Adsorption of Congo Red Dye Using Activated Carbon-Fe_3O_4 Composite

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Abstract

Activated Carbon-Fe_3O_4 composites were synthesized using co-precipitation method and used in batch experiments to adsorb Congo red dyes. The effect of adsorbent dosage, temperature and initial dye concentration was investigated. Increase in the adsorbent dosage resulted in the increase of dye adsorption capacity and the optimum dose was found to be 2 g/L. Increase in temperature had slightly negative impact on the adsorption which indicated the exhothermic nature of the adsorption process. Initial dye concentration also had significant impact on the adsorption process as the adsorption capacity of the AC- Fe_3O_4 adsorbents decreased with increase in dye concentrations. Finally, the obtained adsorption data were fitted to Langmuir adsorption isotherm and the maximum adsorption capacity of Activated Carbon-Fe_3O_4 adsorbent was found to be around 129.87 mg/g. Overall, the results suggested that synthesized AC- Fe_3O_4 composites exhibit significant potential to be used as an adsorbent for the removal of organic pollutants from aqueous solutions.

Keywords: Adsorption; Congo Red Dye; Activated Carbon; Iron oxide; Isotherms; Kinetics

1 Introduction

Water pollution triggered from industrial waste discharge is an evergrowing concern for worldwide. Preservation of water is crucial for the safety and well-being of both human and aquatic life. Large volume of wastewater is being directly discharged to the water bodies without any prior treatment. A large percentage of the industrial waste consists of organic dyes due to their extensive application in textile, tannery, paper and printing industries (Harja et al., 2022). Organic dyes can inhibit the light from going into the aquatic system and disrupt the photosynthetic process (Shan et al., 2015). They are also known to be extremely harmful to human health as they are toxic and carcinogenic as well (Ahmad & Ansari, 2021; Lei et al., 2017). Therefore, it is critical to develop efficient methods to remove these harmful dyes from the industrial wastewater.

Various techniques have been employed to remove dyes from wastewater; including adsorption, photocatalysis, coagulation, flocculation, ion exchange, electro chemical method, chemical oxidation and aerobic and anaerobic degradation using microbes (Lim et al., 2016; Mahmud et al., 2021). Among these techniques, adsorption is the commonly employed technique as it is easy to operate, highly efficient and low cost compared to the others. However, the adsorption process is largely dependent on the nature and type of the adsorbent being used. Various adsorbents like activated carbon, metal oxides, polymers and zeolites have been applied to remove dyes from wastewater (Ewis, et al., 2022a; Ba-Abbad, et al., 2022). However, the different studied adsorbents available in the open literature have several drawbacks such as low sorption capacity, high production and recovery problems. Therefore, development of easily recoverable adsorbents with high sorption capability and low cost is very crucial for their industrial application.

Recently, incorporation of iron oxide with various adsorbents for development of recoverable composites has garnered a lot of interest from the scientific community (Aryee et al., 2022; Deng et al., 2022; Ewis, et al., 2022b; Mahmud, et al., 2022; Mahmud, et al., 2023). Fe_3O_4 are environmentally benign, low cost, biocompatible and magnetically recoverable and have been widely used to modify and improve several adsorbents (Mahmud et al., 2020). Owing to these favorable properties, it is expected that incorporating Fe_3O_4 or iron oxide with activated carbon may well result in the formation of an efficient and recoverable composite (Wang et al., 2022). Therefore, in this study, magnetic Activated carbon- Fe_3O_4 composite were prepared via co-precipitation method and the adsorptive removal Congo red dye using the as-synthesized composites was investigated. Results obtained from these studies can provide useful insight on design and development of highly magnetic and iron oxide-based adsorbents that can be effectively used to remove Congo red dye and optimistically other organic pollutants from wastewater effluents.

2 Material and Methods

2.1 Chemicals

Activated carbon was purchased from Gongyi City Meiqi Industry and Company, China. While precursors for iron oxide namely; $FeCl_2.4H_2O$ and $FeCl_3.6H_2O$ both of purity 99%, 25% NH_4OH, NaOH (Purity 98%) and HCl (Purity 35-38%) were obtained from Reseachlab. Absolute Ethanol (Purity 99.9%) was purchased from Researchlab, India. Deionized water was used for preparation and cleaning of the composites throughout the experiments. All the chemicals were used as received without any further purification.

2.2 Preparation of Activated Carbon-Fe_3O_4 composite

Co-precipitation method was applied to synthesize magnetic activated carbon-Fe_3O_4 composite. The procedure consisted of firstly dissolving 0.2 g of activated carbon into 100 ml of deionized water . The solution was then sonicated for 15-20 minutes at 60 °C. After sonication, 0.87 g and of iron chloride tetrahydrate ($FeCl_2.4H_2O$) and 2.35 g iron chloride hexahydrate ($FeCl_3.6H_2O$) were added to the solution , and the mixture was stirred for 15 - 20 minutes under N_2 atmosphere. Afterwards, 20 ml NH_4OH solution was added to adjust the solution pH to 10. The temperature of the solution was then reduced to 50 ^oC and the solution was stirred for additional 60 minutes. The precipitate obtained was separated using a magnet and cleaned in multiple cycles of DI water and ethanol and dried at 80 ^oC under vacuum. Finally, the obtained magnetic activated carbon-Fe_3O_4 composite was then used for congo red adsorption studies.

2.3 Congo Red Dye Solution

A stock solution of congo red was prepared by dissolving 1 g of analytic grade congo red in deionized water to produce 1000 ppm solution. The required concentrations of working solutions were prepared from this stock solution by dilution.

2.4 Adsorption Experiments

Batch adsorption experiments were performed to investigate the effect of various operating parameters on the adsorption of the Congo red dye. The study on the effect of adsorbent dosage, temperature and initial dye concentration on the adsorption performance was carried out by varying the target parameter, while keeping the other parameters fixed. Adsorption isotherm studies were conducted by adding 2.0 g/L of the as prepared AC-Fe_3O_4 adsorbents to a series of 50 mL conical flasks containing 50 mL Congo Red dye solutions of different concentrations (25-800 mg/L). The flasks were then sealed and stirred at 200 RPM in a Labnet air bath shaker for 24 hours at temperature of 298 K. After the completion of the adsorption experiments, the AC-Fe_3O_4 adsorbents were then separated magnetically and the Congo red dye concentrations in the supernatant was measured by determining the maximum absorbance at 498 nm using HACH UV/Vis spectrophotometer (Model: DR 3000). The amount of Congo red adsorbed by the synthesized adsorbent at equilibrium was determined using the following equation:

$$q_e = \frac{(C_o - C_e)\,V}{m} \quad (1)$$

Where, 'qe' represents the amount of Congo Red Dye adsorbed per gram of the adsorbent, the term 'V' stands for the volume of Congo red solution and 'm' represents the mass of the adsorbent. While, 'Co' and 'Ce' represents the initial and equilibrium concentrations of the Congo Red dye, respectively. While, the terms V and W stands for the volume of the solution and mass of the adsorbent. The removal efficiencies were also calculated using the following equation:

$$\text{Removal}\ \% = 100 \times \frac{(C_o - C_e)}{C_o} \quad (2)$$

3 Results and Discussion

3.1 Effect of AC-Fe_3O_4 Dosage

The effect of AC-Fe_3O_4 dosage ranging from 0.2 – 4 g/L on the removal 200 mg/L of Congo Red Dye was investigated at 298 K, a shaker speed of 200 RPM and at natural pH is shown in Figure 1. The amount of Congo red dye removed increased with the increase in AC-Fe_3O_4 dosage. This behavior can be attributed to the fact that with the increase in the adsorbent dosage, more adsorption sites became accessible, which in turn increased the adsorption surface area favoring adsorption of more Congo Red Dye (Deng et al., 2022). With the initial dose 0.2 g/L, 25 % of the Congo red dye was removed in 24 hours. A gradual increase in Congo Red adsorption (50 to 81 %) was observed between the AC-Fe_3O_4 dosage of 0.5 to 1 g/L. Almost complete removal (99 %) was obtained at adsorbent dosage of 2.0 g/L, hence, it was chosen as the optimum dosage for AC-Fe_3O_4 composites for Congo Red Adsorption experiments.

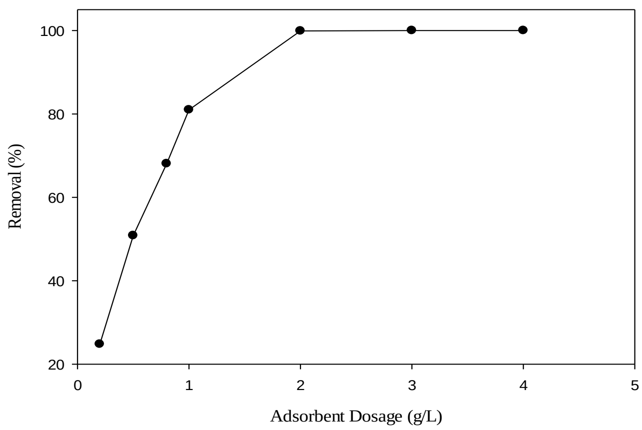

Fig. 1: Effect of Adsorbent Dosage

3.2 Effect of Temperature

The effect of temperature on adsorption of Congo red Adsorption using AC-Fe_3O_4 composites was investigated at three different temperatures (298, 308 and 318 K). Similar to the dosage experiment, the

$AC-Fe_3O_4$ composites dosage was varied between 0.2 – 4 g/L, while, the concentration of Congo red dye and shaker speed was kept fixed at 200 mg/L and 200 RPM, respectively. The dyes natural pH was selected to perform these experiments and obtained results after 24 hours are shown in Figure 2. At all three temperatures, the increase in adsorbent dosage resulted in increase in Congo red dye removal and complete removal of dye was observed at the maximum dosage. However, it was evident from the trends that the increase in temperature resulted in slight decrease in the adsorption capacity. This was an indication that the adsorption process was exothermic in nature (Litefti et al., 2019). Based on these results, 298 K was chosen as the optimum temperature for the dye Adsorption experiments.

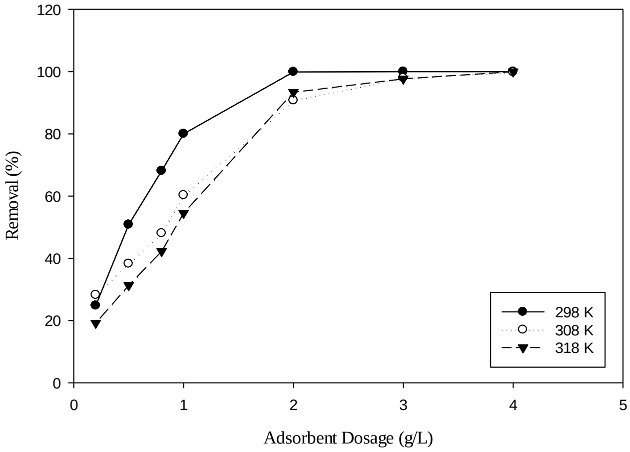

Fig. 2: Effect of Temperature

3.3 Effect of Initial Congo Red Concentration

The effect of Congo red Dye concentration on the adsorption performance was studied by varying the initial concentrations (25-800 mg/L) of the dye under the same experimental conditions (Adsorbent Dose 2.0 g.L-1, natural pH, time 24 hours, shaker speed of 200 RPM and temperature 298 K) as shown in Figure 3. It was observed that the adsorption performance is dependent on the initial dye concentration. Firstly, the complete removal of the congo red dye was observed up to the initial concentration of 200 mg/L. However, starting from initial dye concentration of 300 mg/L and beyond, removal efficiency showed a significant decrease. This phenomenon resulted from the decrease in the availability of the competitive adsorbent sites with the increase in the initial dye concentration rendering it more stable at higher concentrations which in resulted in a decrease in the removal efficiency.

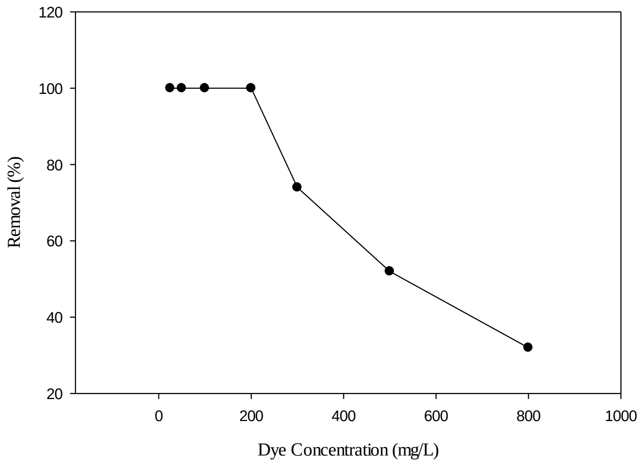

Fig. 3: Effect of Initial Dye Concentration

3.4 Adsorption Isotherm

Analysis of the adsorption isotherms is essential to understand the interactions between the surface of AC-Fe_3O_4 composites and the Congo Red molecules. The Langmuir isotherm assumes that the maximum adsorption occurs due to the formation of a monolayer by the adsorbate on the surface of the adsorbent. It further assumes that the energy required for adsorption process is constant and once the adsorbate i.e. the Congo Red molecule has occupied a site on the surface of the AC-Fe_3O_4 adsorbent, no further adsorption will occur on the same site (Langmuir, 1918). The non-linear form of the governing equation for Langmuir isotherm model is given by equation 3.

$$q_e = \frac{q_m K_L C_e}{1+q_m K_L C_e} \qquad (3)$$

Here, the terms q_m and K_L stands for the maximum amount of Congo red adsorbed by the AC-Fe_3O_4 composite and Langmuir constant, respectively. Both of these terms were determined by non-linear regression. From Figure 4, it can be seen that the model could successfully depict the Congo red adsorption process using the AC-Fe_3O_4 adsorbent with a correlation coefficient, R^2 of more than 0.90. The maximum adsorption capacity of AC-Fe_3O_4 adsorbent at 298 K was be 129.87 mg.g-1. To further predict whether an adsorption process is favorable or not, (Hall et al., 1966) has proposed a dimensionless separation factor or equilibrium parameter, 'R_L' based on the obtained Langmuir constant, 'K_L' and it is given the equation 4.

$$R_L = \frac{1}{1+K_L C_e} \qquad (4)$$

The adsorption process is considered to favorable when the R_L value falls between zero and unity and it is considered to be unfavorable when its greater than unity. Moreover, the adsorption is considered to be linear when R_L equals unity and irreversible when it equals to zero. The calculated values of RL was for Congo red adsorption using AC-Fe_3O_4 adsorbent was observed to be within the range 0.73 to 1, which indicates the adsorption process was favorable.

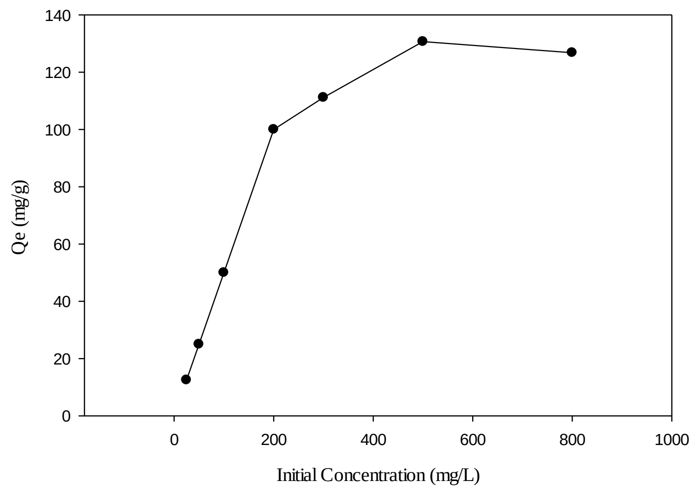

Fig. 4: Observed Isotherm for adsorption of Conge red dye using AC-Fe_3O_4 composite

4 Conclusion

This study showed that the AC-Fe_3O_4 composite is a potential adsorbent for removal of Congo red dyes from aqueous solutions. Congo red adsorption experiments were conducted using the prepared AC-Fe_3O_4 composite. Experimental parameters like adsorbent dosage and initial dye concentration were found to be have a significant effect on the Congo red adsorption process. Adsorption isotherm studies were conducted by fitting the experimental data to Langmuir, isotherm. Langmuir isotherm was found to be suitable in fitting the experimental data and the maximum adsorption capacity of the AC-Fe_3O_4 composite was found to be 129.87 mg/g. Hence, the synthesized AC-Fe_3O_4 adsorbents showed great potential to be used as an adsorbent for removal of Congo red dye as well as other organic pollutants from wastewater streams.

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