REMOVAL OF ALIZARIN RED S FROM AQUEOUS SOLUTION USING SODIUM BENTONITE

[145]

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ABSTRACT

In this work, sodium bentonite (Bn) was used for removal of alizarin red S (ARS) from aqueous solution using batch technique. Fourier transform infrared spectroscopy and X-ray diffraction were used to characterize sodium bentonite. Different parameters that would affect ARS dye removal such as initial pH, contact time, initial ARS dye concentration, bentonite dose, and temperature were explored. The realized data from kinetic studies demonstrated the high fitness of pseudo-second-order kinetic model for better interpretation of the experimental data. The adsorption isotherms studies showed that Freundlich isotherm had a high correlation coefficient among the studied isotherm models. Thermodynamic studies proposed that ARS adsorption onto Bn was spontaneous in nature at the lower temperatures and exothermic.

1. INTRODUCTION

Dyes usually accumulate from the effluents discharged by various industries such as textiles, paper, cosmetics, rubber, and plastics [1, 2]. Dyes are poisonous to organisms and carcinogenic. Manufacturing wastewater having such dyes discharged into receiving water has become a serious environmental problem. One of the major environmental problems is the color removal from textile wastewater because of the difficulty of treating such water by traditional treatment methods [3]. ARS is used for coloring textile such as cotton, wool, and woven fabrics. ARS is an anionic anthraquinone dye and is highly durable and difficult to degrade because of its complex structure. In addition, it is known to possess carcinogenic properties and causes environmental problems [4].

Numerous techniques, such as chemical oxidation, flocculation, precipitation, membrane filtration, biodegradation and electrochemical techniques have been employed for dyes removal. The previously mentioned procedures have several drawbacks such as high cost, generation of secondary contaminants and low removal effectiveness. Adsorption has been shown high efficiency and be an economical process for the dyes removal from wastewater [5]. Currently activated carbons [6, 7] and resins [8] are commonly applied for the removal of dyes; however they are still expensive for practical application. Hence, searching for natural-occurring materials and low cost adsorbent materials for dyes removal seems to be more significant.

Bn clay is a kind of aluminosilicate clay and is mostly composed of montmorillonite that is characterized by one aluminum octahedral layer placed between two silicon tetrahedral layers. This clay is preferred due to its chemical and mechanical stability, high surface area, layered structure, low cost, abundant in most soils and high cation exchange capacity. Bn has a diversity of uses since it becomes a colloidal when mixed with water, swelling in water, and high plasticity. From its developed application is used as a dispersive agent. Bn clay also used as an industrial raw material in catalytic, rheological and sorptive applications. Moreover, it is used in some applications in industry, such as in drilling fluids, paper, cement, pharmaceutical field, dyes and ceramics. Bn has a layer structure, which gives the clay a good ion exchange capacity that is mostly responsible for relatively high viscosity. Bn has been extensively used in the extraction, and separation of a variety of inorganic and organic substances [9-16].

The purpose of this search was to evaluate the potential of Bn to remove ARS from aqueous solution and to determine the several factors that effect on its removal using Bn, such as initial pH, contact

time, initial ARS dye concentration, bentonite mass, and temperature. As well as the kinetics, isotherms, and thermodynamic parameters of ARS removal from aqueous solution are investigated.

2. Experimental

2.1. Materials

Bentonite clay, sodium form was purchased from Thermofisher, Germany. Alizarin red S was purchased from Riedel-de Häen AG, Germany. Chemical structure of the dye is shown in **Fig. 1**. Sodium hydroxide and hydrochloric acid (El Nasr Pharmaceutical Chemicals Co.) were used for initial pH adjustment. A stock solution containing 500 mg L^{-1} ARS was prepared by dissolving the required amount in distilled water. The desired concentrations of solutions in further experiments were obtained by successive dilutions. Distilled water is used throughout the work. All other chemicals and reagents used in this work were of analytical grade.
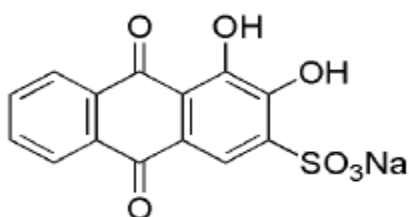

Fig. 1. Chemical structure of ARS

2.2. Instrumentation

The spectrophotometric measurements are performed using a UV-Vis double-beam spectrophotometer (V-630 Jasco, Japan). A Jenco 6173 pH-meter is used for pH measurements. Water bath shaker is used for shaking during experiments. FTIR spectra are recorded on a FTIR spectrometer (FT-IR-6100 Jasco, Japan), using KBr pellets in the range of 4000–400 cm^{-1} at room temperature with spectral resolution 4 cm^{-1}. X–ray diffraction analysis is carried out using an X-ray diffractometer (Brucker D8Advanced, Germany) with Cu Kα radiation (λ = 0.15406 nm) in the 2θ range of 2° to 70°.

2.3. Adsorption studies

Adsorption experiments were carried out using batch technique. To study the effect of pH on the adsorption process, 0.05 g of the adsorbent is mixed with 25 mL of ARS solution with initial concentration of 100 mg L^{-1}. The initial pH is adjusted in the range of 2–10 using drops of 0.1 M HCl and 0.1 M NaOH. For adsorption kinetics studies, 25 mL of the ARS solution with initial concentration of 100 mg L^{-1} at pH 4 is added to 0.05 g of adsorbent. In the adsorption isotherm studies, 0.05 g of the adsorbent is added to 25 mL of the ARS solutions with an initial concentration of 25, 50, 100, 200 and 400 mg L^{-1} at the pH 4. In the thermodynamic studies, 0.05 g of the adsorbent is added to 25 mL of ARS solution with initial concentration 100 mg L^{-1} at different temperatures. After equilibration, the mixtures are centrifuged and the concentration of the ARS is determined spectrophotometrically using UV-Vis spectrophotometer at a wavelength of 420 nm. The percentage of adsorption (%E) and q_e (mg g^{-1}) are calculated as follows:

$$\% = \frac{(C_i - C_e)}{C_i} * 100 \tag{1}$$

$$q_e = \frac{(C_i - C_e)V}{m} \tag{2}$$

where: C_i is the initial dye concentration (mg L^{-1}), C_e is the equilibrium dye concentration (mg L^{-1}), V is the volume of ARS used (L), and m is the mass of adsorbent used (g).

3. RESULTS AND DISCUSSION

3.1. Characterization

3.1.1. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra of Bn are recorded in the range of 4000 - 400 cm^{-1}. The FTIR spectra of Bn are illustrated in **Fig. 2**. Peaks that observed at 3446.2 and 3622 cm^{-1} are due to the vibrations of inner H$_2$O and hydroxyl groups of Bn, respectively. The two peaks at 3237 and 1645 cm^{-1} are resulted from H$_2$O bending and that appeared at 521.7 cm^{-1} and 462.8 cm^{-1} are attributed to Al-O-Si bending and Si- O -Si bending, respectively. The peak at 622.895 cm^{-1} is related to the Al-O and Si-O

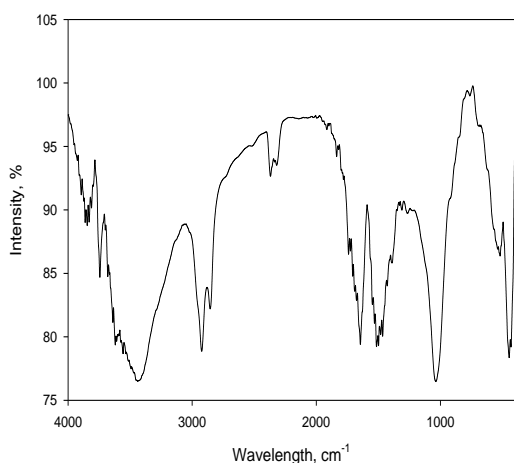out-of-plane vibration. In addition, the peak appeared at 922.8 cm^{-1} caused from Al-OH-Al bending [17].

Fig. 2. FTIR spectra of Bn.

3.1.2. X-ray diffraction (XRD)

The XRD obtained for Bn is shown in **Fig. 3.** The pattern that found for Bn showed the presence of montmorillonite (7.07º and 19.78º) as a majority phase [18].
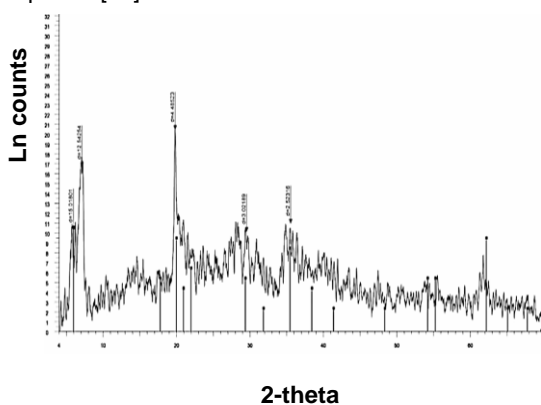

Fig. 3. X-ray diffraction pattern for Bn.

3.2. Adsorption studies

3.2.1. Effect of initial pH

The effect of initial pH on the removal of ARS using Bn from 2–10 is studied and the results are shown in **Fig. 4.** The maximum removal of ARS using Bn is achieved at pH 4, then the removal percentage decreased as pH increased. At pH less

than pk$_a$ of ARS, there is an electrostatic attraction between the cationic form of ARS molecules and the negatively charged surface of Bn. As the pH increase; there is an electrostatic repulsion between the anionic form of ARS molecules and Bn resulting in decreasing the removal percentage of ARS.
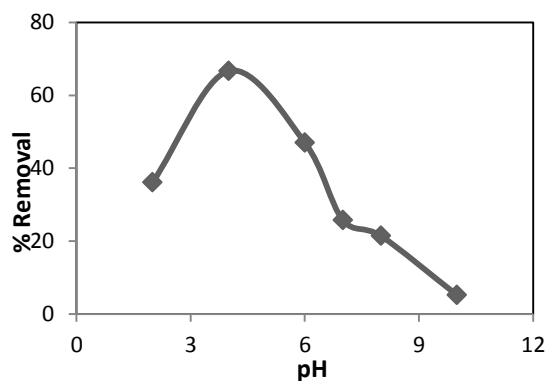

Fig. 4. Effect of initial pH on ARS removal using Bn.

3.2.2. Effect of contact time

The contact time is a significant parameter that used to optimize the processing period. The removal of ARS using Bn is investigated as a function of contact time and it is done in the range from 5 to 120 min. From the results that are shown in **Fig. 5**, it can be concluded that 60 min is the optimum equilibrium contact time for ARS removal by Bn.
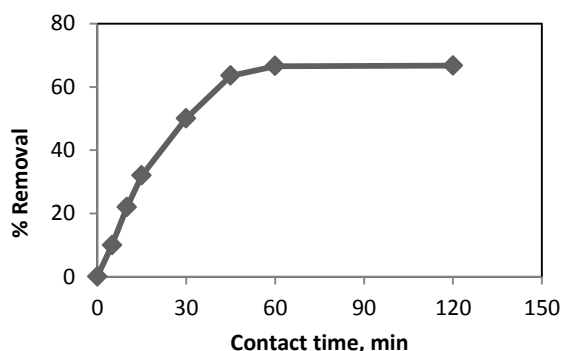

Fig. 5 Effect of contact time on ARS removal using Bn.

3.2.3. Effect of adsorbent mass

Fig. 6 shows the removal percentage of ARS using Bn. The results indicated that the removal %

increase with increasing adsorbent dose from 0.01 to 0.2 g. The increase in the adsorption efficiency of ARS can be attributed to a large total surface area of Bn and the accessibility of large number of adsorption sites [19, 20]. At Bn dosage that is higher than 0.05 g, the concentration of the ARS on Bn surface is in equilibrium with the ARS concentration in solution [21].
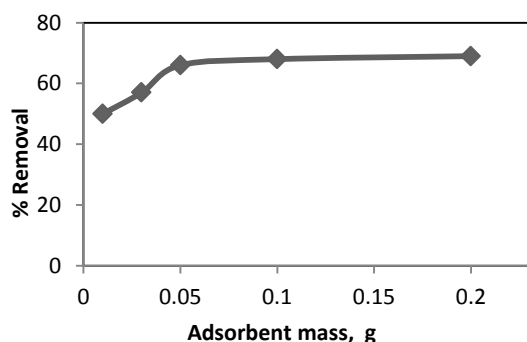

Fig. 6. Effect of adsorbent mass on ARS removal using Bn.

3.2.4. Effect of ARS initial concentration

The effect of ARS initial concentration on its removal using Bn is studied and the results are shown in **Fig. 7**. The Bn and dye solution of different initial concentrations of 10 to 400 mg L^{-1} are contacted for 60 min at pH 4 with an adsorbent dose of 0.05g. The adsorption capacity of ARS increased from 4.25 to 122.15 mg g^{-1} by increasing the initial ARS dye concentration from 10 to 400 mg L^{-1}. This indicates that the ARS adsorption on Bn is concentration dependent [22].
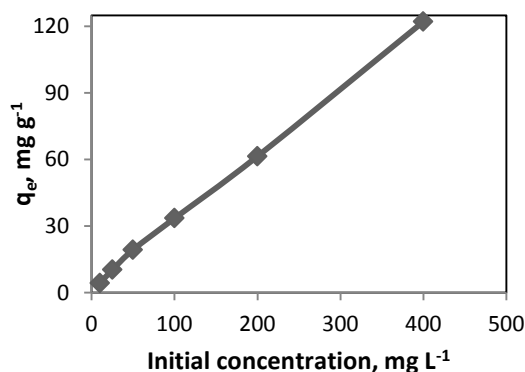

Fig. 7. Effect initial concentration of ARS on its removal using Bn.

3.2.5. Effect of temperature

The study of the adsorption process of ARS onto Bn at different temperatures (30, 40, 50, and 60 ºC) at pH 4 using 0.05 g of Bn for 60 min was revealed in **Fig. 8**. The removal percentage decreased as the temperature increased. The obtained results indicated the exothermic nature of ARS adsorption onto Bn.
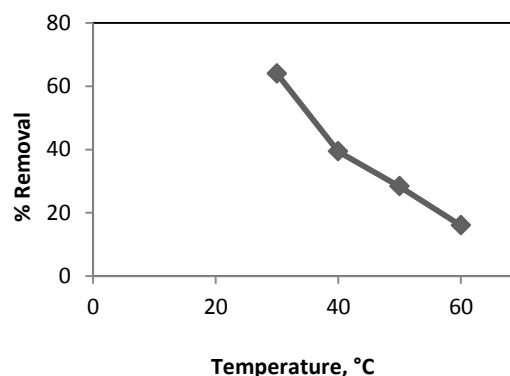

Fig. 8. Effect of temperature on removal of ARS using Bn.

3.3. Isotherm Studies

Langmuir [23] and Freundlich [24] models are used to analyze the equilibrium isotherm adsorption data:

Langmuir isotherm

Langmuir isotherm model presume a monolayer for adsorption onto the surface of adsorbent with a definite amount of identical sites. Once an active site is occupied, no additional adsorption can occur at that site and Langmuir model is given by:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \tag{3}$$

Where: C_e and q_e are the equilibrium concentration of ARS(mg L^{-1}), and the quantity of ARS adsorbed per unit mass of Bn at equilibrium concentration (mg g^{-1}), respectively. q_{max} is the full monolayer adsorption (mg g^{-1}) and K_L is the Langmuir constant related to the affinity of Bn binding sites (L mg^{-1}) and the these parameters values are registered in **Table 1**.

Freundlich model

Freundlich model is based on a multilayer for adsorption on a heterogeneous surface and is set by:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \qquad (4)$$

Where: n and K_F are Freundlich constants indicating the intensity and adsorption capacity, respectively. The values of n and K_F are calculated from the slope and intercept of the plot of $\ln q_e$ versus $\ln C_e$ and they are presented in Figure 9 and recorded in **Table 1**. From the magnitudes of the correlation coefficients values for the two models, the Freundlich model isotherm has better R^2 value than the other isotherm model **(Table 1)**. This recommends that the ARS adsorption onto Bn is a physical process.
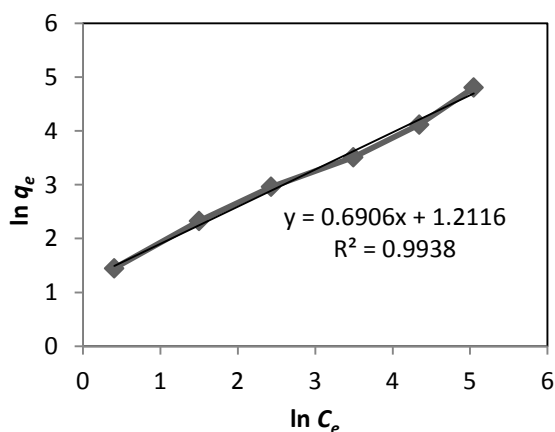

Fig. 9. Freundlich isotherm of adsorption of ARS onto Bn.

Table 1. The parameters of Langmuir and Freundlich isotherm models for the adsorption of ARS onto Bn.

Langmuir isotherm			Freundlich isotherm		
K_L	q_{max}, mgg^{-1}	R^2	K_F, mgg$^{1(}$Lmg$^{1)1/n}$	n	R^2
0.01	169.5	0.7391	3.36	1.45	0.9938

3.4. Kinetics Study

The mechanism of the ARS adsorption onto Bn is explained using two kinetic models: Lagergren pseudo-first-order [25] and pseudo-second-order [26]. The Lagergren pseudo-first-order model equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t , \qquad (5)$$

Pseudo-second-order kinetic equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} , \qquad (6)$$

Where: q_t and q_e are the quantities of ARS that are adsorbed per unit mass of Bn (mg g^{-1}) at time t (min) and that adsorbed at equilibrium, respectively. The values of rate constants (k_1, k_2) represent pseudo-first-order constant (min^{-1}), and pseudo-second-order rate constant (g mg^{-1} min). **Figure 10** represents the plot of pseudo-second-order, while the data of k_1, k_2 and R^2 are demonstrated in **Table 2**. The ARS adsorption onto Bn fitted well with the pseudo-second-order kinetic model and this is indicated by the values of R^2 as shown in **Table 2**.

Table 2. Parameters of the kinetics models for ARS adsorption onto Bn.

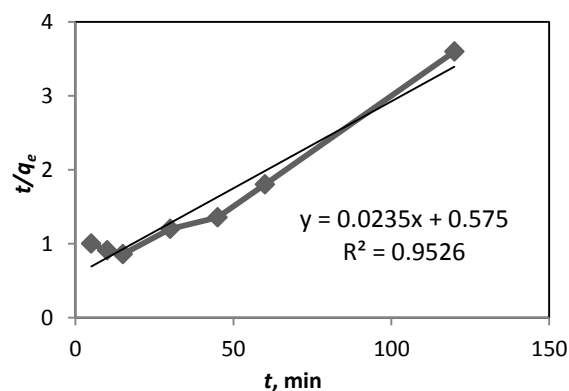| Kinetic model	Parameter	Value
Pseudo–first–order	q_e (mg g^{-1})	34.81
	k_1(h^{-1})	0.0815
	R^2	0.907
Pseudo–second–order	q_e (mg g^{-1})	42.55
	k_2(h^{-1})	0.000961
	R^2	0.9526

Fig. 10. Pseudo–second–order rate plot for the adsorption of ARS onto Bn.

3.5. Thermodynamic Parameters

Van't Hoff equations [27] are used to calculate the thermodynamic parameters, such as enthalpy ($\Delta H°$), entropy ($\Delta S°$) changes and Gibb's free energy change ($\Delta G°$), and the results are given in Table 3. The values of $\Delta S°$ and $\Delta H°$ are determined from the intercept and the slope of the plots **(Fig. 11)** of $\ln k_d$ versus T^{-1}.

$$k_d = \frac{q_e}{C_e} \tag{7}$$

$$\ln k_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{8}$$

$$\Delta G^o = \Delta H° - T\Delta S° \tag{9}$$

Where: k_d is the distribution coefficient, q_e is the equilibrium concentration of ARS on Bn (mg L^{-1}), R is gas constant (J mol^{-1} K^{-1}) and T is the temperature (K). The negative values of both $\Delta H°$ and $\Delta S°$ showed that the nature of ARS adsorption is exothermic, and adsorption is accompanying with entropy decrease due to the limit of the mobility of ARS that resulted from binding to the Bn surface [28]. The values of $\Delta G°$ are found to be negative at the lower temperature and positive at the higher temperatures, which indicated that the non-spontaneous nature of ARS adsorption onto Bn at the higher temperatures [29]. The observed increase in $\Delta G°$ value with temperature suggested that lowering temperature enhances the process of adsorption of ARS onto Bn.

Table 3. Thermodynamic parameters for the adsorption of ARS onto Bn.

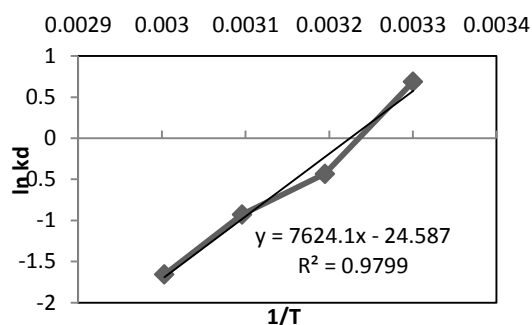| Temperature, K	$\Delta G°$, KJ mol^{-1}	$\Delta H°$, KJ mol^{-1}	$\Delta S°$, J mol^{-1}
303	-1.44862	-63.38676	-204.419
313	0.59554		
323	2.639703		
333	4.683866		

Fig. 11. Plot of ln K_d versus 1/T for ARS adsorption onto Bn at different temperatures.

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إزالة أليزارين الأحمر S من المحلول المائي بإستخدام البنتونيت الصوديومى

[145]

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الكلمات الدالة: ازالة، اليزارين الاحمر(أرس)، بنتونيت

الموجـــــز

في هذا العمل، تم استخدام البنتونيت الصوديومى لإزالة أليزارين الأحمر (أرس) من محلول مائي باستخدام تقنية الدفعة. تم وصف البنتونيت الصوديومى (بن) باستخدام تحويل فورييه الطيفي بالأشعة تحت الحمراء وحيود الأشعة السينية. تم التحقق من عدة عوامل والتى تؤثر على إزالة الصبغة مثل درجة الحموضة، وقت الاتصال، تركيز الصبغة الأولي، جرعة البنتونيت، ودرجة الحرارة. أظهرت البيانات المحققة من الدراسات الحركية الملاءمة العالية للنموذج الحركي الزائف من الدرجة الثانية من أجل تفسير أفضل للبيانات التجريبية. أظهرت دراسات الإيزوثرم الإمتصاصية أن معامل فروديليتش لديه معامل ارتباط عالي بين نماذج الإيزوثرم المدروسة. وأشارت دراسات الديناميكا الحرارية أن امتصاص (أرس) على ال (بن) يكون تلقائيا في الطبيعة عند درجات الحرارة المنخفضة وطارد للحرارة.

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