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Article

Synthesis of Magnetic Composites of Chitosan-Fly Ash-Fe_3O4 Nanoparticle to Improve Congo Red Dye Adsorption

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Abstract

Chitosan, an environmentally friendly adsorbent, is derived from the deacetylation of crab shell chitin. In this study, the chemical and physical properties of chitosan were enhanced through the direct compositing process of magnetic chitosan (Chi) with fly ash powder particles (FA). This research is of considerable importance in the development of environmentally friendly adsorbent materials for the treatment of wastewater contaminated with synthetic dyes, particularly azo dyes such as congo red. The utilization of crab shell waste as a source of chitosan, in conjunction with fly ash and Fe_3O_4 to form Chi-FA-Fe_3O_4 magnetic composites, has been demonstrated to exhibit considerable promise in enhancing adsorption efficiency. The magnetic composite of Chi-FA-Fe_3O_4 was characterized by XRD and SEM. The present study investigated the effect of adsorption process parameters on CR dye removal. The parameters that were investigated included contact time (30-150 minutes) and initial concentration of CR dye at an adsorbent dosage of 0.06 grams in 100 milliliters and a pH of 4. The maximum removal efficiency of the Chi-FA-Fe_3O_4 composite for CR dye was recorded as 99.82% at an initial concentration of 100 parts per million (ppm) CR dye for 150 minutes. Pursuant to the analysis of XRD, it has been confirmed that the compositing process was successfully executed, thereby yielding 2θ values indicative of Fe_3O_4 and FA. Additionally, an enhancement in the intensity of the Chi-FA-Fe_3O_4 composite was observed following the adsorption of CR dye. Concurrently, SEM analysis revealed that the Chi-FA-Fe_3O_4 composite and the Chi-FA-Fe_3O_4 composite exhibited an augmented intensity.

Keywords: chitosan, composites, magnetic, fly ash, congo red

1. Introduction

Water contamination represents a grave environmental concern, significantly contributing to overall pollution levels and posing a substantial

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threat to public health. Annually, a substantial quantity of dye-containing waste is produced from industrial activities, including textiles, food, pharmaceuticals, paper, and cosmetics [1], [2]. These dyes have been shown to impede the penetration of sunlight through water, exhibit chemical persistence, and are not biodegradable [1], [3]. Congo red (CR) is a type of azo (diazo) dye, which is the predominant class of synthetic dyes and is extensively utilized by numerous industries. The compound is classified as a carcinogen due to its structural elements, specifically the presence of aromatic amines. The aromatic structure of these dyes renders them resistant to natural degradation, a property that is characteristic of azo dyes. Dyes that persist in the environment for extended periods, exerting detrimental effects on fauna and flora [4]. Therefore, water treatment is necessary to eliminate CR dyes.

A substantial amount of progress has been achieved in the domain of wastewater treatment research. A variety of techniques have been employed to remove dyes from wastewater, including photocatalytic decomposition, coagulation, flocculation, ion exchange, membrane separation, nanofiltration, electrochemical oxidation, and adsorption [5]. Among these methods, adsorption technology is ideal for wastewater treatment due to its cost-effectiveness, high efficiency, and low energy consumption [2]. In the field, numerous researchers have developed various materials that function as adsorbents for dye removal. These include activated carbon [6], zeolite [7], silica [8], cellulose [9], and chitosan [10]. In recent years, significant attention has been directed towards the development of environmentally friendly adsorbents, particularly those derived from chitosan. Chitosan (Chi) is a cationic polysaccharide composed of D-glucosamine units. Chi is typically derived from the deacetylation of chitin found in shrimp shells, crab shells, lobster shells, and oyster shells, thereby ranking as the second most prevalent biopolymer in nature after cellulose [11]. The distinctive molecular configuration of Chi is attributable to the presence of amine (-NH2) and hydroxyl (-OH) functional groups, which function as dynamic adsorption sites capable of removing various water pollutants, including dyes [1].

Chi can be modified by compositing to increase porosity and surface area, and to reduce internal diffusion resistance. Such modifications can be achieved through the incorporation of ZnO nanoparticles, TiO_2 nanoparticles, clay nanocomposites, magnetic (Fe_3O_4), and fly ash (FA) [3]. Adsorption is a promising method of removing pollutants from water, and FA is a promising adsorbent. The chemical composition, surface area, porosity, particle size, and water-holding capacity of FA all suggest that it has the potential to increase its adsorption capacity. The composition of FA predominantly consists of metal oxides, including silica (SiO_2), alumina (Al_2O_3), and magnetite (Fe_2O_3), in addition to unburned carbon [12]. Another modification that can be made is adding Fe3O4 nanoparticles as a magnetic core in composite materials to achieve effective separation and easy collection of adsorbents from aqueous media with an external magnetic field [2]. Ferrite (Fe_3O_4) are frequently utilized magnetic particles due to their exceptional properties, including elevated surface area, biocompatibility, magnetic responsiveness, and chemical stability [13].

The primary objective of this study was to develop a novel magnetic chitosan-fly ash-Fe_3O_4 (Chi-FA-Fe_3O_4) composite that functions as an adsorbent. It is characterized by high chemical stability, and can be both recovered and separated. The effectiveness of Chi-FA-Fe_3O_4 was examined based on its capacity to remove CR dye from an aqueous environment. The synthesis and application of Chi-FA-Fe_3O_4 as an adsorbent are contingent upon two primary parameters: contact time and initial concentration of CR dye.

2. Material and Method

2.1. Materials

Fly ash (FA) is a byproduct of the combustion of coal, a material that is a fundamental component of the power generation industry. Chi is derived from deacetylation of crab shell chitin. The following reagents were procured from Merck: iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$), congo red ($C_{32}H_{22}N_6Na_2O_6S_2$), acetic acid ($CH_3CO_2H$), and sodium hydroxide (NaOH). All experiments were conducted using distilled water.

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2.2. Synthesis of Chi-FA-Fe_3O_4 composite

A mixture of 1 g of Chi and 1 g of FA particles was prepared in an acetic acid solution (5%, 50 mL). The solution was subjected to gentle stirring for a period of 24 hours at room temperature. This procedure was intended to ensure complete dissolution of Chi and the subsequent loading of FA particles into the molecular structure of Chi. Subsequently, 3.9 g of $FeCl_3.6H_2O$ and 2.7 g of $FeSO_4.7H_2O$ were dissolved in 10 mL of distilled water and added to the Chi-FA solution under slow stirring (80 rpm) for a duration of one hour. The obtained solution was subsequently introduced into a sodium hydroxide solution (2M, 1000 mL) with a rate of 10 mL over a period of 6 hours, under conditions of slow stirring. This process resulted in the instantaneous formation of magnetic Chi-FA-Fe_3O_4. The newly synthesized magnetic Chi-FA-Fe_3O_4 was subjected to a thorough wash with distilled water, with the objective of eradicating residual sodium hydroxide solution. Following this step, the material was dried in a controlled environment. After a thorough examination of the pulverization process, it was determined that the desired result, i.e., the Chi-FA-Fe_3O_4 composite powder, was finally obtained.

2.3. Characterization

The characterization of the Chi-FA-Fe_3O_4 composites was carried out by various analytical methods and techniques. The morphology of the Chi-FA-Fe_3O_4 samples was analysed using a scanning electron microscopy (SEM, FeI Inspect S50-AMETEX). The analysis of the Chi-FA-Fe_3O_4 composites before and after the adsorption of CR dye is the subject of this investigation. X-Ray Diffraction (XRD, Bruker D8 Advance Eco, Germany) was utilized to examine the crystallinity and amorphous nature of Chi-FA-Fe_3O_4 composites and Chi-FA-Fe_3O_4 composites following CR dye adsorption.

2.4. Adsorption experiments

The effect of contact time (0-150 minutes) was studied using initial CR adsorbate concentrations of 100 and 150 ppm. The adsorption process was carried out with a dose of 0.06 g of adsorbent in 100 ml of CR adsorbate at pH 4. Subsequent to this, the mixture was separated between the filtrate and the residue. The filtrate from the adsorption process was analyzed using a UV-Vis spectrophotometer (Agilent Cary 60 Spectrophotometer; λ = 497 nm) to determine the concentration of CR adsorbed in the adsorbent. The calculation of removal efficiency can be performed using equation 1.

$$\%Removal = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

Where C_o and C_e are the initial concentration of CR and the final concentration of CR in ppm.

3. Results and Discussion

3.1. XRD analysis

The crystal structure of the adsorbent was determined by XRD analysis. As illustrated in Figure 1, the XRD patterns of the Chi-FA-Fe_3O_4 composite adsorbent and the Chi-FA-Fe_3O_4 composite after CR dye adsorption are shown. The highest peaks of the Chi-FA-Fe_3O_4 composite prior to adsorption are located at 2θ = 35.492° and 62.8168°. The presence of Fe_3O_4 particles is indicated by characteristic peaks at 2θ = 30°, 35°, 43°, 53°, 57°, and 62°. Furthermore, the prominent peaks observed at 2θ = 16°, 22°, 26°, 33°, 39°, 41°, 50°, 60°, 61°, and 68° correspond to the crystalline phases of the FA particles, including alumina (Al_2O_3), quartz (SiO_2), and hematite (Fe_2O_3) [12]. The presence of these peaks is indicative of the insertion of FA particles into the molecular structure of magnetic chitosan. Following the adsorption process, an increase in intensity at 2θ = 17.36° is observed, suggesting that a change occurs during the adsorption process, indicating that the CR dye molecules are inserted into the adsorbent pore [4].

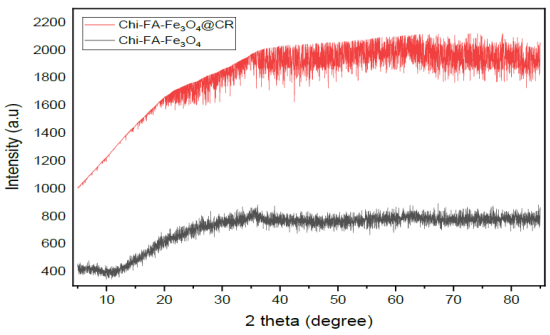

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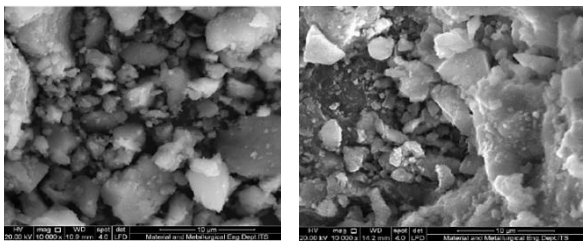
Fig 1. XRD analysis of Chi-FA-Fe_3O_4 composite adsorbent and Chi-FA-Fe_3O_4 composite after CR dye adsorption

3.2. SEM analysis

The surface morphological structure of the Chi-FA-Fe_3O_4 composite adsorbent and Chi-FA-Fe_3O_4 composite after CR dye adsorption was examined by SEM analysis. Figures 2a and b illustrate the SEM images of the Chi-FA-Fe_3O_4 composite and Chi-FA-Fe_3O_4 composite following CR dye adsorption, respectively. As illustrated in Figure 2a, the surface morphology of the Chi-FA-Fe_3O_4 composite is characterized by its roughness, porosity, and the presence of crevices and cracks. Figure 2a also demonstrates the discrepancy in size of the embedded spherical objects that are clearly visible on the surface of the Chi-FA-Fe_3O_4 composite. This indicates the successful incorporation of FA particles into the molecular structure of the Chi-FA-Fe_3O_4 composite. The surface of the Chi-FA-Fe_3O_4 sample exhibited a more compact morphology following MB dye adsorption, as observed in Figure 2b. This change was accompanied by the emergence of crevices on the surface, suggesting the presence of CR molecules adsorbed on the surface of Chi-FA-Fe_3O_4.



(a) (b)

Fig 2. SEM analysis with 10,000x magnification (a) Chi-FA-Fe_3O_4 composite and (b) Chi-FA-Fe_3O_4 composite after adsorption of CR dye

3.3. Effect of contact time and initial concentration of CR dye

Contact time and initial concentration of CR dye are one of the most important factors affecting the adsorption efficiency. As shown in Figure 3, the removal efficiency of CR in solution by Chi-FA-Fe_3O_4 increased with time at an initial concentration of 100 ppm of CR dye. However, at the initial concentration of 150 ppm CR dye, there was a decrease in the removal efficiency after 120 minutes. The increase in removal efficiency is because there are many active sites on the surface of Chi-FA-Fe_3O_4, and with the extension of time, the adsorption gradually tends to equilibrium saturation [14]. After passing the equilibrium condition, the removal efficiency starts to decrease slowly. This decrease occurs because the adsorbent experiences desorption, which occurs when the adsorbate on the surface of the adsorbent is released back into the solution because the active groups on the adsorbent are saturated [15].

In addition, the initial concentration of CR dye also affects the removal efficiency. As the initial concentration increases, the removal efficiency of CR dye on Chi-FA-Fe_3O_4 gradually decreases. This occurs because the adsorption capacity of activated carbon is limited, i.e., the adsorption sites on its surface are limited [16]. At low solution concentration, the activated carbon does not reach adsorption saturation, and CR ions can fully occupy the adsorption sites on its surface, and the removal rate is high, but the adsorption amount per unit is relatively small. As the solution concentration increases, the diffusion rate of CR ions also increases, and the amount of CR ions adsorbed on the surface of the activated carbon unit increases [14].

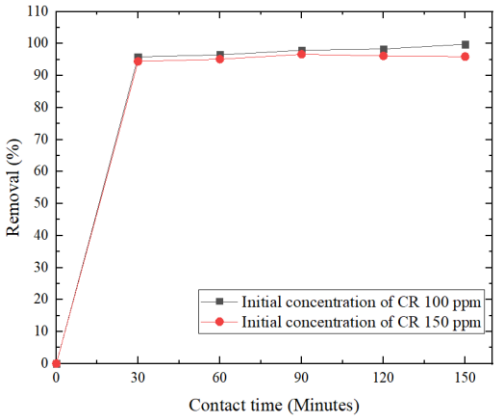


Fig 3. Effect of contact time and initial dye concentration on the adsorption of CR dye with Chi-FA-Fe_3O_4 composite adsorbent

4. Conclusions

Magnetic chitosan-fly ash-Fe_3O_4 (Chi-FA-Fe_3O_4) composites were successfully synthesized and applied as effective bio adsorbents for the

removal of azo (diazo) dyes. The Chi-FA-Fe_3O_4 composite was easily separated and collected from aqueous solution after the adsorption process by external magnetic field. The results showed that the highest CR dye removal efficiency (99.82%) was obtained from the significant interaction effect between contact time and initial concentration of CR dye at pH 4. This study introduces an innovative and efficient adsorbent for removing diazo dyes from water.

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