



## Adsorption of Acid Blue 92 Dye on Modified Diatomite by Nickel Oxide Nanoparticles in Aqueous Solutions

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### ARTICLE INFO

#### Article history:

Received: 14-05-2012

Final Revised: 13-09-2012

Accepted: 14-09-2012

Available online: 15-09-2012

#### Keywords:

Adsorption

Diatomite

Nickel oxide nanoparticles

Adsorbent isotherm

Kinetic model

Acid Blue 92.

### ABSTRACT

**A**pplication of diatomite for the treatment of dye-bearing effluents has high significance in environmental research. In this research, adsorption of Acid Blue 92 (AB 92) from aqueous solutions on raw and nickel oxide nanoparticles-modified diatomite (NONMD) was studied. The effect of different operation parameters on adsorption process was evaluated. The surface morphology of adsorbents was characterized by SEM, BET, FTIR, XRD, EDX and elemental analysis. The maximum removal percentage of AB 92 using 0.1 g of modified diatomite at pH 2,  $25 \pm 1^\circ\text{C}$ , agitation speed of 200 rpm, initial dye concentration of 50 mg/L after 90 min was 95.21% (47.61 mg/g). Furthermore, under same conditions, the maximum adsorption of dye on raw diatomite was 56.95% (28.48 mg/g). The experimental data showed that the adsorption of dye on raw diatomite follows the Langmuir model, but its adsorption on modified diatomite follows the BET model. The kinetics effect of the adsorbent was pseudo-second-order. Prog. Color Colorants Coat. 5(2012), 101-116. © Institute for Color Science and Technology.

## 1. Introduction

Water is a scarce resource. Only 0.03% of the world's water reserves are available for human activities. Population growth and industrial booms have increased demand for water, while water source has remained constant. Moreover, inappropriate water management has reduced the amount of available resources. In the textile

industry, regulations concerning the discharge of wastewaters have become more and more stringent. Synthetic dyes, suspended solids and dissolved organics are the main hazardous materials found in textile effluents [1]. In addition to the undesirable colours of textile effluents, some dyes may degrade to produce

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carcinogens and toxic products [2]. Furthermore, the coloured effluents reduce light penetration and potentially prevent photosynthesis [3, 4].

Many treatment systems have been proposed for the removal of synthetic dyes from aqueous solutions. Coagulation [5], flocculation [6], photocatalytic degradation [7-9], membrane filtration [10], microbiological decomposition [11], electrochemical oxidation [12], fungus biosorbent [13] and adsorption [2-5,14-18] are the most commonly used methods for removing dyes from waste effluents systems. The microbiological, photocatalytic and electrochemical decomposition procedures are not efficient because many dyes can not be easily decomposed [12]. Adsorption is considered to be particularly competitive, economically cost effective and efficient process for the removal of dyes, heavy metals and other organic and inorganic hazardous impurities from aqueous solutions [19-21]. Although activated carbon is the most efficient and popular adsorbent and has been used with great success, the high cost of activated carbon sometimes restricts its applicability for dye removal [17,20,22]. Therefore, in recent years, considerable attention has been devoted to the study of different types of low-cost and efficient materials as sorbent for the removal of dyes from aqueous solutions, which included wood and saw dust [23,24], fly ash [25], wheat straw [26], apple pomace [26], orange peel [27-29], banana peel [30], peanut hull [3], leaf [31], soy meal hull [32], egg shell membrane [33], etc.

AB 92 dye is used in huge quantities in Iran and produces many environmental problems. So, search for an appropriate and low-cost adsorbent is an important consideration for designing a suitable treatment plant for minimising pollution load [38].

Diatomite ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) is a pale-coloured, soft, lightweight siliceous sedimentary rock made up principally from the skeletons of aquatic plants called diatoms. Diatomite contains a wide variety of shape and sized diatoms, typically 10-200  $\mu\text{m}$ , in a structure including up to 80-90 % pore spaces [34]. Diatomite's extremely porous structure, low density and high surface area make it suitable as an adsorbent for organic and inorganic chemicals. Diatomite is found in abundance in Iran. Several studies have been carried out on the use of diatomite as an adsorbent for removing some contaminants such as heavy metals [34], basic dye (Methylene blue) [2], basic and reactive dyes (Methylene blue, reactive black, reactive yellow) [4,35] and some

textile dyes (SifBlau BRF, Everzol Brill Red 3BS, Int Yellow 5GF) [36]. Furthermore, the unique properties of diatomite caused its applications as filtration media in a number of industries [34,36]. Diatomite is approximately 500 times cheaper than commercial activated carbon [36] and has the potential of being successfully used as a cost-effective alternative to activated carbon.

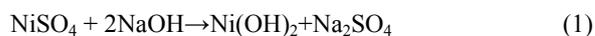
In the present investigation, the possibility of utilization of nickel oxide nanoparticles-modified diatomite (NONMD) as an adsorbent for removal of AB 92 dye from an aqueous medium has been studied. The equilibrium and kinetic study are investigated to observe the effects of various process parameters such as pH, contact time, initial dye concentration, calcinations and sorbent dosage on the adsorption process. Equilibrium data are attempted by various adsorption isotherms including Langmuir, Freundlich and Brunauer-Emmett-Teller (BET) isotherms in order to select an appropriate isotherm model. Moreover, a kinetics study of the adsorption process is also considered to describe the rate of sorption.

## 2. Experimental

### 2.1. Preparation of adsorbent

Diatomite sample was obtained from Tabriz, Iran. The sample was washed several times with distilled water and HCl (1 M) to remove fines and other adhered impurities and to achieve neutralization. The sample was finally filtered, dried at 60°C for 24 h, and stored in closed containers for further use.

The nanoparticles of NiO were synthesized according to the following reaction (Equation1):



The nanoparticles of NiO were synthesized by adding  $\text{NiSO}_4$  and NaOH (1M) to the solution. It means that 2.0 g of previously dried diatomite was added to 25 ml of Nickel hydroxide (1 M), stirrer speed of 200 rpm, for 1 h. The new material, Ni-diatomite was sequentially separated by filtration. The calcination process was carried out by placing Modified diatomite sample in the furnace at 250°C for 4.5 h. The sample was then allowed to cool in a desiccator. The modified sample was used to examine the effect of silanol groups and the role of pore size distribution on the adsorption process.

## 2.2. Reagents and solutions

AB 92 dye was obtained from Ciba Ltd. and was used without further purification. The chemical structure of this dye is shown in Figure 1. Distilled water was throughout employed as solvent. For adsorption experiments, various concentrations of dye solutions (25, 50, 75, 100 and 150 mg/L) were prepared. The pH measurements were made using Hach pH meter. The pH adjustments of the solution were made by adding a small amount of HCl or NaOH (1 M). These chemicals were of analytical grade and purchased from Merck, Germany.

## 2.3. Adsorption procedure

The adsorption experiments were performed by mixing various amounts of diatomite (0.02–0.12 g) in 100 mL of dye solutions with varying concentrations (ranging from 25-150 mg/L) at various pH values (2-12). The pH studies were carried out to determine the optimum pH at which maximum dye removal could be achieved with diatomite. Adsorption experiments were conducted at various concentrations of dye solutions (25, 50, 75, 100 and 150 mg/L) using optimum amount of diatomite (0.1 g) at pH 2, an agitation speed of 200 rpm and temperature  $25 \pm 1^\circ\text{C}$  for 2 h to attain equilibrium conditions. The changes of absorbance were determined at certain time intervals (5, 10, 30, 60, 90 and 120 min) during the adsorption process. After adsorption experiments, the dye solutions were centrifuged for 10 min in a Hettich EBA20 centrifuge at 4000 rpm in order to separate the sorbent from the solution and dye

concentration was then determined.

## 2.4. Analysis

The residual dye concentrations in aqueous medium were determined using a Perkin-Elmer spectrophotometer corresponding to maximum wavelength ( $\lambda_{\text{max}}$ ) of AB 92 dye. The XRD analysis was performed on raw and modified diatomite samples using a Philips Xpert x-ray diffractometer. Scanning electron microscopic (SEM) of both raw and modified diatomite were carried out using LEO 1455VP scanning electron microscope before and after modification process.

## 3. Results and discussion

### 3.1. Surface characterization

In order to explore the surface characteristics of diatomite, an FTIR analysis was performed in the range of 450 to 4000  $\text{cm}^{-1}$ . Figure 2 shows the Infra-Red spectra of raw and modified diatomite samples.

In the first spectrum (Figure 2(a)), the peak positions showing major adsorption bands were observed at 3622, 3421, 2506, 1636, 1038, 915, 794, 692, 671, 627, 596, 522 and 470  $\text{cm}^{-1}$ .

The bands at 3622 and 3421  $\text{cm}^{-1}$  illustrate the (H) atom that is attached to heteroatoms (Si-H), the peaks at 2506  $\text{cm}^{-1}$  is due to the free silanol group (Si-O-H), the band at 1636  $\text{cm}^{-1}$  represents (H-O-H) bending vibration of water, the band at 1038  $\text{cm}^{-1}$  reflects the siloxane (-Si-O-Si-) group stretching. The bands at 915 and 794  $\text{cm}^{-1}$  correspond to (SiO-H) vibration.

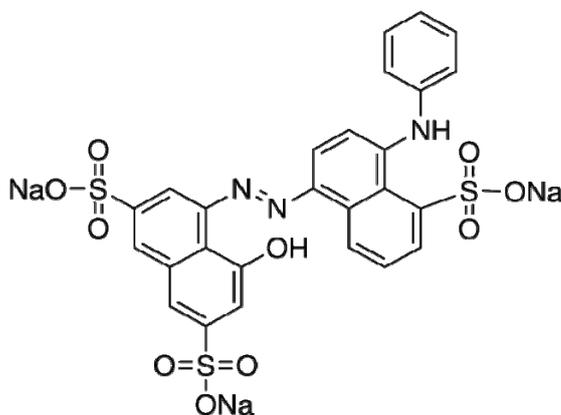


Figure 1: Chemical structure of AB 92 dye.

The peak positions of 692, 671, 627, 596, 522 and 470  $\text{cm}^{-1}$  are attributed to the Si-O-Si bending vibration. The peak positions of the major bands in the spectrum of modified diatomite (Figure 2(b)) is seen more or less at the same position as in the spectrum of raw diatomite, except for a trace of ammonia ions because of calcinations at high temperature and existence of nitrogen in air.

Comparison of these two spectra shows that there is only slight difference between the band positions of these two adsorbents, especially at 2364  $\text{cm}^{-1}$  position that it is not very important in adsorption process. The most important difference of these spectra is in the intensity of the fingerprint part. Although, the amount of silanol group has decreased slightly, the raise of metal oxide content at the modified diatomite can be the main reason for increasing the adsorption capacity.

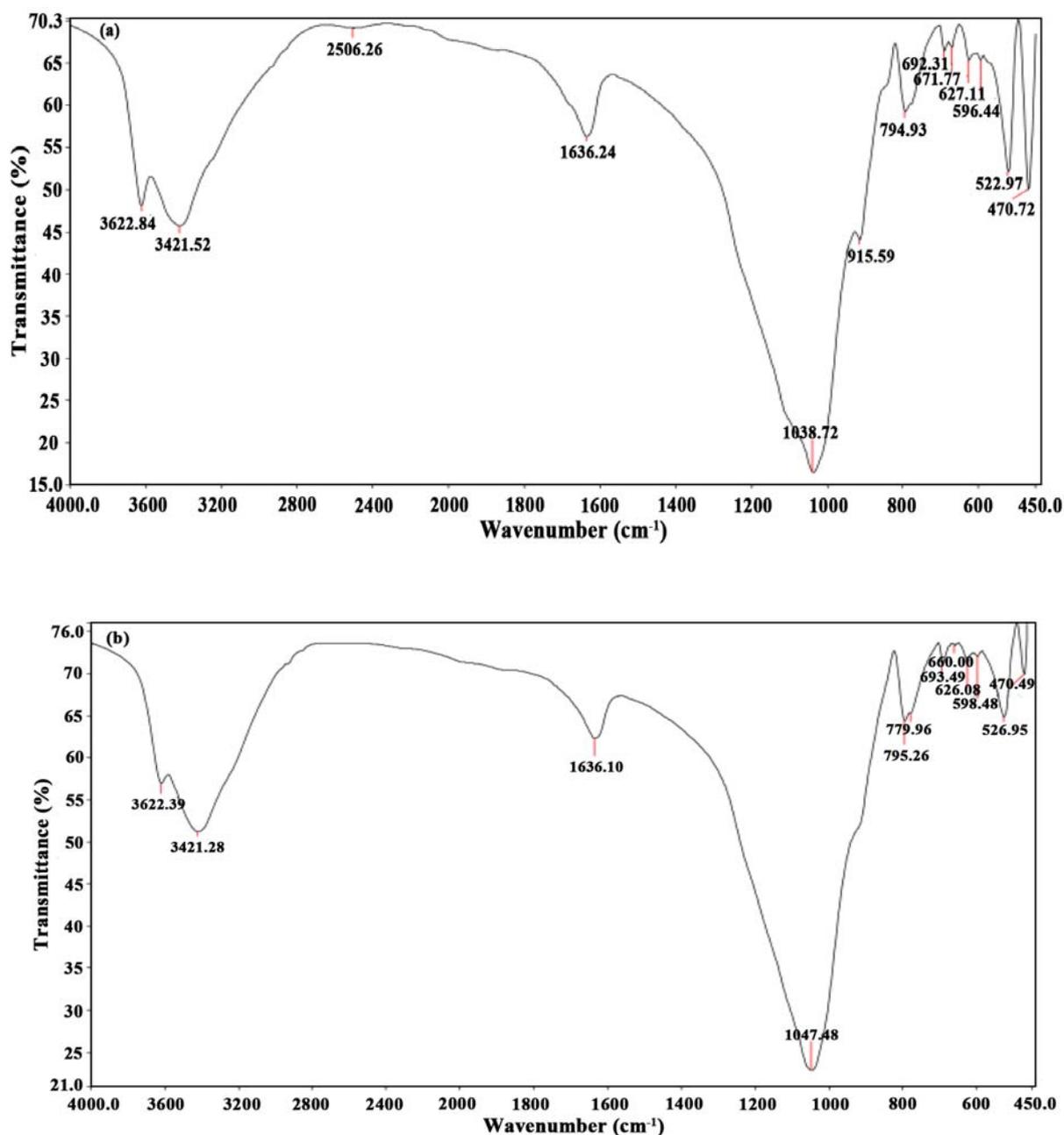
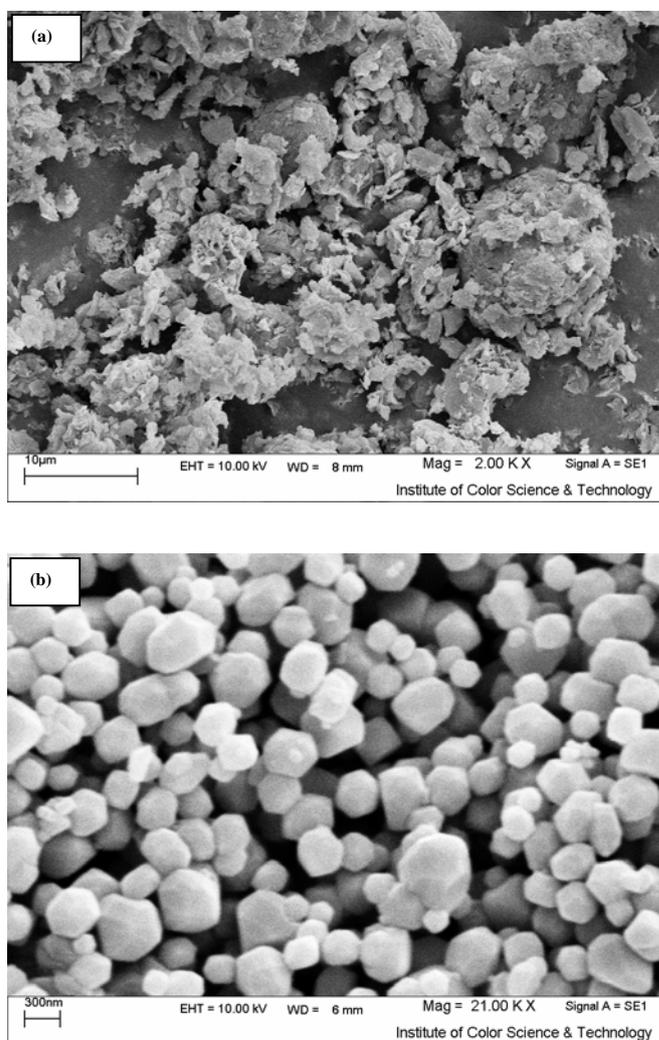


Figure 2: FT-IR spectra of (a) raw and (b) modified diatomite.

Scanning electron micrographs of raw and modified diatomite are shown in Figures 3(a) and 3(b), respectively. As evident from Figure 3(a), raw diatomite does not have considerable numbers of pore spaces for adsorption of dyes. An important change in the surface characteristics and the size of the pore spaces of the diatomite is seen after modification and calcination process at 250°C. From Figure 3(b), the modification treatment of the diatomite increases the volume of the pore spaces and improves the surface functional groups from the raw diatomite. In addition, the modified diatomite has considerable numbers of pore spaces for dye adsorption. As a result, the adsorption of dye enhances by modified diatomite.

XRD analysis results of the raw and modified diatomite are shown in Figure 4. It can be seen from Figure 4 that the x-ray pattern of the raw diatomite is different from that of modified diatomite, suggesting that a phase transformation probably occurred during the calcination process.

The main composition of raw diatomite is quartz, anorthite and muscovite. It is evident that sanidine was appeared; while anorthite and muscovite were completely removed as the diatomite was calcined at 250°C. In fact, some peaks in the diatomite disappeared and some peaks were created by modification process. Similar behaviour was previously reported by other researchers [4].



**Figure 3:** Scanning electron micrographs of (a) raw diatomite and (b) modified diatomite.

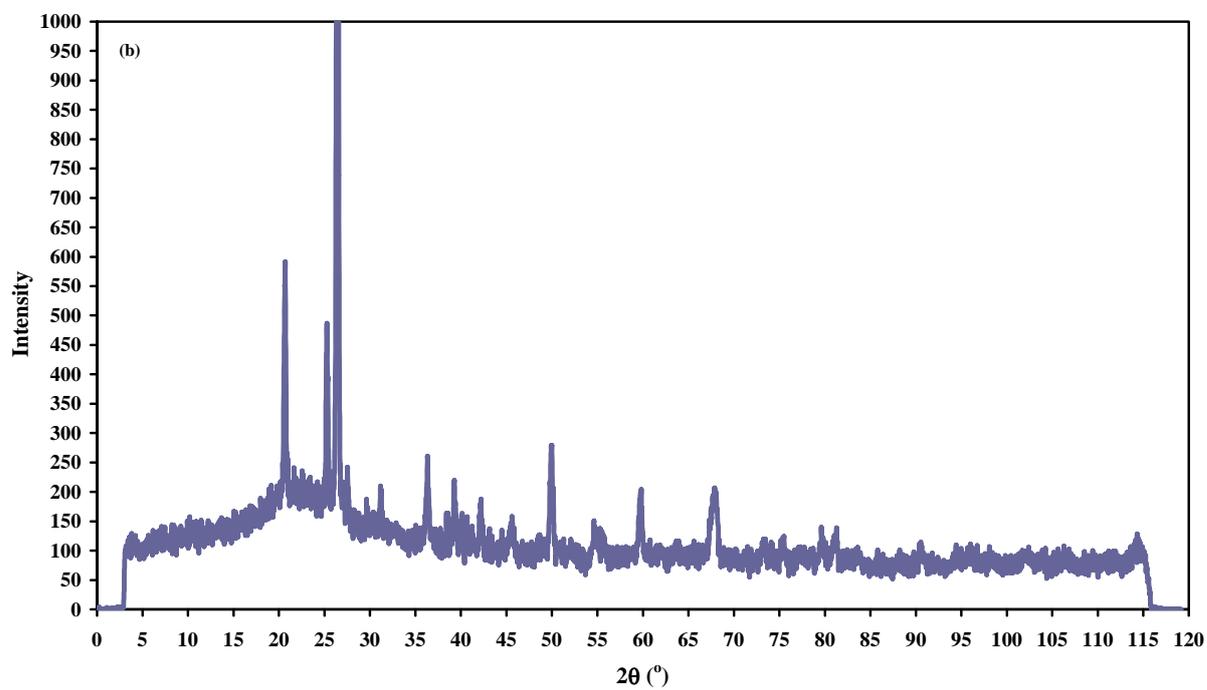
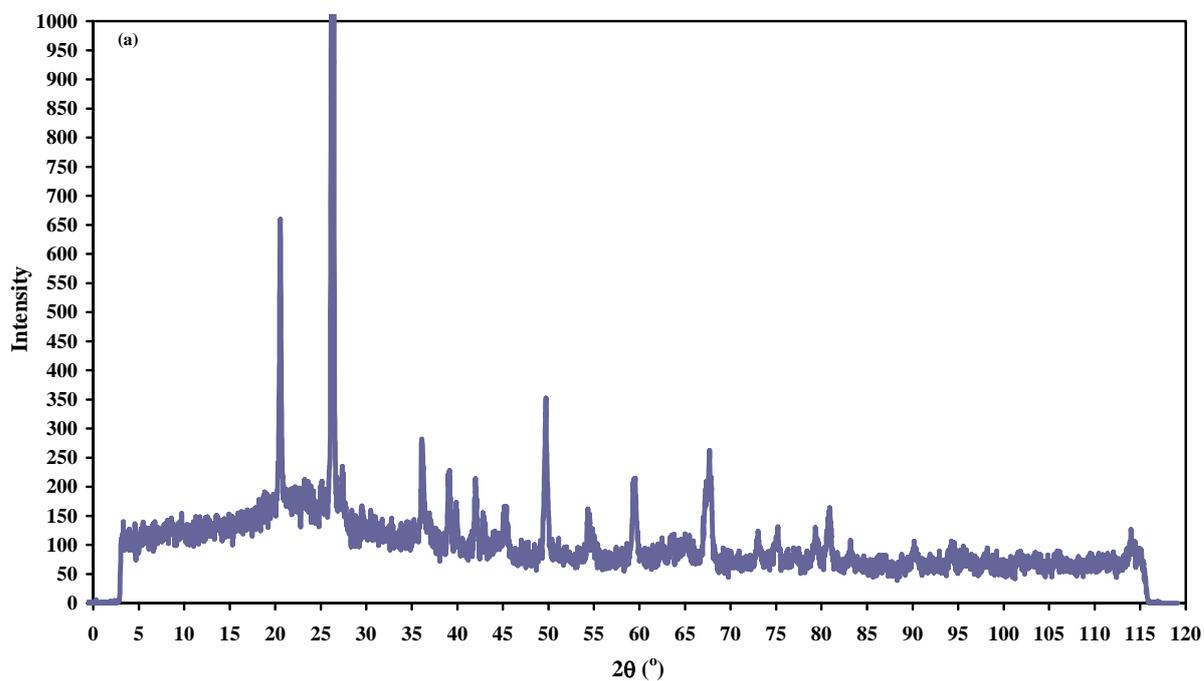


Figure 4: XRD patterns of (a) raw and (b) modified diatomite.

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EDX analyses in Figure 5 showed that the concentration of Ni metal in the NONMD was 3.96 (%W), although before modification process there was not any Ni in the raw diatomite.

The surface area of the diatomite was determined by BET method (Figure 6). By using nitrogen adsorption method the BET specific surface area adsorbents was

measured, using Autosorb-1MP apparatus from Qantachrome at 77 K.

In this investigation, the values of 7.5 m<sup>2</sup>/g for raw and 28.45 m<sup>2</sup>/g for modified diatomite were obtained. A particle size analysis was carried out to determine the distribution of particles of the adsorbent.

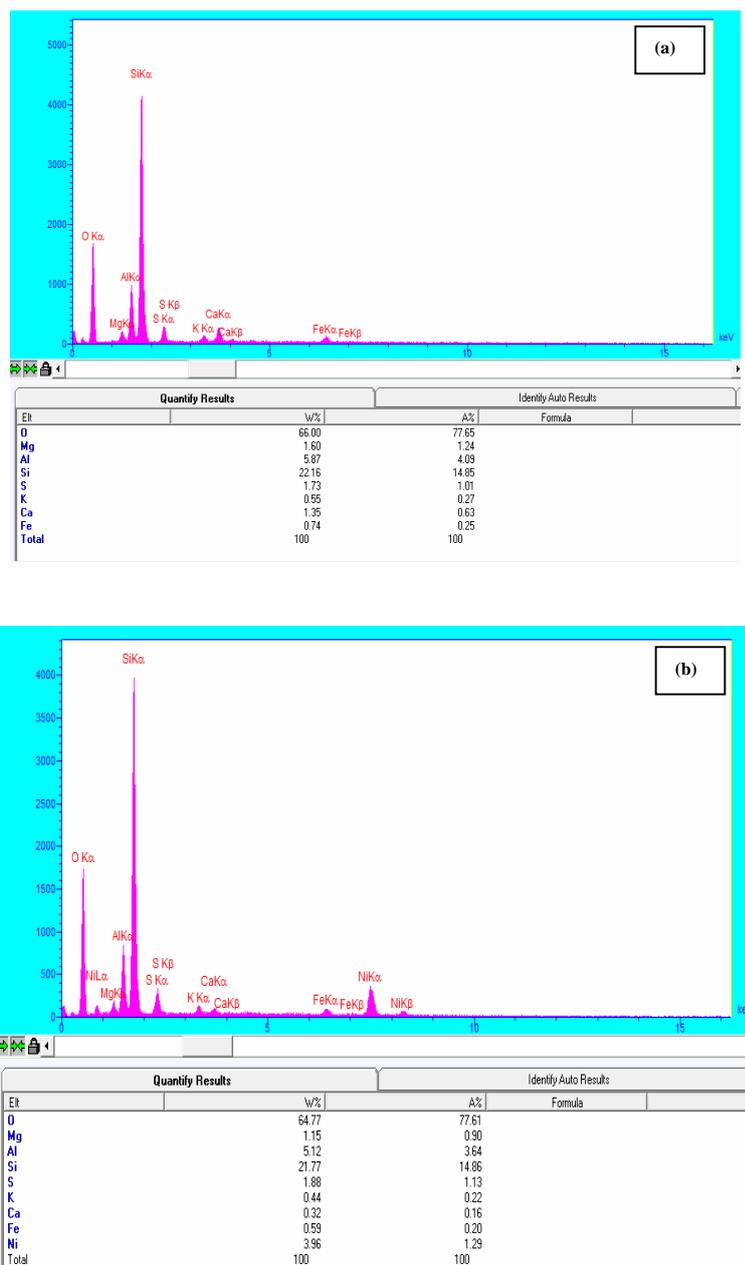


Figure 5: EDX patterns of (a) raw and (b) modified diatomite.

The maximum distribution of particles is varied from 200 to 400 nm.

### 3.2. Effect of adsorbent dosage

The adsorption of AB 92 dye on raw and modified diatomite dosage was investigated at  $25 \pm 1^\circ\text{C}$  by varying the adsorbent amount from 0.02 to 0.12 g while keeping the volume of dye solution constant equal to 100 mL, with an initial dye concentration of 50 mg/L. Figure 6 shows the percentage removal of AB 92 dye versus

adsorbent amount.

As it is clear from the figure, the percentage removal of dye increased with an increase in the adsorbent amount. The main reason for this fact is due to the greater availability of the adsorption sites at higher concentrations of the adsorbent [36, 37]. Based on the results shown in Figure 7, 0.1 g of the raw and modified diatomite was used for further experiments. Similar behaviour was previously reported by other researchers [38].

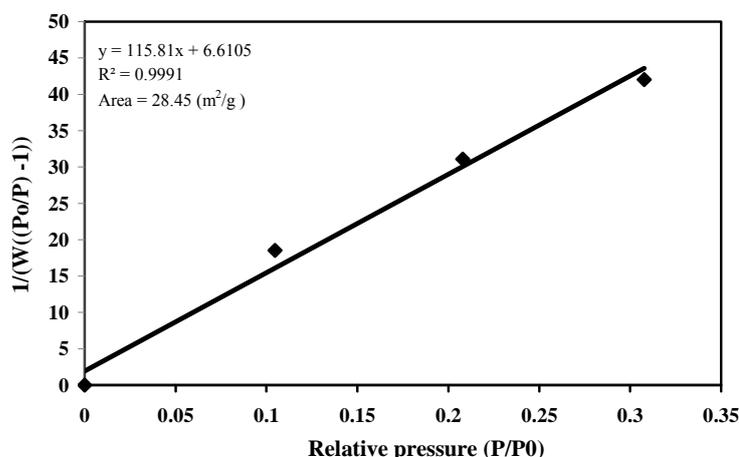


Figure 6: BET surface area of modified diatomite.

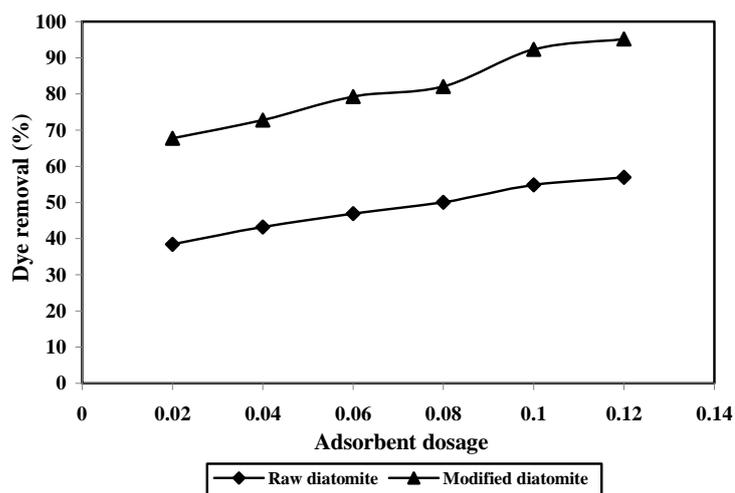
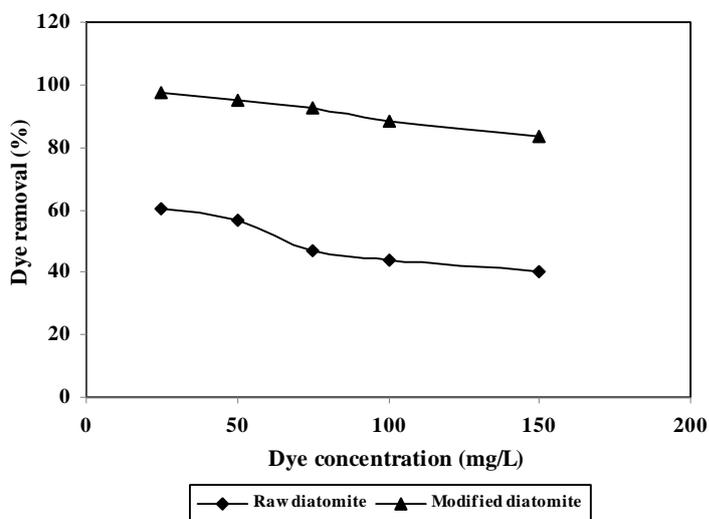


Figure 7: Effect of adsorbent dosage on the removal percentage of AB 92 dye by raw and modified diatomite.  $25 \pm 1^\circ\text{C}$ , initial dye concentration of 50 mg/L, pH 2, agitation speed of 200 rpm.



**Figure 8:** Effect of initial dye concentration on adsorption of AB 92 dye by raw and modified diatomite, contact time of 120 min,  $25 \pm 1^\circ\text{C}$ , pH 2, agitation speed of 200 rpm.

### 3.3. Effect of initial dye concentration

A change in the initial dye concentration can considerably affect the adsorption process. Figure 8 depicts the effect of dye concentration on the removal percentage of AB 92 dye by adsorbents. As it is evident from the figure, when the dye concentration increased from 25 to 150 mg/L, the removal percentage of AB 92 dye decreased from 97.3 to 83.21% for modified and from 60.21 to 40.22 for raw diatomite.

As expected, when the concentration of dye is increased, the limited capacity of the adsorbent checks any further adsorption of dye and hence the overall removal percentage decreases. Similar behaviour was previously investigated by other researchers [37].

### 3.4. Effect of contact time

The adsorption of AB 92 dye onto diatomite was evaluated as a function of contact time. Figure 9 shows the effect of contact time on the removal percentage of AB 92 dye in the aqueous phase by raw (Figure (9a)) and modified diatomite (Figure (9b)).

The initial dye concentration was varied from 25 to 150 mg/L. At all investigated initial dye concentrations, the adsorption occurs very fast initially. After 5 min, the amount of adsorption by raw diatomite reaches to 82 and 80% of the ultimate adsorption of AB 92 dye for initial

dye concentrations of 25 and 50 mg/L, respectively.

As illustrated in Figure 9(b), the adsorption is also fast at early stages of the adsorption process for modified diatomite. Typically about 85% of the ultimate adsorption of AB 92 dye with an initial concentration of 50 mg/L takes place within the first 5 min of contact and it almost remains constant thereafter.

It means that the most of mass transfer resistance is in bulk of fluid and high rate agitation would decrease this resistant. In addition, these results show that the most of the dye molecules are adsorbed on the external surface of the adsorbent, and transferred to the pores and internal surface layers. More experiments are necessary to be carried out to prove this investigation. As expected, when the concentration of dye is increased, the limited capacity of the adsorbent checks any further adsorption of the dye, hence the overall removal percentage decreases. Similar behaviour was previously reported by other researchers [38].

### 3.5. Effect of pH

The pH is the most important factor affecting the adsorption process. The pH studies were conducted to determine the optimum pH at which maximum colour removal could be achieved with diatomite for AB 92 dye.

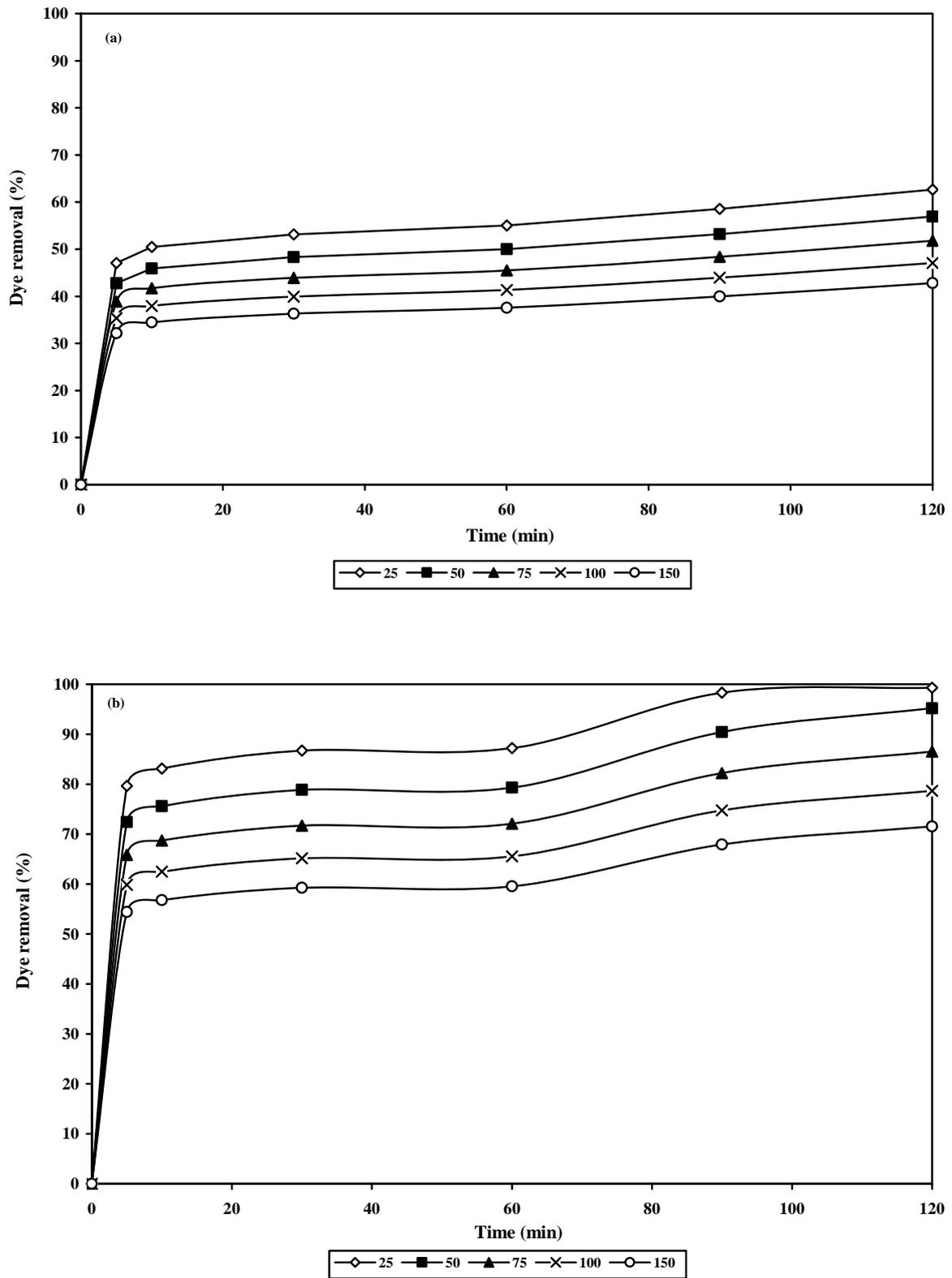


Figure 9: Effect of contact time on adsorption of AB 92 dye on (a) raw and (b) modified diatomite, equilibrium time of 120 min, pH 2, agitation speed of 200 rpm, adsorbent dosage of 0.1 g.

The effect of pH was observed by studying the adsorption of dye over a broad pH range of 2-12. The results are shown in Figure 10. As depicted in the figure, for both raw and modified diatomite, the maximum adsorption of AB 92 was occurred at pH 2.

The dye removal decreased as the solution pH was increased from 2 to 4. The amount of sorbed dye increased slightly when pH was raised from 4 to 6. From pH 6 to 8, the dye removal increased again by modified diatomite and reached to 82.03% at pH 8. But, in this range (pH 6-8), the amount of dye sorbed on raw diatomite was almost increased with a slow rate to 46.28%.

The adsorption of AB 92 dye decreased from 82.03 to 68% with increasing the pH of dye solution from 8 to 12 when modified diatomite was used as the adsorption medium, whereas, the quantity of the sorbed dye increased from 46.28 to 53.83% in the pH range of 8 to 12 using raw diatomite as adsorbent. Because the maximum dye adsorption occurred at pH 2 and the corresponding sorption capacities were 95.21 and 56.95% for modified and raw diatomite, respectively, so the effective pH was 2 and it was used in all adsorption experiments.

### 3.6. Effect of temperature

The temperature has a significant effect on the adsorption process. Increasing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate. Furthermore, an increase in temperature can raise the rate of diffusion of the dye molecules in the internal pores of the adsorbent [15]. In this study, the removal of AB 92 dye from aqueous solution using modified diatomite has been investigated at four different temperatures ranged from 25 to 55°C.

By increasing temperature, the adsorption efficiency of the modified diatomite has extended from 95.21 to 100%. Therefore, the remediation process incorporating adsorption method can be performed under normal temperature for an industrial scale. It was well depicted in Figure 11 that the adsorption process was not sensitive to the temperature. It was shown that the energy balance was not important in this process.

### 3.7. Adsorption isotherms

The distribution of dye between the adsorbent and the dye solution at equilibrium is important in establishing the capacity of the adsorbent for dye removal from aqueous systems. The adsorption isotherms of AB 92 dye on both raw and modified diatomite are shown in Figure 12.

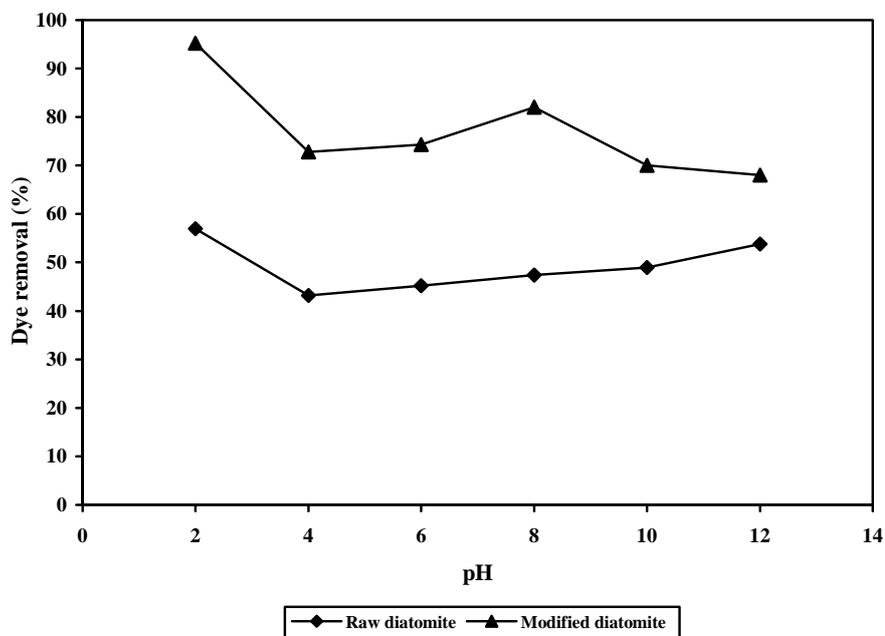
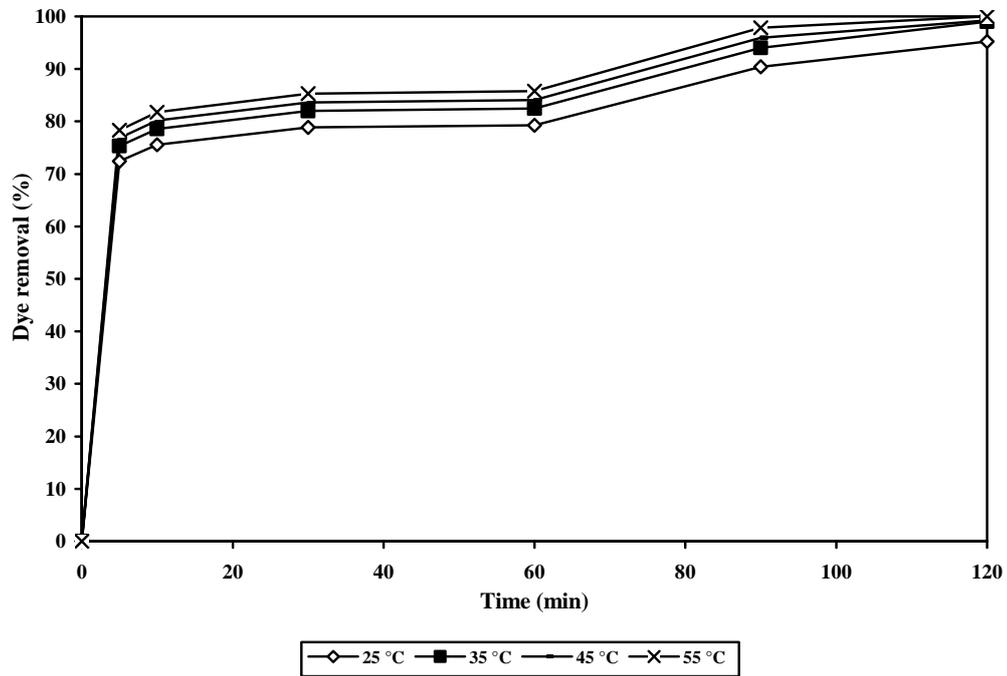
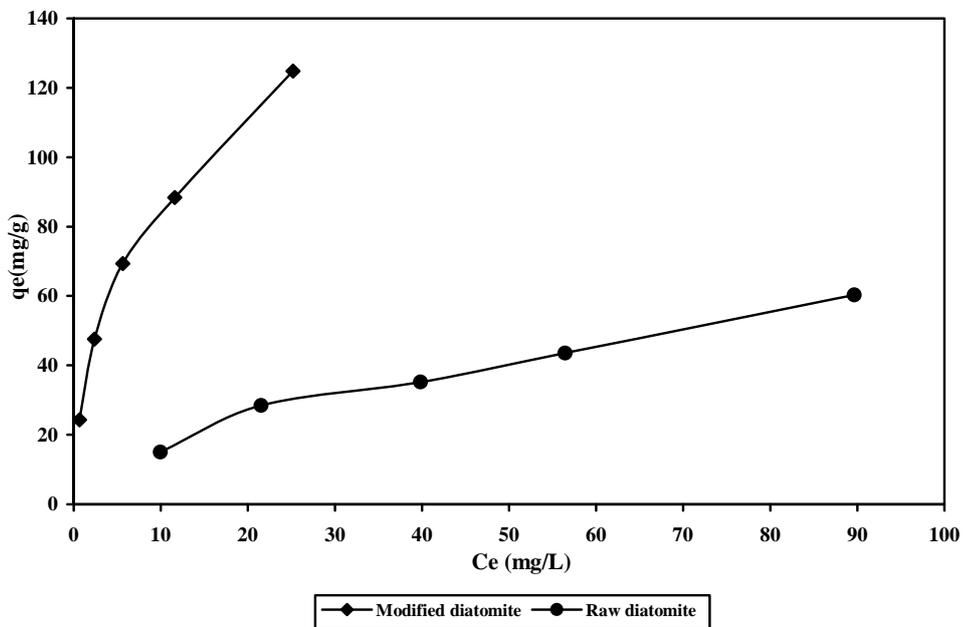


Figure 10: Effect of pH on the adsorption of AB 92 dye by raw and modified diatomite, agitation speed of 200 rpm, 25 ± 1°C, equilibrium time of 120 min.



**Figure 11:** Effect of temperature on adsorption of AB 92 dye on modified diatomite. equilibrium time of 120 min, pH 2, agitation speed of 200 rpm, adsorbent dosage of 0.1 g.



**Figure 12:** Adsorption isotherms of AB 92 dye onto raw and modified diatomite.

It is clearly seen from Figure 12 that the amount of adsorbed AB 92 dye on raw diatomite was much lower than that of modified diatomite.

The experimental data obtained were evaluated by various isotherm models incorporating Langmuir, Freundlich [5,13,17] and Brunauer-Emmett-Teller (BET) [13,37] isotherms.

Langmuir isotherm is applicable for monolayer adsorption on a surface containing a finite number of identical adsorption sites [17]. A linear expression for the Langmuir isotherm is as follows:

$$1/q_e = \left( \frac{1}{K_L Q_0} \right) (1/C_e) + 1/Q_0 \tag{2}$$

where  $C_e$  is the concentration of dye under equilibrium condition (mg/L),  $q_e$  denotes the amount of dye adsorbed at equilibrium (mg/g),  $Q_0$  indicates the maximum adsorption capacity and  $K_L$  is the Langmuir isotherm constant (l/mg). The values of  $K_L$  and  $Q_0$  were calculated from the slope and intercept of the linear plot of  $1/q_e$  versus  $1/C_e$ .

Freundlich equation was also applied for the adsorption of AB 92 dye on diatomite as given below:

$$q_e = K_F C_e^{1/n} \tag{3}$$

where  $C_e$  is the equilibrium dye concentration in aqueous system (mg/L),  $q_e$  is the amount of dye adsorbed per weight of the adsorbent used (mg/g),  $K_F$  and  $n$  are Freundlich isotherm constants incorporating all factors affecting the adsorption process. Taking  $\log_{10}$  from both sides of the Eq. (3) yields the following equation:

$$\log_{10} q_e = \log_{10} K_F + \frac{1}{n} \log_{10} C_e \tag{4}$$

Linear plot of  $\log_{10} q_e$  versus  $\log_{10} C_e$  gives the values of  $K_F$  and  $n$ .

Brunauer-Emmett-Teller (BET) model was also used to fit the adsorption data according to the linear form of its rearranged adsorption isotherm model, which may be expressed as:

$$\frac{C_e}{(C_s - C_e)q_e} = \frac{1}{K_b q_m} + \left( \frac{K_b - 1}{K_b q_m} \right) \left( \frac{C_e}{C_s} \right) \tag{5}$$

where  $C_e$  is the concentration of dye in solution (mg/L),  $C_s$  denotes the saturation concentration of dye (mg/L),  $q_e$  is the amount of dye adsorbed per weight of the diatomite used (mg/g),  $q_m$  is the amount of dye adsorbed in forming a complete monolayer (mg/g),  $K_b$  indicates a constant explaining the energy of interaction with the surface. The values of  $K_b$  and  $q_m$  were calculated from the slope and intercept of the linear plot of  $\left( \frac{C_e}{C_s - C_e} \right) \frac{1}{q_e}$  versus  $\frac{C_e}{C_s}$ .

The  $Q_0$ ,  $K_L$ ,  $r_1^2$  (correlation coefficient for Langmuir isotherm),  $K_F$ ,  $1/n$ ,  $r_2^2$  (correlation coefficient for Freundlich isotherm),  $K_b$ ,  $q_m$  and  $r_3^2$  (correlation coefficient for BET isotherm) are given in Table 1. The negative values of  $K_b$  in the BET isotherm model describe that the adsorption process for raw diatomite did not follow the BET isotherm model, since this constant is indicative of the surface binding energy. It is evident from Table 1 that the isotherm data for the adsorption of AB 92 dye by raw diatomite were best-fitted using Langmuir model with a correlation coefficient of 0.9896 which is justified by the uniformity of raw diatomite.

**Table 1:** Parameters of various isotherms for adsorption of AB 92 dye onto raw and modified diatomite.

| Adsorbent          | Langmuir     |              |         | Freundlich                        |      |         | BET   |              |         |
|--------------------|--------------|--------------|---------|-----------------------------------|------|---------|-------|--------------|---------|
|                    | $Q_0$ (mg/g) | $K_L$ (L/mg) | $r_1^2$ | $K_F$ (mg/g)(L/mg) <sup>1/n</sup> | 1/n  | $r_2^2$ | $K_b$ | $q_m$ (mg/g) | $r_3^2$ |
| Raw diatomite      | 80.00        | 0.023        | 0.9896  | 3.99                              | 0.60 | 0.9814  | -1.71 | 1.32         | 0.8191  |
| Modified diatomite | 104.16       | 0.442        | 0.9814  | 30.51                             | 0.44 | 0.9937  | 18.52 | 0.0082       | 0.9996  |

**Table 2:** Kinetics constants for AB 92 dye adsorption by raw and modified diatomite.

| Adsorbent          | Pseudo-first-order    |                           |                | Pseudo-second-order   |                              |                |
|--------------------|-----------------------|---------------------------|----------------|-----------------------|------------------------------|----------------|
|                    | q <sub>e</sub> (mg/g) | K <sub>1,ad</sub> (1/min) | R <sup>2</sup> | q <sub>e</sub> (mg/g) | K <sub>2,ad</sub> (g/mg min) | R <sup>2</sup> |
| Raw diatomite      | 111.249               | 0.775                     | 0.9851         | 185.185               | 0.0088                       | 0.9977         |
| Modified diatomite | 33.02                 | 0.529                     | 0.9951         | 105.26                | 0.053                        | 0.9996         |

Furthermore, the BET model is most appropriate for the adsorption of AB 92 dye on modified diatomite with a correlation coefficient of 0.9996. This is attributed to the changes in the structure of diatomite surface and its uniformity after presence of Ni. It can cause multilayer adsorption on produced composite and the BET isotherm can explain this situation.

In addition, it is clear from Table 1 that the adsorption capacity of modified diatomite is more than raw diatomite. The Langmuir isotherm (or equilibrium) constant (K<sub>L</sub>) and the maximum adsorption capacity (Q<sub>0</sub>) for modified diatomite are 19.21 and 1.3 times more than raw one, respectively.

### 3.8. Adsorption kinetics

The prediction of the adsorption kinetics of dye from aqueous system is important in order to design a suitable treatment system. The kinetics of adsorption of AB 92 dye on diatomite may be described by the pseudo-first-order Lagergren rate equation [3,13,17] and the pseudo-second-order rate expression developed by Ho and McKay [39]. The Lagergren equation is a simple kinetic analysis of adsorption representing as follows:

$$\log(q_e - q_t) = \log q_e - \frac{K_{1,ad}}{2.303} t \quad (6)$$

where q<sub>e</sub> and q<sub>t</sub> are the amounts of dye (mg/m) adsorbed at equilibrium and at time t (min) and K<sub>1,ad</sub> is the pseudo-first-order rate constant (1/min).

The Ho and McKay equation is based on adsorption equilibrium capacity which is given below:

$$\frac{t}{q_t} = \frac{1}{K_{2,ad} q_e^2} + \frac{t}{q_e} \quad (7)$$

where q<sub>e</sub> and q<sub>t</sub> are the amounts of dye (mg/m) adsorbed at equilibrium and at time t (min) and K<sub>2,ad</sub> is the rate constant of the pseudo-second-order model (g/mg min).

Linear plot of log<sub>10</sub>(q<sub>e</sub> - q<sub>t</sub>) against t gives the rate constant of K<sub>1,ad</sub>. Moreover, the value of K<sub>2,ad</sub> is obtained from the intercept of the linear plot of t/q<sub>t</sub> versus t. Adsorption kinetics constants of the pseudo-first-order and pseudo-second-order models at pH 2, 25 ± 1°C, an agitation speed of 200 rpm, an initial concentration of 50 mg/L and a time period of 120 min are given in Table 2.

From Table 2, the high values of correlation coefficients of the pseudo-second-order model for both raw and modified diatomite showed that the adsorption data conformed well to the Ho and McKay kinetics model (Eq. (7)), indicating the process is chemisorption controlled and the adsorption mechanism depends on the adsorbate and adsorbent.

### 4. Conclusion

Diatomite has been studied for the removal of AB 92 dye from aqueous solution. Modification treatment of the adsorbent was useful and its adsorption capacity increased. The adsorption process was also influenced by solution pH. The maximum sorption capacity occurred at pH 2, but there is no big difference between pH 2 (95.21% at 25°C) and 8 (82.03% at 25°C). By increasing the temperature, the adsorption efficiency of the modified diatomite has extended from 95.21 to 100%. Therefore, the remediation process incorporating adsorption method can be performed under normal temperature for an industrial scale. It was well depicted that the adsorption process was not sensitive to the temperature.

It was found that in order to obtain the highest possible removal of AB 92 dye, the experiments can be carried out at pH 2, 25°C, agitation speed of 200 rpm, initial dye concentration of 50 mg/L, centrifugal rate of 4000 rpm, adsorbent dosage of 0.1 g and process time of 120 min.

The results of this investigation show that NONMD has suitable adsorption capacity to remove AB92 from aqueous solutions. The most important thing to design and run an industrial adsorption plant is the knowledge of adsorption kinetics and isotherms. Hence, the experimental results were analyzed by using the Langmuir, Freundlich and BET equations. Equilibrium

data for the adsorption of AB 92 dye by raw diatomite fit well to the Langmuir isotherm model. Furthermore, the BET model is most appropriate for the adsorption of AB 92 dye on modified diatomite. In addition, the rate of adsorption process obeys the pseudo-second-order kinetics model.

### Acknowledgments

The authors are thankful to Petroleum University of Technology for providing the financial help and to Institute for Color Science and Technology (ICST), for supporting this research.

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