Short Communication

Removal of Rhodamine dye from textile wastewater using chemically modified XAD-4

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Abstract. Textile wastewater has been a potential threat around the world. This study reports the abatement of rhodamine dye from textile wastewater using modified amberlite XAD-4 resin. Modification of resin was carried out by introducing amino group and characterized through FTIR. The peaks appeared at 1232 and 1624 cm^{-1} can be attributed to C-N stretching and N-H bending respectively, witnessed the presence of amino group on XAD-4. The effects of contact time, adsorbent dosage, initial dye concentration, and pH on dye removal were investigated. Maximum removal was recorded 93% at pH 9, adsorbent dosage 50 mg and 25 mgL^{-1} initial concentration dye solution and 60 min. The adsorption isotherm of dye showed good fitting to Langmuir and Freundlich isotherms models, respectively.The maximum adsorption capacities were calculated is 82.5 mg/g and 58 mg/g respectively.

1. INTRODUCTION

Water pollution has been a serious threat to living creatures. Huge number of industries dispense their waste into water streams which may affect the human life. Due to industrial effluents less availability to fresh water streams, water pollution treatment has gained serious attention of researchers all around the world. Among the industrial effluents, textile dyes are considered as potential water pollutants which may result in carcinogenic, toxic and can pollute the process of photosynthesis in water streams (Tony et al., 2019, Javaid and Qazi 2019). Large number of dyes are used in textile industries such as basic, acidic, azo, disperse, and metal complex dyes and anthraquinone. In the dying process noticable amount of synthetic dye does not bind effectively and discharged as waste into water streams (Weber and Adams 1995). The dye with concentration of 1 ppm contaminates the drinking water and other streams (Malik et al., 2007).

Present research is focussed on the removal of Rhodamine dye, one of the most important environmental dye. It is water soluble cationic dye, mostly used as medicine for the treatment of animals. It is reported as toxic and cancer causing (Noureddine et al., 2007). It affects the penetration of sun light into the depth of water which affects the processes of respiration and photosynthesis. It causes kindney failure and respiratory diseases (Hachem et al., 2001).

To overcome this effect, various techniques have been applied for the abatement og organic dye from wastewater including ion exchang ,coagulation, flocculation, ozonation and adsorption. Among these methods, adsorption has been a cost effective, rapid and easy manipulated potential technique for removal of organic dyes in the industrial process (Zhang et al., 2021, cao et al., 2021).

In the last several decades, multiple porous adsorbents has been reported such as zeolites (Shaw et al., 2016), activated carbons (mohan et al., 2008) and metal−organic frameworks (Hou et al., 2016) have been investigated for the removal of water pollutants. The drawback of these materials is instability, low removal rate, and poor adsorption capacity.

Large number of articles have been reported the use of Amberlite XAD series resin due to large surface area and greater pore size (Ahmad et al., 2015). But the main demrit of commercial Amberlite resins is that they do not possess selectivity among the metal ions, which results in interferences of co-existing species with the analyte ion which decreases the efficiency (Mottol and Steimetz 1992).

Number of chelating agents have been applied to modify Amberlite XAD surface such as 1,6-*bis*(2-carboxy aldehyde phenoxy)butane has been covalently bonded with polystyrene-divinylbenzene, through a –C=N– group, for the removal and preconcentration of Cu(II) and Cd(II) prior to their determination by FAAS (Mohan and Singh 2002), Octa-O-methoxyresorcine (Oral et al., 2011) arene on Amberlite XAD-4 resin (Vyas et al., 2013), Lemos and Baliza reported a new sorbent (Amberlite XAD-2-2-aminothiophenol) via azo coupling (–N=N–) (Lemos et al., 2005). Present study reports the modification of amberlite XAD-4 and applied for the removal of rhodamine dye from industrial wastewater.

2. MATERIALS AND METHODS

2.1. Rhodamine Dye solution
The standard solutions of Rhodamine dye (Rhd) were prepared from stock solution (1000 mg L^{-1}) by taking a calculated amount of Rhodamine in double distilled water. HCl, CH_3COONa and $NaHCO_3$ buffer solutions were used for pH of 2, 6 and 10, respectively.

Dye (Fig. 1): The dye used in this work was Rhodamine (Rhd) and is one of the commonly used in textile factories. Rhd has a maximum absorption wavelength of 555 nm and the structure of the dye is shown below.The concentration of rhodamine dye was determined by using spectrophotometer,
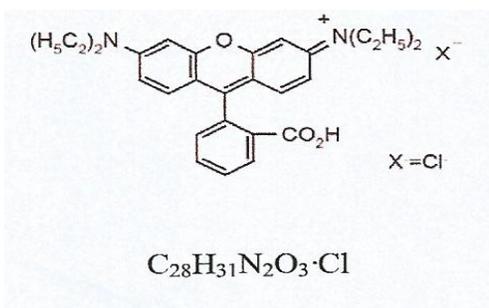

$$C_{28}H_{31}N_2O_3 \cdot Cl$$

Figure 1: Chemical structure of dye in this study

2.2 Synthesis of sorbent
Amberlite XAD-4 resins (5 g) were nitrated using the mixture of concentrated HNO_3 and H_2SO_4. The mixture was heated at 60°C with constant stirring for 30 min. The reaction mixture was poured off into ice water. The nitrated resins were filtered and washed repeatedly with distilled water until free from acid and there after treated with a reducing mixture of 40g of $SnCl_2$, 45mL of concentrated HCl and 50mL of ethanol. The mixture was refluxed for 12h at 90°C. The solid precipitates were filtered and washed with water and 2 $molL^{-1}$NaOH to release amino resin (R–NH$_2$) form (R-NH$_4$)$_2$ SnCl$_4$ (where R is resin matrix). The amino resins were first washed with 2 mol L^{-1}HCl and finally with distilled water to remove the excess of HCl.

2.3. Batch adsorption experiments
The removal of rhodamine dye on resin was optimized by batch adsorption experiments in terms of; dye concentration (10-100 mgL^{-1}), pH (2-9), amount of resin (10-100mg) and time (10-120 minutes). All the experiments were carried out at 25 °C keeping volume and agitation speed respectively at 20 mL and 150 rpm.

Removal efficiency of resin surface was calculated using Eq. (1):

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

Where C_o and C_e are concentrations (mg L^{-1}) of dye at initial and equilibrium stages, respectively. The equation used to determine the dye amount adsorbed at equilibrium per unit mass of adsorbent given below:

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{2}$$

Where q_e is the dye uptake at equilibrium or sorption capacity (mg of dye g^{-1} of the Sorbent), V is the volume of dye solution and m is the amount of resin.

3. RESULTS AND DISCUSSION

3.1. Characterization
Fig. 2 shows the FT-IR spectrum of chemically modified XAD-4. The peaks appeared at 1232 and 1624 cm^{-1} can be attributed to C-N stretching and N-H bending respectively, witnessed the presence of amino group on XAD-4.

3.2. Effect of pH
pH of solution has been a most important parameter that affects the uptake of pollutants affecting the protonation of functional groups of the sorbent surface. The uptake of rhodamine dye was investigated by changing the pH of solution from 2-9 as shown in fig. 3. The maximum adsorption was recorded at pH 9 about 92%. The decrease in uptake of dye at pH less than 9 is due to the presence of excess positive ions that compete with the dye cationic group, which results in low adsorption capacity. At higher pH (9.0-12) values, cation dyes are easily attached on the surface of negatively charged samples through electrostatic force attraction (Anbia and Asl.hariri 2010).

3.3. Effect of initial concentration of rhodamine dye
In order to examine the optimized response of resin, initial concentration of dye was varied from 10-100 mg L^{-1} while other parameters pH, adsorbent dosage, shaking time were kept at constant. It can be seen in the Fig. 4 that the removal of dye decreases with increase in the initial concentration of dye solution. Maximum removal was achieved at 25 mgL^{-1} of dye solution. It can be evaluated that the increase in ratio of dye cations to the amount of resin and the number of active adsorption sites required to accommodate the remaining resin surface.

3.4. Effect of contact time
The uptake of dye on modified resin was examined in terms of contact time in the range of 10-120 min to investigate the equilibrium time for the optimum sorption at pH 9, adsorbent dosage 50 mg and 25 mgL^{-1} initial concentration dye solution. Maximum removal 93% was obtained after 60 min as shown in fig. 5. This can be attributed to the existence of equilibrium point at which the rate of adsorption and desorption were same and no further uptake of dye from the solution was achieved.

3.5. Effect of adsorbent dosage
In order to investigate the efficiency of adsorbent for the uptake of dye, different amounts were used like 10, 20, 30, 50 and 100 mg. An increase in the uptake of dye with increase in adsorbent dosage was recorded up to 50 mg as shown in fig. 6. This can be attributed to the increase in available active sites, where maximum uptake of dye is possible. After 50 mg, it seemed constant due to equilibrium existence between adsorbent surface and dye.

3.6. Adsorption Isotherms
The data obtained from varying initial concentration of dye (10-100 mg L^{-1}) were subjected to different adsorption isotherms. Langmuir the monolayer adsorption model (Eq. 3), Freundlich (Eq.4) and D-R isotherm (Eq.5) were plotted and obtained parameters are presented in Table 1.

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \qquad (3)$$

$$log C_{ads} = log K_F + \frac{1}{n_F} log C_e \qquad (4)$$

$$\ln C_{ads} = K_{D-R} - \beta \, \varepsilon^2 \qquad (5)$$

Where Cads is the amount of dye adsorbed per unit mass of adsorbent and Ce is the amount of dye in liquid phase at equilibrium, Q, b, K, 1/n, and β are the, Freundlich, Langmuir, and D-R constants respectively (channa et al., 2014). Experimental data was validated by all three isotherms with the co-efficient of co-relation values (r) 0.92, 0.93 and 0.92 respectively. Sorption capacities for the uptake of dye were evaluated from their linear curves. Energy for the uptake of dye was calculated from slope of D-R isotherm. Calculated parameters are given in Table 1.
The feasibility of arsenic uptake on adsorbent can also be explained by dimensionless separation factor (RL), can be calculated using (Eq. 7):

$$R_L = 1/(1+bC_i) \qquad\qquad\qquad (6)$$

It describes the type of Langmuir isotherm (Ruthven 1985) to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). R_L factor calculated for the uptake of dye was found to be in the range of 0.0016-0.00053 indicating the favourable sorption.

4. CONCLUSION

Adsorption of dye onto the modified resin is simple fast and cost effective. This study has proved that a modified amberlite XAD-4 was found to have a higher potential for the adsorption dye. In a batch method, removal of dye increased with increasing contact time 60. The adsorption data was fit to the Langmuir and Freundlich models. The increase in adsorption capacity for the modified resin was attributed mainly to the addition amino group.

Table 1. Sorption parameters of Dye onto modified resin

Langmuir			Freundlich			D-R		
Q (mg g^{-1})	b(1mol^{-})	R	A (mg g^{-1})	1/n	R	Xm (mg g^{-1})	E (KJ mol^{-1})	r
82.5	102	0.92	58	0.953	0.93	25.6	12	0.92

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