SELECTIVE DECOLORIZATION OF ANIONIC TEXTILE DYE FROM BINARY SOLUTIONS BY ADSORPTION ONTO CHITOSAN-POLYANILINE/Fe₃O₄ NANOCOMPOSITE

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Abstract. In this study, chitosan-polyaniline/Fe₃O₄ nanocomposite material (CS-PANI/Fe₃O₄) was prepared by means of in-situ emulsion polymerization method. The synthesized material was then utilized as an adsorbent for the removal of Reactive blue 198 (RB198) from a single and binary dye system. The effects of pH, contact time, and initial dye concentration on the removal efficiency of the adsorbent were systematically investigated. The obtained results indicated that the adsorption ability toward RB198 of the prepared adsorbent decreased with an increase in the initial dye concentration and pH media. Meanwhile, the removal percentage of dye increased with increasing contact time. Importantly, approximately 92.4% RB198 was removed for an adsorption time of 120 min in single dye system. Adsorption experiment using a binary system of dyes indicated that the removal percentages of RB198 were 72.8% and 94.7% in the RB198-RR198 and RB198-CY mixture, respectively.

Keywords. Chitosan, PANI, textile dye, nanocomposite

1. INTRODUCTION

Wastewaters released from the industries based on textile dyeing, rubber processing, leather, paper, cosmetics, plastics, food, and pulp manufacturers contain a lot of synthetic organic dyes that were used to tint the commodities. The emission of untreated-wastewater containing a few of dyes into the environment can generate risks to human beings, aquatic creatures, and biodiversity [1]. Textile industries produce the greatest problems associated with effluents due to their complex composition and elevated coloration. The dying process generates large amounts of effluents that carry colorful inorganic salts and chemical compounds used throughout these processes. Therefore, there should be the solutions for treatment of dyes in wastewater before discharging them into the water resources to minimize the pollution of water and soil. There have been several methods applied for treating dye in wastewaters such as coagulation and flocculation, reverse osmosis, electroflotation, membrane filtration, irradiation and ozonation, and adsorption [2-3]. Among them, adsorption is well-known as one of the most promising approaches for the dealing of colorants in aqueous media due to its ease of application and high efficiency. However, the efficiency of this route depending on the development of adsorbent materials. So far, many materials have been used for the removal of dyes including teawaste [4], chitosan [5], kaolin [6], banana waste [7] and composite materials [8-9], etc. Lebron et al. investigated the sorption of methylene blue and eriochrome black T from aqueous solutions using a low-cost and eco-friendly biosorbent [3]. However, these studies only focused on the adsorbents’ ability toward textile dyes from a single dye system. It is well-known that industrial wastewater could involve multi-components of dyes, and they can compete with each other during the adsorption process. Thus, a highly selective adsorbent is highly desired to develop. Besides, the recovery of used adsorbents has been considered as one of the important factors that evaluates their practical applications. In this work, a cost-effective and easily recovered chitosan-polyaniline/Fe₃O₄ nanocomposite was prepared by in-situ emulsion polymerization. The synthesized CS-PANI/Fe₃O₄ composite was applied for decolorization of anionic Reactive Blue 198 dye in aqueous solution. The effects of pH solution, contact time, and dye concentration on the dye removal efficiency were systematically investigated. Moreover, the competitive adsorption of RB198 in the presence of anionic Reactive Red 198 (RR198) and cationic CY dye was also investigated using binary dye systems.

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2. EXPERIMENTAL SECTION

2.1. Materials
Aniline (C₆H₅NH₂, 98%) and ammonium peroxodisulfate ((NH₄)₂S₂O₈, 98%) were supplied by Aldrich-Sigma company. Iron(III) chloride hexahydrate (FeCl₃·6H₂O, 98%), iron(II)chloride tetrahydrate (FeCl₂·4H₂O, 98%), and sodium hydroxyl (NaOH, 98%) was purchased from TCI Chem Co. The Reactive Red 198 textile dye (Mₚ = 983.5, λₘₐₓ = 516 nm), Reactive Blue 198 dye (Mₚ = 1304.8, λₘₐₓ = 604 nm) and cationic Yellow dye (CY) were obtained from Thanh Cong textile and dyeing company. Chitosan with deacetylation degree of 90% was obtained from Aldrich-Sigma company. All chemicals were used as received without further purification.

2.2. Methods

2.2.1. Synthesis of chitosan-PANI/Fe₃O₄ composite
Chitosan-polyaniline/Fe₃O₄ composite was prepared via in-situ emulsion polymerization following our previous procedure[10]. Briefly, a calculated amount of chitosan in acetic acid 1% was added to the aniline solution in HCl 1M under stirring condition, and the mixture was aged for 10 min to obtain a uniform solution (Chitosan: Aniline =1:1 molar ratio). To the resulting mixture, a desired amount of ammonium peroxydisulfate in HCl (1.0 M) was added. The obtained reaction mixture was kept at 5°C for 5h under stirring condition. Then, a desired amount of Fe₃O₄ nanosuspension was added dropwise into the above reaction mixture. The obtained greenish-black solid was collected by filtering and washing with deionized water until the filtrate became colorless. The prepared composite was finally desiccated at 60°C for 24h and used as an adsorbent for decolorization of dyes.

2.2.3. Characterization of prepared materials
The functional groups of the synthesized composite material was analyzed using an FT-IR spectroscopy (Tensor 27, Bruker, Germany) with the scanning wavenumber in the range of 400 to 4000 cm⁻¹. X-ray diffraction (XRD) of Fe₃O₄ and CS-PANI/Fe₃O₄ were conducted on LabX XRD-6100 (Japan). The surface morphology of CS-PANI/Fe₃O₄ was measured by FE-SEM equipment (HITACHI-SU8000, Japan).

2.2.4. Adsorption experiments
Adsorption experiment was performed using Erlenmeyer flasks (250 ml). Firstly, the solution of textile dye (50 mL) with concentration ranged from 25 to 100 ppm was prepared in these flasks. The pH media was adjusted using NaOH 0.1M and HCl 0.1M. 0.1g of composite materials was added to the dye solution under stirring condition (200 rpm) at room temperature. After an interval adsorption time, the aqueous solution was withdrawn and separated by an external magnet. The concentrations of dye were measured using UV–Vis spectrophotometer. The dye removal efficiency was calculated by the following equation:

\[
\text{Removal efficiency} \% = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]  

where \(C_0\) and \(C_t\) are the initial dye concentration and dye concentration at t time (ppm), respectively. All experiments were measured triplication to obtain average values.

Adsorption experiment using binary dye system was conducted as the same as that the single dye. Equimolar dye mixture solution was prepared by mixing RR198 and RB198 (v/v=1/1, 50 ppm), RR198 and CY (v/v=1/1, 50 ppm). After an interval time, the aqueous solution was withdrawn, and the optical density of dye solution was measured by UV-Vis spectrometer. The concentration of each dye in binary solutions was determined as previous report [11]. All the experiments were carried out in triplicate. For UV-vis analysis, linear relation between absorbance (A) and concentration of dye (C) (mg/L) which was given by Beer-Lambert law in (1) was applied.

\[
A = K.C + E
\]

Where
- \(A\) is the absorbance of light at a maximum wavelength (\(\lambda_{\text{max}}\));
- \(C\) is the concentration of dye in solution (ppm);

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K is the absorbance coefficient (slope of linear relation);
E is the intercept of a linear relation.

For the binary system, total absorbance $A_1$ at $\lambda_{1\max}$ is the sum of absorbance of each component $R_i$ (RR 198) and $B_i$ (RB 198), the equation (2) can be rewritten as:

$$A_1 = kR_1 . CR + kB_1 . CB \quad (3)$$

Additionally, total absorbance $A_2$ was determined at $\lambda_{2\max}$:

$$A_2 = kR_2 . CR + kB_2 . CB \quad (4)$$

Based on the equation (3) and (4), the concentration of each component in solution was determined as follows $CR$ (RR 198) and $CB$ (RB 198):

$$CR = \frac{kR_2 . A_1 - kB_1 . A_2}{kR_1 . kB_2 - kB_2 . kB_1} \quad (5)$$

$$CB = \frac{kR_1 . A_2 - kR_2 . A_1}{kR_1 . kB_2 - kB_2 . kB_1} \quad (6)$$

Binary components of RR198–RB198, in which $kR_1, kB_1, kR_2, kB_2$ are the calibration constants for dye RR198 and RB198 at wavelength of 542 nm and 604 nm, respectively. As shown in Figure 1, the calibration constants for RR198 – RB198 are $kR_1 = 0.0198, kB_1 = 0.006$ at $\lambda_{1\max} = 542$ nm, $kR_2 = 0.0005, kB_2 = 0.0107$ at $\lambda_{2\max} = 604$ nm. Based on the f equation (5) and (6), the concentration of each component in solution was determined:

$$CR = \frac{0.0197 . A_1 - 0.005 . A_2}{2.0886 \times 10^{-4}}$$

$$CB = \frac{0.0198 . A_2 - 0.0005 . A_1}{2.0886 \times 10^{-4}}$$

Figure 1: Calibration curves for RR198–RB198 at (a) $\lambda_{1\max} = 542$ nm and (b) $\lambda_{2\max} = 604$ nm
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For the binary system of RR198–CY, the calibration constants for RR198–CY are \( kR_1 = 0.0038, kI_1 = 0.0197 \) at \( \lambda_{1\text{max}} = 410 \) nm, \( kR_2 = 0.0201, kI_2 = 0.0003 \) at \( \lambda_{2\text{max}} = 542 \) nm (Figure 2) Based on the equation (5) and (6), the concentration of each component in solution was determined:

\[
CR = \frac{0.0003A_1 - 0.0197A_2}{0.00039} \\
CB = \frac{0.0038A_2 - 0.0201A_1}{0.00039}
\]

Based on the equation (5) and (6), the concentration of each component in solution was determined:

3. RESULTS AND DISCUSSION

3.1. Characterization of CS-PANI/Fe3O4 composite

The details for structure of CS-PANI/Fe3O4 composite was reported in our previous work[10]. FT-IR spectra of CS-PANI/Fe3O4 composite shows a wide peak located 3100-3600 cm\(^{-1}\), assigned to O-H and N-H stretching vibration of chitosan. The vibrational mode of PANI is presented at 1585 cm\(^{-1}\), which is due to the stretching vibration of C=C in the quinoid ring, while peak at around 1496 cm\(^{-1}\) is attributed to C=C stretching vibration of the benzenoid ring. The vibrational mode of C–N in the secondary aromatic amine was observed at the wavenumber of 1293 cm\(^{-1}\) [10]. Additionally, the peak located at 563 cm\(^{-1}\) was assigned to magnetic Fe3O4. SEM image shows that the formation of aggregated composite materials.

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addition, it can be seen that Fe$_3$O$_4$ nanoparticles coated by CS-PANI (Figure 3). XRD pattern of the synthesized Fe$_3$O$_4$ and CS-PANI/Fe$_3$O$_4$ nanocomposite show the diffraction peaks at 10 to 70°. The peaks at 2θ = 38.8°, 45.2°, 65.6° and 78.8°, assigned to the characteristic peak of Fe$_3$O$_4$'s cube structure [12].

Figure 4 shows the TGA curve of the CS-PANI/Fe$_3$O$_4$ composite material. The weight loss of composite material underwent several periods. The first weight loss (15.35 wt%) occurred between 40 and 140 °C could be due to the removal of adsorbed water and solvents. The second weight loss stage happened from 140 to 408 °C, the last weight loss of 38.67 % was due to the degradation of glycosidic bonds (C-O-C) in chitosan. The weight loss occurred between 408 to 700 °C was due to decomposition of chitosan and polyaniline in oxygen atmosphere. The residual mass was stable during the heat treatment process could be assigned to Fe$_3$O$_4$ nanoparticles.

3.2 Adsorption of RB198 in single system

3.2.1 Influence of initial RB198 concentration

The influence of initial dye concentration and contact time on the removal efficiency of RB198 on the prepared CS-PANI/Fe$_3$O$_4$ nanocomposite were presented in Figure 5. As shown, the removal efficiencies were 76.8, 90.0, 90.5 and 92.4% corresponding to the initial dye concentration of 100, 75, 50 and 25 ppm, respectively. It was noticed that the removal efficiency of RB198 increased significantly with an increase in contact time in the period of 0-30 min. With longer adsorption time, however, the adsorption rate increased slightly. Under the investigated condition, the adsorption equilibrium reached after 120 min. The high adsorption rate of RB198 on the synthesized-PANI/Fe$_3$O$_4$ at the first stage could be attributed to there were many available active sites of the adsorbent. Longer adsorption time (> 30 min) and higher dye concentration (>50 ppm) decreased the removal efficiency of dye because most of adsorption sites were filled by the RB198 molecules. The effect of contact time on the removal efficiency of dye on the adsorbent was also investigated and presented in Figure 5. Fig. 6 shows the UV-Vis spectra of RB198 as a function of contact time. From Fig. 6, it can be seen that the absorbance intensity decreased with increasing of the contact time, indicating that the removal efficiency of dye increased with an increase in adsorption time.
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3.2.2 Influence of pH

Fig. 7 shows the effects of pH media on the adsorption ability toward RB198 over the synthesized adsorbent. As presented, the removal efficiency decreased with increasing pH media. Specifically, the removal efficiency of RB198 decreased from 81.64% at pH 3, to 37.6% when pH media increased from 3.0 to 9. This could be explained due to the fact that the surface charge of prepared CS-PANI/Fe3O4 was changed with the change in pH media. In deed, at acidic media (pH 3), the amino groups of CS-PANI/Fe3O4 were protonated to form the positive charge surface on the adsorbent, which enhances the adsorption ability toward anionic dye RB198 due to the electrostatic interaction. The similar result for the removal of RR198 by PANI/Fe3O4 nanocomposite was also reported in the literature [13].
3.3 Adsorption of RR198 for Binary System

Equimolar dye mixtures including RB198-RR198 and RB198-CY were used to test their competitive adsorption using the prepared CS-PANI/Fe₃O₄ material and the obtained results presented in Figure 8 and 9, respectively. As shown, the removal efficiency of each dye over CS-PANI/Fe₃O₄ increased rapidly with increasing the adsorption time for both systems. In particular, the maximum dye removal was 88.4% for RR198 and 72.8% for RB198 in the RR198-RB198 system. Meanwhile, the maximum dye removal of RR98 and CY in the RR198-CY system was 94.7 and 56.8%, respectively. The higher removal efficiency for RR198 in the RR198-CY mixture as compared to that in the RR198-RB198 mixture could be due to the fact that the RR198 and RB198 are anionic dyes, while the CY is cationic dye. As above-mentioned, the adsorbent’s adsorption ability can be improved due to the electrostatic interaction between the negative charge of anionic dye and the positive charge surface of the adsorbent.

Figure 8: Effect of contact time on the removal of RR198 dye in the presence of RB198 dye
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4. CONCLUSION

In this present work, CS-PANI/Fe3O4 was successfully prepared and applied for the removal of RB198 dye in aqueous solution. The synthesized CS-PANI/Fe3O4 composite was characterized by FT-IR, SEM and TGA techniques. Adsorption experiment on a single dye system indicated that CS-PANI/Fe3O4 exhibited 92.4% removal efficiency of RB198 at pH 3 and room temperature. The removal efficiency of dye on the prepared material were strongly affected by contact time, pH media, and dye concentration. The obtained results from the adsorption experiment using equimolar dye mixtures showed that CS-PANI/Fe3O4 exhibited high selective adsorption toward anionic dye over cationic dye. These findings suggested that the prepared CS-PANI/Fe3O4 can be a promising adsorbent for removal of anionic dyes in wastewater.

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LOẠI BỎ CHỌN LỌC CHẤT MÀU ANION TỪ DUNG DỊCH MỘT VÀ HAI CẤU TỬ BẰNG VẬT LIỆU NANOCOMPOSITE POLYANILINE/Fe₃O₄

Tóm tắt. Trong nghiên cứu này, chất màu Reactive Red 198 (RR198) và Reactive Blue 198 (RB198) được loại bỏ từ dung dịch một và hai cấu tử bằng hấp phụ lên vật liệu nanocomposite chitosan-polyaniline/Fe₃O₄ (CS-PANI/Fe₃O₄). Ảnh hưởng của pH, thời gian tiếp xúc và nồng độ ban đầu của chất màu đến hiệu suất loại bỏ cũng được nghiên cứu. Kết quả nghiên cứu cho thấy, hiệu suất loại bỏ RB198 từ hệ một cấu tử và hai cấu tử tăng với tăng thời gian tiếp xúc. Trong hệ một cấu tử 92.4% chất màu được loại bỏ, trong khi hiệu suất loại bỏ trong hệ hai cấu tử cho RR198 và RB198 lần lượt là 88.4 và 72.8%. Ngoài ra, hiệu suất loại bỏ RR198 tăng lên 94.7% khi RB198 được trộn với chất màu cation CY.

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