotometrically by monitoring the absorbance before and after the treatment at wavelength of 665 nm. The % removal rate of BET can be calculated by the equation

$$\% \text{ removal} = \frac{At - Ao}{Ao} \text{ X } 100$$

Here A_t and A_0 are absorbance at various intervals of time (t) and original dye solution. Ao and At are proportional with Co and Ct, respectively, where Co is the initial concentration of dye and Ct is the concentration of dye at any time, based on Beer–Lambert’s law.

III. RESULT AND DISCUSSION

a. Dosage effect

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The percent adsorption of Eriochrome black-T on PFAC was studied at different adsorbent doses (10, 20, 30, 40, 50, 60 and 70 mg /100ml respectively) keeping methylene blue concentration (10.0 mg/L), at pH neutral and room temperature, constant at constant stirring time (45 min). It is evident from Fig.4 that dye adsorption increases in an adsorbent dose. The percentage adsorption increases from 87.00% at equilibrium as the PFAC dose was increased 10.0 to 70.0 mg /100 ml. This was attributed to equilibrium to an increase in the Parthenium flowers activated carbon, which increased the available surface area and finally it reaches equilibrium [12].

b. Effect of pH

The experiment was conducted to determine the optimum pH at which maximum colour removal could be achieved with PFAC for EBT dye. The pH of the dye solution is an important parameter which controls the rate of adsorption. Waste water containing dyes is discharged at different pH, therefore it is important to study the effect of pH on degradation of dye. The pH manipulation was done in order to elucidate the nature of hydroxyl radicals in degradation of EBT. In order to study the effect of pH, adsorption was carried out using PFAC (70 mg) with 10 ppm EBT solution by stirring for 45 minutes. The pH of the solution studied was 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 with the addition of either HCl or NaOH. The relationship observed between absorption of EBT and varying pH is presented in Fig.5. When the pH of the solution was increased from 4.0 to 6.0, the removal of EBT dye increased from 87.0 % to 92.00 %. The maximum EBT adsorption was observed at neutral pH range.

c. Effect of dye concentration

To study the effect of contact time on the rate of % removal, 100 ml of 10 ppm dye solution was taken in a 250 ml beaker and the optimized quantity of 70 mg of the adsorbent was added to it an and varying time from 5min,15min 30min and 45 min. The solution was stirred on a magnetic stirrer and a small aliquot of the solution was taken out at regular intervals of 12 minutes centrifuged. The UV-Visible spectra were recorded for every aliquot of the solution taken as shown in Fig.6. From the figure, it can be noticed that saturation is reached around 90.6% for a contact time of 45 minutes.

d. Effect of dye concentration

A view glance to respective results, show that at each initial concentration by increasing the amount of adsorbent, the removal time significantly reduced, while the adsorption capacity has opposite relation [20]. At fixed adsorbent concentration, the increase in initial EBT value lead to shortening equilibrium time and enhance in adsorption. As the initial EBT concentration increases from 10 to 50 mg/L, its removal percentage decrease from 92.0 to 27.4% using 0.10 and 0.70 gram and most of the total EBT amount removal occurs in the initial concentration (10 mg/1000 ml). In the 45 min, the major portion of equilibrium adsorbed value is around 92.00 for initial EBT concentrations of 10–50 mg/L using 0.70 g adsorbent, respectively, while at 0.70 g adsorbent the removal percentage was in the range of 27.4–92.00%. This observation is related to the high initial concentration gradient that represents high driving force for the EBT transfer to the PFAC surface. It is also clear from typical curve (Fig.7) that the required contact time for EBT solutions with initial concentrations of 10–50 mg/L was less than 45 min at all conditions. Absolute amount of adsorbed EBT azo dye has strong and positive correlation with initial EBT concentration. It could be said that the higher the adsorbate concentration, the more diffusion would occur from the adsorbent surface into the microspore. So, the initial rate of adsorption was greater for high initial EBT concentrations and the resistance to the EBT uptake diminished as the mass transfer driving force increased [17]. Increase in the adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites, while the unit adsorbed of EBT decreased with increase in PFAC dose. This may be due to the decrease in total adsorption surface area available to EBT resulting from overlapping or aggregation of adsorption sites [18].

e. Desorption and adsorbent regeneration

Desorption and adsorbent regeneration is a critical step, which contributes to the process costs and pollutant recovery. A successful regeneration process should restore the initial characteristics of the adsorbent, allowing the solid reuse during the maximum number of cycles and thus decreasing the costs of the overall separation process. However, in a large number of sorption studies available in the literature dealing with the use of carbon nano particles for the removal of heavy metals and dyes, desorption and reuse of the adsorbents has not been accurately analyzed [21]. The selection of a suitable eluent depends on the adsorbate and the adsorbent, but other operation variables, such as pH, temperature, contact time between the solid and liquid phases and the presence of competitive ions in the solution, may also affect the efficacy of the desorption process [22].70 mg of the PFAC was added to 100 mL of aqueous EBT azo dye solution, after the adsorption studies, the adsorbent was collected (5-10 g) by filtration and washed with deionized water twice to remove any residual dye molecules from the surface of the adsorbent. To this cleaned adsorbent, 100 mL of 0.05 M HCL and stirred for 6 hrs after which it was centrifuged at 1200 rpm for 30 min. The supernatant was analysed for estimating the concentration of dye molecules. From this analysis the percentage of dye molecules was calculated and plotted as % desorption vs. time in min as shown in Fig. 6. It shows percentage of desorption decreases

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like 87 >72 > 33 > 21 for every recycling process in the order of Cycle 1 > Cycle 2 > Cycle 3 > Cycle 4.

f. Comparison of proposed methods with different adsorbents as low cost materials

The adsorption capacities for the removal of Eriochrome black-T on conventional carbon-based adsorbents, including AC, CNTs, charcoal and coal, It can be seen that PFAC has lower adsorption affinity to EBT compared with other carbonaceous materials. However, the practical application of these materials on a large scale is limited by source materials, i.e., non-renewable source of coal, and cost of regeneration and potential toxicity (ie., CNTs) [22,23,27]. Besides, traditional carbon-based adsorbents predominantly consist of micro pores and wide pore size distributions. Adsorption of bulky organic chemicals may be impeded by the size-exclusion effect. PFAC has relative less structure but more O-containing groups and porous structure than the carbon-based adsorbents reported [23-26]. These features make PFAC a promising adsorbent for removing bulky organics such as dyes. Another notable advantage of PFAC is its lower cost (Rs 620/- per kg) in comparison with commercial carbon-based materials in India (Rs 950/- per kg (collagen scientific supplements)). Therefore, this new bio sorbent is expected to have applicability in the removal of dyes and even other organic pollutants from wastewater.

IV. CONCLUSIONS

Among several low cost adsorbents, PFAC showed good adsorptive properties. PFAC material as an adsorbent is effective for EBT removal from dye solution. The adsorption of EBT was dependent on pH, initial dye concentration, adsorbent dose as well as contact time which were optimized. The uptake of EBT is possible between pH of 4 and 6 whereas the maximum color removal was achieved at pH 6. The removal rate increased with the increase in adsorbent dose and contact time while the rate decreased with the increase in EBT concentration and pH. The present study concluded that the Parthenium flowers activated carbon material as an adsorbent can be effectively utilized for the removal of EBT from aqueous environment.

Figure caption:

Fig 1: Structure of Eriochrome Black-T .

Fig 2: Morphology of PFAC studied under SEM.

Fig. 3: FT-IR spectra of (a) after and (c) before adsorption PFAC.

Fig. 4: UV visible spectrum for adsorption of EBT for different adsorbent loading.

% adsorption of EBT vs amount of PFAC.

Fig. 5: UV visible spectrum for degradation of EBT for different pH.

% adsorption of EBT vs pH variation.

Fig. 6: UV visible spectrum for adsorption of EBT for different contact time.

% adsorptions of EBT vs contact time.

Fig.7:Effect of dye Concentration.

(a) 10 ppm, (b) 20 ppm, (c) 30 ppm, (d) 40 ppm, (e) 50 ppm.

Fig.8: Regeneration studies

1-cycle1, 2-cycle2, 3-cycle3, 4-cycle4

Figures

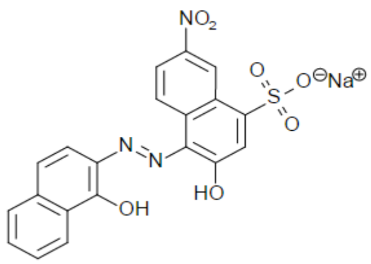

Fig. 1

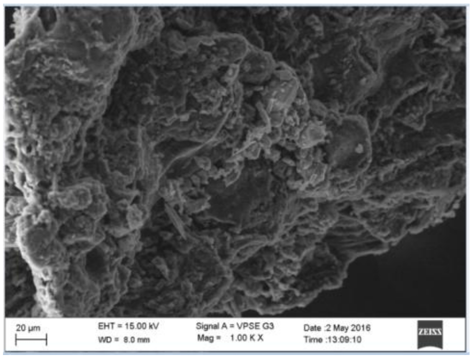

Fig.2

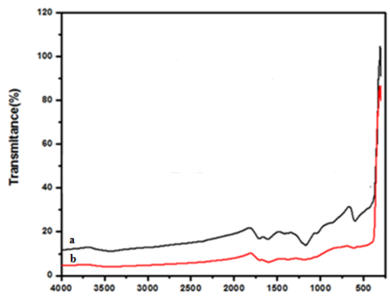

Fig.3

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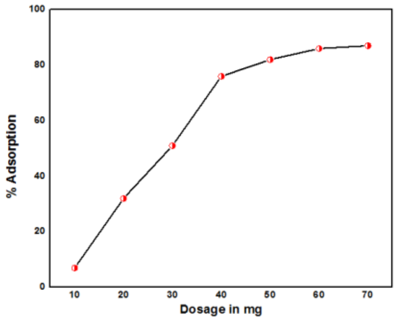

Fig.4

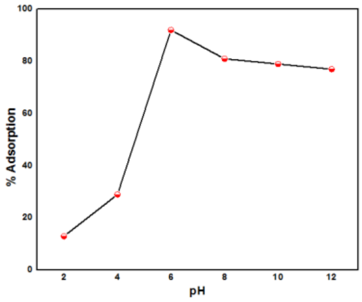

Fig. 5

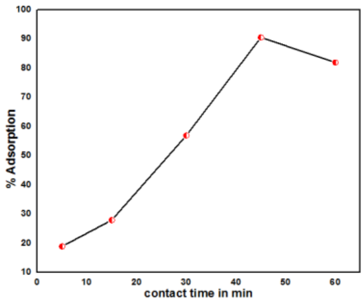

Fig. 6

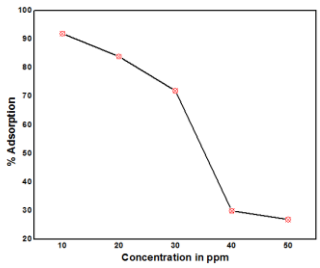

Fig. 7

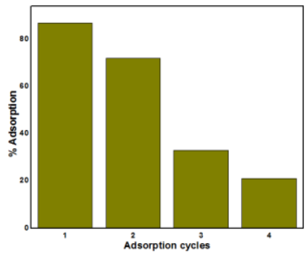

Fig.8

V. Conclusion

Among several low cost adsorbents, PFAC showed good adsorptive properties. PFAC material as an adsorbent is effective for EBT removal from dye solution. The adsorption of EBT was dependent on pH, initial dye concentration, adsorbent dose as well as contact **time** which were optimized. The uptake of EBT is possible between pH of 4 and 6 whereas the maximum color removal was achieved at pH 6. The removal rate increased with the increase in adsorbent dose and contact time while the rate decreased with the increase in EBT concentration and pH. The present study concluded that the Parthenium flowers activated carbon material as an adsorbent can be effectively utilized for the removal of EBT from aqueous environment.

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