Journal of Molecular Liquids 212 (2015) 675–685

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

# Removal of Safranin dye from aqueous solution using magnetic mesoporous clay: Optimization study

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ARTICLE INFO

*Article history:*
Received 17 June 2015
Received in revised form 22 September 2015
Accepted 26 September 2015
Available online xxxx

*Keywords:*
Magnetic adsorbent
Safranin removal
Central composite design
Sepiolite
Response surface methodology

ABSTRACT

Iron oxide/sepiolite magnetite composite (MSep) was prepared by a chemical precipitation method. The composite was characterized by using X-ray diffraction, scanning electron microscopy, Fourier transform infrared spectroscopy and specific surface area analysis. The response surface methodology (RSM) based on central composite design (CCD) was successfully applied to the optimization of the Safranin removal process. Three independent variables namely initial pH, dye ion concentration and adsorbent dosage were investigated. Analysis of variance (ANOVA) of the quadratic model suggested that the predicted values were in good agreement with experimental data. Detailed kinetic and equilibrium studies were performed for liquid phase adsorption of Safranin using MSep. The adsorption process could be well described by Langmuir isotherm and the maximum monolayer adsorption capacity was calculated as 18.48 mg $g^{-1}$. The adsorption kinetics was evaluated by pseudo-first-order and pseudo-second-order models; pseudo-second-order model was found to describe the process better. The adsorption was analyzed thermodynamically and the results revealed that the adsorption process was spontaneous and endothermic.



## 1. Introduction

Dyes and pigments are extensively used in the textile, leather, plastics, printing, rubber, pharmaceutical, cosmetic, food, paper and carpet industries to color their product. There are more than 10,000 different dyes weighing approximately $7 \times 10^5$ tons that are produced annually for various industrial processes [1]. The dyes generally have complex aromatic structure and thus most of them are highly resistant to breakdown by chemical, physical, and biological treatments [2,3]. The discharge of dye-bearing wastewater into water bodies possesses a serious pollution problem as the dyes give water undesirable color, reduce sunlight penetration and gas solubility in water [4,5]. Safranin (3,7-dimethyl-10-phenylphenazin-10-ium-2,8-diamine chloride) is a water-soluble organic dye, widely used in textile industries [6]. However, Safranin can cause eye burns which may be responsible for permanent injury to the cornea and conjunctiva in human and rabbit eyes [7]. Contact with Safranin dye also causes skin and respiratory tract irritation [8]. Because of this, industrial wastewaters containing such dye need to be treated before being delivered to the environment [9,10]. A wide range of physical and chemical processes such as flocculation, adsorption, membrane filtration, coagulation, precipitation, ozonation, electrochemical techniques, and fungal decolonization have been investigated extensively for removing dyes from aquatic bodies [11,12]. Among these, liquid phase adsorption has been found to be superior to other techniques for removal of colors, odor, oils, and organic pollutants from process or waste effluents. This is attributed to its initial low cost, high efficiency, simplicity of design, and ease of operation [13]. The major drawback of this method is the high price of adsorbents that increase the cost of treatment. A number of scientists for this purpose have used different adsorbents such as charcoal [14], zeolites [15], bagasse [16], fly ash [17], clay [18] and sawdust [19].

Sepiolite (magnesium hydro-silicate) is a natural clay mineral characterized by its fibrous morphology and intracrystalline channels with a unit cell formula of $Si_{12}Mg_8O_{30}(OH)_4(OH_2)_4 \cdot 8H_2O$ [20]. The hollow needlelike crystal structure of sepiolite is responsible for its unique physiochemical properties. The average size of fibrous sepiolite crystals is $800 \times 25 \times 4$ nm, which results in a solid with an external surface area of the same order of magnitude as the area of macroporous [21]. Like other clay minerals, natural sepiolite has an electronegative surface because of isomorphic substitutions. In addition, the abundant molecular

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http://dx.doi.org/10.1016/j.molliq.2015.09.045
0167-7322/

sized channels allow the penetration of organic and inorganic species into the structure of sepiolite and assign sepiolite important industrial applications [22–24].

During the past few years, magnetic nanoparticles (MNPs) as an efficient adsorbent with large specific surface area and small diffusion resistance have been recognized [25,26]. The magnetic separation provides a desirable path for online separation. A distinctive superiority of this technique is that the MNPs with affinity to target species can be readily isolated from sample solutions using an external magnetic field without additional filtration or centrifugation steps.

Response surface methodology (RSM) is a well known statistics-based procedure for designing experiments, understanding the effects of different factors and their interactions on targeted response, building models and finding out optimum conditions [27–29]. The use of RSM has been accentuated for developing the complex processes, optimizing their performance, and improving design of new products. The main advantage of RSM is the reduced number of experimental trials needed to evaluate multiple parameters and their interactions [30]. Central composite design (CCD) is the most frequently used method of RSM, which is suitable for fitting a quadratic surface and helps optimize the effective parameters with a minimum experimental runs, in addition to analyzing the interaction between parameters [31].

The focus of this research was to explore the feasibility of new kind of $Fe_3O_4$/sepiolite magnetic nanocomposite (MSep) being utilized in removal of Safranin as a cationic dye from aqueous solutions and also optimization of the process variables using the response surface modeling approach. CCD was selected to study the individual and synergetic effects of factors such as Safranin concentration (mg $L^{-1}$), adsorbent dosage (g) and pH on the percentage removal of dye as response.

## 2. Experimental

### 2.1. Instruments and reagents

All reagents and chemicals used in the study were of analytical reagent grade. Safranin dye (C.I.: 50240; chemical formula: $C_{20}H_{19}ClN_4$; M.W.: 350.84 g $mol^{-1}$, $\lambda_{max}$: 520 nm) was procured from Merck. The chemical structure of the dye is shown in Fig. 1. Safranin stock solution with an initial concentration of 1000 mg $L^{-1}$ was prepared by dissolving the required amount in double-distilled water. The test solutions were prepared by diluting the stock solution to the desired concentrations. The pH was adjusted and measured using a 713 pH-mV meter (Metrohm, Switzerland) at the laboratory ambient temperature. Absorbance spectra of Safranin were acquired with a Cary 50 single detector double beam in-time spectrophotometer (Varian, Australia). A newly found Iranian sepiolite (Sep) sample with a particle size of ≤0.075 mm (200-mesh) from Yazd region (central Iran) was applied in this study [32]. The mineral sample was powdered and sieved using a 0.05 mm mesh. The chemical composition of the mineral used in this study is shown in Table 1.

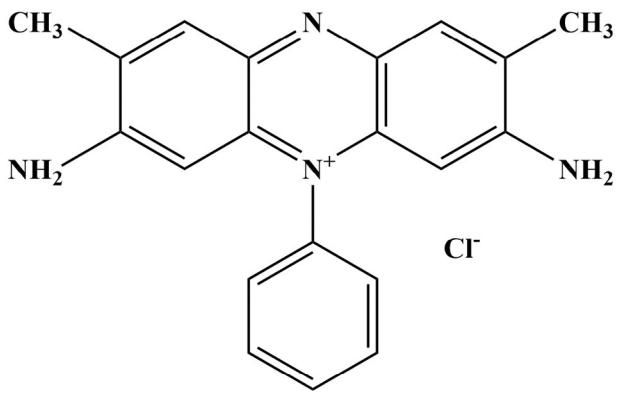


**Fig. 1.** Chemical structure of Safranin.

### 2.2. Preparation of iron oxide–sepiolite composite

In brief, 2 g of Sep was added into a 100 mL solution of 1.55 g $FeCl_3 \cdot 6H_2O$ and 1.2 g $FeSO_4 \cdot 7H_2O$ and refluxed for 3 h in an oil bath at 110 °C under $N_2$. When the mixed solution was cooled to 60 °C, ~5 mL $NH_4OH$ solution (25%) was added dropwise under $N_2$ with vigorous stirring to precipitate the surface-immobilized $Fe^{2+}$ and $Fe^{3+}$ ions. The pH of the final mixtures was controlled in the range of 10–11 to ensure the complete transformation of iron ions to iron oxides. The mixtures were aged at the same temperature for 2 h and then washed with deionized water repeatedly. The obtained composite was dried at 100 °C for 5 h.

X-ray diffraction (XRD) analysis of the natural sepiolite and MSep composite was performed using a PANalytical X'Pert PRO MPD instrument (PANalytical B.V., Almelo, The Netherlands) equipped with a back monochromator operating at a tube voltage of 40 kV and a tube current of 30 mA using a copper cathode as the X-ray source ($\lambda$ = 1.542 Å). The 2θ angle that ranges from 5° to 80° was scanned with a step size of 0.02° and a time per step of 0.5 s.

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker tensor 27 spectrometer (Madison, WI, USA) using the standard KBr disk method (sample/KBr = 1/100). All transmittance spectra were taken at the spectral resolution of 4 $cm^{-1}$ for 64 scans over the wave number region 4000–500 $cm^{-1}$.

The morphology of MSep composite was also determined with scanning electron microscopy (SEM, KYKY-EM 3200, Zhongguancun Beijing, China), operated at 20 kV. The samples were sputter-coated with a thin layer of gold for 2 min prior to SEM analysis.

A vibrating sample magnetometer (VSM, Lake Shore, 7410, USA) was applied to determine the magnetic property of the resultant composite.

The zeta potentials of materials were measured with a Malvern Zetasizer (Nano-ZS, Malvern Instruments, Worcestershire, UK) according to literature [33]. In the preparation of the samples, 0.5 g of solid sample was mixed with 100 mL electrolyte (NaCl, 0.01 mol $L^{-1}$) in an Erlenmeyer flask and pH was adjusted using NaOH or HCl in the range between 2.0 and 11.0. After stirring for 1 h at room temperature, the samples were allowed to stand for 15 min to let larger particles settle. An aliquot taken from the supernatant was used to measure the zeta potential.

To determine the specific surface area of samples, Brunauer–Emmett–Teller (BET) measurements of $N_2$ adsorption were carried out at 77 K using a Belsorp-mini II (BEL Japan, Inc.). The samples were dried and out-gassed at 120 °C for a minimum of 6 h under vacuum before the $N_2$ adsorption experiments.

### 2.3. Adsorption studies

Batch experiments were carried out in 20 sets of 50 mL Erlenmeyer flasks with 10 mL dye solution agitated for 30 min using an incubator shaker at 150 rpm. The experiments were performed under varying initial concentrations (40–80 mg $L^{-1}$), pH (6–10) and adsorbent dosage (0.03–0.07 g). The pH of the solution was adjusted using 0.1 mol $L^{-1}$ KOH. After adsorption, the MSep composite was separated by a magnet and the sample absorbance was measured. The residual concentration of the dye in the solution was then determined using the UV–vis

**Table 1**
Main chemical composition of sepiolite sample.

| Component (wt.%) | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | $Na_2O$ | $K_2O$ | MgO | LOI |
|---|---|---|---|---|---|---|---|---|
| Sepiolite | 53.9 | 0.21 | 0.01 | 2.94 | 0.01 | 0.01 | 24.22 | 18.7 |