Application of surfactant-coated magnetic zeolite NAA as a new sorbent to remove Safranin O dye from aqueous solutions

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In the present study, a novel modified magnetic zeolite NaA was produced and applied to remove cationic Safranin O dye using a batch equilibration method. The results indicated that sodium dodecyl sulfate coated magnetic zeolite NaA had higher adsorption capacities for Safranin O than unmodified magnetic zeolite NaA. The effects of sorbent dose (0.05-0.4 g), contact time (5–25 min), dye concentration (120-1123 mg L^{-1}), solution pH (3–9), and sorption temperature (299–323 k) were examined. Under optimal conditions, the adsorption was 98% at pH 4 for Safranin O dye. The maximum adsorption capacity was 149.25 mg/g, and the k_F value was 9.05 mg/g for Safranin. The kinetics of Safranin dye onto SDS-coated magnetic zeolite NaA was best described by the pseudo-second-order kinetic model. Safranin Dye adsorption equilibrium data were fitted well to the Langmuir and Freundlich isotherms. The negative values of free energy and enthalpy change indicated the spontaneity and exothermic nature of the adsorption process. Accordingly, magnetic zeolite NaA was shown to be a very efficient and low-cost sorbent and a promising alternative for eliminating dyes from industrial waste waters.

Keywords: SDS-coated magnetic zeolite NaA; adsorption; safranin O; sorbent

1.INTRODUCTION

The discharge of dye effluents to the environment, especially to water system, has been a major concern due to their toxicity. These dyes are usually originated from industries such as textiles, dye stuff manufacturing, dyeing, and printing. The dissolved oxygen required by aquatic life, can be consumed by these dyes. Some of dyes have direct toxicity to microbial populations and even can be toxic and/or carcinogenic to mammals. However, the problems related to dye pollution can be reduced by physical, chemical, and biological processes such as microbial degradation, chemical oxidation, coagulation, filtration and membrane separation but these processes pose their disadvantages and limitations such as high cost, generation of secondary pollutants, and poor removal efficiency. Thus adsorption has been found to be the most effective economic alternative with high potentials to remove and recover dyes from wastewater [1, 2]. In this regard activated carbon is one of the most widely used adsorbents [3-5], yet it suffers from high cost of production and regeneration [5, 6]. Alternatively, relatively cheap natural adsorbents or their modified products are a choice. For instance, clay minerals, as low-cost natural ones, are natural scavengers of pollutants from water through ion exchange and adsorption [7-10]. Zeolite, as an abundant resource, available globally, has already found many applications because of its high cation-exchange capacity and high surface area. Structurally, it is mostly composed of aluminosilicates with a three-dimensional framework structure. This structure bears AlO_4 and SiO_4 tetrahedra which are connected to each other by sharing all of their oxygens to form interconnected cages and channels containing mobile water molecules and alkalis and/or alkaline earths [11, 12]. So, zeolite is a good adsorbent for heavy metal ions from wastewater [13-15] and for organic dyes [5, 16-18]

Recently, magnetic separation has been applied in many areas to remove, isolate and/or concentrate the desired components from a sample solution. Nanosized magnetic iron oxide particles have been studied extensively as a new adsorbent with large surface area and small diffusion resistance [19] for the separation and removal of chemical species such as metals [20, 21], dyes [22, 23] and gases [24].

To modify and increase the adsorption/desorption of sorbents, the core–shell mechanism was applied. In this way, magnetic particles were loaded on a suitable support and are used as a sorbent to remove target analytes from different real samples [25, 26]. One of the best materials that can be used for the core in core/sell mechanism is zeolite. Many kinds of natural and synthetic zeolites have been known and they have various applications. In general, chemical structure, availability, and economic cost are important factors for various applications of zeolites. In recent years, various methods have been developed for preparing

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magnetic zeolite; the most important ones are hydrothermal and mechanical methods [27].

Safranin, a contaminant agent, is widely used as food dye to flavour and color candies and cookies, textile industries, leather, paper as well as in researches related to histology, textile, cytology and bacteriology [28]. Safranin is a phenazine dye used also as a photosensitizer in electron and energy-transfer reactions. Moreover, it is frequently used as a redox indicator in analytical chemistry and Safranin has been used as an analytical reagent for the determination of nitrite in acidic medium. Safranin reacts with nitrite to form a diazonium cation, charging the reddish-orange colour of the dye solution to blue. Safranin was selected in the present study as a representative cationic dye.

The objective of this study was to investigate the adsorption of Safranin onto SDS-coated magnetic zeolite NaA using a batch equilibration method. In this research, for the first time, SDS-coated magnetic zeolite NaA as a new magnetic sorbent was successfully prepared. This study helps to understand the adsorption properties and potential applications of modified magnetic zeolite NaA for dye removal from aqueous environments. The effects of many factors such as SDS-coated magnetic zeolite dose, initial pH, initial dye concentration, temperature and contact time are also investigated. Moreover, the kinetics and thermodynamics were analyzed by fitting the data to various kinetics models and isotherms equations.

2. EXPERIMENTAL

2.1. Chemical and apparatus

Pure zeolite NaA powder was synthesized from the raw and accessible materials using a hydrothermal method described in the literature [29].

All the reagents were of analytical reagent grade and were used as supplied. Safranin O ($C_{20}H_{19}N_4^+Cl^-$) as a cationic dye was obtained from Sigma–Aldrich. Ferric chloride ($FeCl_3.6H_2O$), ferrous chloride ($FeCl_2.4H_2O$), Sodium dodecyl sulfate (SDS), sodium hydroxide and hydrochloric acid were prepared from Merck. The molecular structure of Safranin O is shown in Fig. 1. All the solutions were prepared with doubly distilled water. A stock standard solution of Safranin O dye at a concentration of 1000 mgL^{-1} was prepared in doubly distilled water and was diluted with distilled water to prepare stock solutions with concentration of 5, 10 and 50 mgL^{-1} of Safranin O. These solutions were used to optimize the effective parameters and also to plot the calibration curve in order to calculate the dye removal efficiency using spectrophotometry. All of the spectrophotometric measurements of the dye

were done at its λ_{max} (520 nm) by a cintra 6 UV–Vis spectrophotometer (Australia).

2.2. Preparation of magnetic zeolite NaA

Fe_3O_4 NPs were prepared by a chemical co-precipitation method. At first, 10.4 g of $FeCl_3.6H_2O$, 4.0 g of $FeCl_2.4H_2O$ and 1.7 mL of HCl (12 mol L^{-1}) were dissolved in 50mL of deionized water for preparing the stock solution of ferrous and ferric chloride. After that, it was degassed with nitrogen gas for 20 minutes. Simultaneously, 500 mL of a 1.5 mol L^{-1} NaOH solution was degassed for 15 min and heated to 80 °C. Then, the stock solution was added dropwise during 30 min under nitrogen gas protection and vigorous stirring. During the whole process, the solution temperature was kept at 80 °C and nitrogen gas was purged to prevent the intrusion of oxygen. The magnetite nanoparticles were formed according to the following reaction:

$Fe^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Fe_3O_4 + 4H_2O$

After the reaction, the obtained Fe_3O_4 NPs precipitate was separated from the reaction medium using the magnet, and then washed with 500 mL deionized water several times. Finally, Fe_3O_4 NPs were resuspensioned in 100 mL of degassed deionized water. 2 g of calcined zeolite NaA was added to the above solution after heat treatment at 150 °C under vacuum over night. The total mixture was vigorously stirred for 10 hours. Then it was separated by using a magnet and washed with deionized water several times. After that it was dried and kept in desiccator for later use [30].

2.3. Magnetic zeolite NaA modifications

The adsorption capacity of unmodified magnetic zeolite NaA are low for Safranin dye, but when magnetic zeolite A was modified with SDS, the adsorption capacity was increased remarkably. In this study, SDS was used at concentrations lower than its critical micelle concentration [31]. In the absence of SDS, dye removal was low due to weak attraction between the positive dye and magnetic zeolite NaA. Accordingly, the negative groups of SDS can interact with the magnetic zeolite surface to form double layer on its surface. By increasing the surfactant concentration, admicelles were formed dominatingly on the surface of magnetic zeolite and the negative charge increased. At this condition, Safranin dye can be adsorbed to the surface of zeolite via electrostatic interactions.

To prepare the modified magnetic zeolite, 100 ml of SDS solution (0.1 gL^{-1}) was prepared and 5 g of magnetic zeolite NaA was added to the SDS solution. The mixture was shaken for 2 h. Then the modified magnetic zeolite NaA was quickly

separated from the sample solutions using a magnet. After that, it was dried in an oven at 120 ℃ and then stored in a desiccator for later use.

2.4. Analytical procedure

Sorption measurements were performed using batch experiments. An amount of 0.2 g of SDS-coated magnetic zeolite NaA was added to 25 ml of 120 mgL⁻¹ Safranin solution; then the mixture was shaken using Shaker at 150 rpm for 15 min. At predetermined time, the bottles were taken from the shaker, and the sorbent was quickly separated (1min) from the sample solutions using a magnet (1.4 T), and the residual dye concentration in the solution was measured using UV-Visible spectroscopy at the wavelength that corresponded to the maximum absorbance of the sample at 520 nm. Dye concentration in the reaction mixture was calculated from the calibration curve. Sorption experiments were conducted by varying initial solution pH, contact time, sorbent dose, initial dye concentration and temperature. In addition the sorption kinetics, sorption isotherm and thermodynamic were studied. The amount of equilibrium sorption q_e (mg/g) was calculated using the Equation (1):

$$q_e = (C_0 - C_e)/M \qquad (1)$$

where C_e (mgL⁻¹) is the liquid concentration of dye at equilibrium, C_0 (mgL⁻¹) is the initial concentration of the dye in the solution, V is the volume of the solution (L), and M is the mass of dye sorbent (g). The Safranin removal percentage can be calculated using Equation (2):

$$\text{Removal efficiency\%} = (C_0 - C_e)/C_0 \times 100 \qquad (2)$$

where C_0 is the initial Safranin concentration, and C_e (mgL⁻¹) is the concentrations of dye at equilibrium.

3. RESULTS AND DISCUSSION

3.1. Influence of pH on Safranin adsorption

Adsorption tests as a function of pH were carried out, and the results are shown in Fig. 2. In the experiments, 25 ml of 120 mg L⁻¹ Safranin and 0.2 g of modified magnetic zeolite NaA were used, and the initial pH varied from 3 to 9. As shown in figure 2, the adsorbed Safranin reached its maximum at pH 4. At pH higher than 4, the electrostatic attraction between the negatively charged –SO₃⁻ anion and the positively charged dye decreased. The reason underlying the high adsorption capacity at low pH is because of the strong electrostatic interaction between the anionic surfactant head groups and cationic dye molecules. At higher pH values, the density of –SO₃⁻ groups on the outer surface of the adsorbent decreased and consequently the

adsorption capacity decreased. The maximum adsorption capacity of Safranin O occurred at around acidic pH 4. So, pH 4 was selected for all further adsorption experiments.

3.2. Effect of initial dye concentration

It has been observed that for adsorbents, adsorption of dye increases with increasing concentration, Due to the increase in the number of ions competing for the binding sites available on the sorbent surface. Initial dye concentration also provided an important driving force to overcome all mass transfer resistances of dye between the aqueous and solid phases.

Fig. 3 presented the percentage of removal versus initial dye concentration. It was observed that when the concentration of the dye increased from 120 to 1123 mg L⁻¹, the percentage of removal decreased from 98 to 86%, but the amount of adsorbed dye increased (Fig. 4).

3.3. Influence of contact time on Safranin adsorption

In order to optimize the contact time, a series of experiments were performed at 25 ml of 120 mg L⁻¹ Safranin solutions with modified magnetic zeolite NaA. The initial pH for each dye solution was also set at 4.0. The suspensions were shaken in certain time intervals, and then the dye concentrations were analyzed to calculate the adsorbed Safranin on the modified zeolite. These experiments were performed in different time periods (5, 10, 15, 20, 25 min). The effect of contact time on the adsorption of Safranin onto the modified magnetic zeolite NaA is presented in Fig. 5. The results demonstrated that the adsorption process was quick, and the equilibrium was attained in 15 minutes. For this reason, 15 min was selected as the optimum contact time for the next experiments in our study.

3.4. Influence of adsorbent amount used on Safranin adsorption

In order to obtain the optimum SDS coated magnetic zeolite NaA amount required for adsorption at pH 4.0, a series of experiments were carried out with different amounts of adsorbents in 25 ml of 120 mg L⁻¹ Safranin solutions. The Safranin concentration was tested after 15 min of shaking. The removal percentage against the added modified magnetic zeolite NaA amounts is shown in Fig. 6. Examination of this figure revealed that the percentage of dye removal increased when the amount of the adsorbent increased. The percentage of dye removal using 0.2 g SDS-coated magnetic zeolite NaA can reach 98.25. At higher amounts of

adsorbent the removal percentage becomes nearly constant. So 0.2 g of SDS- coated magnetic zeolite NaA was used in the further experiment.

3.5. Effects of ionic strength

The effect of ionic strength on the adsorption of the dye (25 ml of 120 mg L^{-1} (pH 4)) was investigated by adding of NaCl, CaCl$_2$, Na$_2$SO$_4$ and NH$_4$Cl to the range of 0–10% (w/v). The results indicated that increasing salt concentration had little effect on the Safranin O adsorption which could be ignored. According to the results, the presence of high ionic content in sample does not change the dye removal efficiency.

Real waters especially dyeing waste waters have high salt contents, so modified magnetic zeolite NaA is expected to be an effective and economical adsorbent for removal of Safranin O from aqueous systems.

3.6. Influence of temperature on Safranin adsorption (ΔG^0, ΔH^0 and ΔS^0)

The effect of temperature on the adsorption of Safranin onto modified magnetic zeolite NaA was investigated. A series of experiments were performed at different temperatures in 25 ml of 120 mg L^{-1} Safranin solutions (pH 4.0) as described in section 2.4.

Using the equilibrium concentration obtained at different temperatures, various thermodynamic parameters such as change in free energy ΔG^0, enthalpy ΔH^0 and entropy ΔS^0 were determined using the following equations:

$$\Delta G^0 = -RT\ln K \qquad (3)$$
$$K = (C_0 - C_e)/C_e \qquad (4)$$
$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (5)$$

where K is the equilibrium constant, T is the temperature expressed in K, and R is the gas constant. The ΔH^0 and ΔS^0 values were obtained from the slope and intercept of Van't Hoff plot. The results $(\Delta S^0 = -0.064$ kJ/mol.K and $\Delta H^0 = -29/02$ kJ/mol) illustrated that adsorption was a spontaneous and exothermic process.

3.7. The study of kinetics of adsorption

To select optimum operating conditions, the study of kinetics of dye adsorption onto the modified magnetic zeolite NaA was required. The kinetic parameters, which are helpful for the prediction of the adsorption rate, provide important information for designing and modeling the adsorption processes. Kinetic studies were performed according to section 2.3 (Analytical procedure) at different time intervals ranging from 5 to 40 mins. The residual Safranin O concentration in the solution was measured by spectrophotometer. The kinetic data for the adsorption of the dye onto SDS-coated magnetic zeolite NaA were analyzed using pseudo-first order [32], pseudo-second order [33] and intra-particle diffusion [34] models to find out the adsorption rate expression. The conformity between the experimental data and the model-predicted values was expressed by the correlation coefficients (R^2, values close to 1). The removal rate was very fast during the initial stages of the adsorption processes. The kinetics of the adsorption was obtained as a pseudo-second order. The rate of pseudo-second order reaction may be dependent on the amount of the solute sorbed on the surface of the adsorbent and the amount sorbed at equilibrium. The kinetic rate equations can be rewritten as Equation (6):

$$t/q_t = 1/k_2 q_e^2 + t/q_e \qquad (6)$$

where q_t and q_e, are the values of the adsorbed dye at each time and at equilibrium, and k_2 is the pseudo-second order rate constant. The pseudo-second order rate constants, k_2, was obtained as 0.012 g mg^{-1} min^{-1}, and the equilibrium adsorption capacity was obtained as 148.2 mg g^{-1}. The linear correlation coefficient value (R^2) was found to be 0.9964. The pseudo-second order kinetic model in the present system showed the adsorption of the dye followed by chemisorption mechanism via electrostatic attraction.

3.8. Adsorption isotherms of Safranin

Equilibrium isotherm equations were used to describe the experimental sorption data. The parameters obtained from the different models provide important information on the sorption mechanisms and the surface properties and affinities of the sorbent. The equilibrium adsorption isotherm was also determined using batch studies. An amount of 25 mL of the dye solution with various initial dye concentrations 120–1123 mg L^{-1} was prepared and then the modified magnetic zeolite was added to the dye solution. After that the solution was shaken for 15 min according to section 2.4. The amount of dye uptake by the SDS-coated magnetic zeolite NaA, q_e (mg g^{-1}), was obtained by using equation 7:

$$q_e = (C_0 - C_e)/m_s \qquad (7)$$

where C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of the dye in the solution, respectively, and m_s is the concentration of modified magnetic zeolite NaA (g L^{-1}). The adsorption data obtained in a concentration range of 120–1123 mg L^{-1} were correlated with the following linear forms of Langmuir (Eq. 8) [35] and Freundlich (Eq. 9) [36] adsorption isotherm models:

• Langmuir equation: $C_e/q_e = (1/K_L\, q_{max})+(1/q_{max})C_e$, and $\quad$ (8)

• Freundlich equation: $\log q_e = \log K_f + (1/n)\log C_e$ $\quad$ (9)

where q_e is the equilibrium dye concentration on the adsorbent (mg g^{-1}), C_e the equilibrium dye concentration in the solution (mg L^{-1}), q_{max} the monolayer capacity of the adsorbent (mg g^{-1}), K_L the Langmuir constant (L mg^{-1}) related to the free energy of the adsorption, K_F the Freundlich constant (L g^{-1}), and n (dimensionless) is the heterogeneity factor.

In the Langmuir model, a plot of C_e/q_e versus C_e indicates a straight line of slope $1/q_{max}$ and an intercept of $1/(K_L\, q_{max})$. Using this model the maximum absorbed Safranin amount on the modified zeolite NaA was 149.25 mg g^{-1}. In most cases the exponent between 1 $<n<$ 10 shows beneficial adsorption. So, the value of n (1.91) reached in the current study, represents favorable adsorption conditions.

4. CONCLUSIONS

The sorption of pollutants from aqueous solutions plays a significant role in water pollution control. For this purpose, the utilization of the SDS-coated magnetic zeolite NaA as an efficient adsorbent was successfully carried out to remove the Safranin O dye from wastewater samples.

Optimal experimental conditions including pH, adsorbent dosage, temperature, salt concentration and contact time were also established. The experiments showed that the adsorption process was quick and the equilibrium was attained in 15 minutes using 0.2 g of the adsorbent. The optimum pH for dye removal was determined 4.0. The maximum equilibrium capacity of the modified magnetic zeolite was calculated from Langmuir equation that was 149.25 mg g^{-1}. It was seen that the increase in the salt concentration had little effect on the Safranin O adsorption which could be ignored. Using the equilibrium concentration obtained at different temperatures, various thermodynamic parameters, such as ΔG^0, ΔH^0 and ΔS^0 were calculated. The results illustrated that adsorption was a spontaneous and exothermic process and modified magnetic zeolite NaA was expected to be an effective and economical adsorbent to remove Safranin O from aqueous solutions.

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