

Adsorption of Methylene Blue from Aqueous Solutions using Fe_3O_4 /Bentonite Nanocomposite

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Abstract

Magnetic Fe_3O_4 /bentonite nanocomposite was prepared by chemical co-precipitation method. The product was characterized by X-ray diffraction and Scanning electron microscope. Batch adsorption experiments were carried out for the removal of methylene blue from aqueous solutions using Fe_3O_4 /bentonite nanocomposite. Effects of pH of the initial dye solution, mass of the adsorbent and the contact time on the adsorption capacity were studied. The results showed that the adsorption capacity for the dye increased by increasing the contact time and initial pH of the solution. However, it decreased with increasing the mass of the adsorbent. The adsorption behaviors of the nanocomposite showed that the adsorption kinetics and isotherms were in good agreement with pseudo 2nd order kinetic equation and Langmuir equation, respectively, and the maximum adsorption capacity was 1600 mg/g. For this the prepared nanocomposite could be regarded as a potential adsorbent for MB removal in a wastewater treatment.

Keywords: Bentonite; Nanocomposites; Fe_3O_4 ; Adsorption; Methylene blue

Introduction

Adsorption is an economically and effective technique for the removal of dyes and colored pollutants from waste water [1]. The ease of operation, ease of availability and simplicity of design represent other reasons for the use of such technique [2,3]. Activated carbon is usually used as adsorbent due to its high adsorption capacity, high surface area, microspores structure and high degree of surface reactivity. But, there is some problems with its use concern the high cost and the loss in the regeneration. For this reasons, many researchers divert to low cost and effective substitutes, like coconut husk [4] spent tea leaves [5] fly ash [6-9] and surface soils [10]. Naturally occurring clays are bellowing to low cost materials with good adsorption ability [11-14]. This ability comes from their high specific surface area, chemical and mechanical stability, layered structure and high cations exchange capacity (CEC). Bentonite, naturally occurring clay, a cheap and a widespread material have been used as an alternative material for the removal of dyes.

Clays can be modified to improve their sorption ability. One of these modification methods is coating with magnetic particles [15,16]. Use of the magnetic particle in the nano scale have attracted by many authors [17]. The extremely fine size of nano-particles yields favorable characteristics. With reduction in size, more atoms are located on the surface of a particle results to a remarkable increase in surface area of nanopowders. This imparts a considerable change in surface energies and surface morphologies. All these factors are altering the basic properties and the chemical reactivity of nano-materials [18,19]. Fe_3O_4 nanoparticles, a fine brown powder, were used recently in several applications like magnetic storage media, solar energy transformation, electronics, ferrofluids and catalysis [20]. Several methods have been reported to synthesize Fe_3O_4 powders, including hydrothermal synthesis [21], microemulsion [22] and chemical co-precipitation [23]. Ultra small magnetic ferrite nano particles (diameter smaller than 15 nm) will be dispersed in a liquid carrier and provide a colloidal solution known as magnetic fluid (or Ferro fluid). Such solution, including both the fluid and magnetic properties was used in numerous industrial applications [24].

The aim of the present work is to prepare Fe_3O_4 /bentonite nano composite has high capacity of the removal of basic dyes like methylene

blue. Batch adsorption experiments are carried out and the adsorption kinetics for adsorption of MB on modified bentonite are studied.

Experimental

Materials

The materials used in this study were natural occurring bentonite clay supplied from the Red Sea for Phosphate Company, Egypt and methylene blue MB (BDH). The bentonite samples were ground and sieved by 200-mesh sieve and washed with distilled water for 3-4 times. Other used agents were all analytical grade and all solutions were prepared with distilled water.

Preparation of Fe_3O_4 /bentonite nanocomposite

Magnetic Fe_3O_4 /bentonite nanocomposite was prepared as follow [25]: 20 g of bentonite was added into a solution containing iron (II) chloride (0.02 molar) and iron (III) chloride (0.04 molar) at room temperature. The pH adjusted to around 10 by adding NH_4OH solution (5 mol/L). Stirring continued for 30 min and then stopped. 40 ml of 2M HNO_3 was added with stirring for 5 minutes. 60 ml of 0.35M $\text{Fe}(\text{NO}_3)_3$ was added and the solution boiled for one hour. The suspension was left to settle down then filtrated. The solid obtained washed with distilled water several times and dried in an oven at 80°C for 2 h.

The characterization and morphology of the formed composites are identified using X-ray diffraction (XRD) and Scanning electron microscope (SEM). For X-ray examination, a stabilized X-ray

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generator was used fitted using copper target and nickel filter under working conditions of 40 kV and 25 mA. For SEM examination, a freshly fractured surface of the dried sample coated with a thin film of gold (about 300–400 x 10⁻⁶ m thickness) using a vacuum evaporation technique. A JEOL-JSM-5400 high resolution scanning electron microscopy was used (Shimadzu Co., Japan). Surface area of the modified bentonite was measured using Sears' method [26].

Adsorption experiments

Effect of pH: The effect of pH on the adsorption was studied by agitated 50 ml of MB solution (2000 mg/L) with 50 mg of Fe_3O_4 /bentonite nanocomposite at different pH values (2 - 10) with shaking for 24 hours at 25°C. This was carried out using (THZ-98A) shaker at a constant speed of 120r/min. After equilibrium, filtration was carried out and the concentration of residual MB in the filtrate was measured by using UV-spectrophotometer (Specord 200) at 666 nm corresponding to a maximum absorbency of methylene blue. The concentrations of the samples were determined by using a linear regression equation obtained by plotting a calibration curve for MB over a range of concentrations.

Effect of adsorbent mass: The effect of mass of Fe_3O_4 /bentonite nanocomposite on the adsorption capacity was studied using 50 ml of methylene blue (2000 mg/L at pH 5) onto 50 - 300 mg of modified bentonite with shaking at 25°C for 24 hours. After 24 hours, the solid particles were removed and the remaining concentration of MB in the filtrate was measured by using the same spectrophotometer.

Adsorption kinetics: For kinetic study, 50 ml of dye solutions (2000 mg/L) was agitated onto 50 mg of modified bentonite with shaking at 25°C for 20, 40, 60, 80, 100, 120, 150, 180 and 200 minutes. At each time interval the solid particles was removed and the adsorption capacity qt was calculated by applying equation (1):

$$qt = (C_0 - C_t) \cdot V / 1000 \cdot m \quad (1)$$

Where: qt is the adsorption capacity (mg/g) at time t and C₀ and C_t is the concentration of the MB solution before and after adsorption process (mg/L), V is the volume of the solution (ml) and m is the mass of the adsorbent (g).

Results and Discussion

Characterization of Fe_3O_4 /bentonite nano composite

Figure1 shows XRD pattern of Fe_3O_4 /bentonite nano composites. From the pattern, we can conclude that quartz is the major constituent of modified bentonite. Nano Fe_3O_4 was identified from the peak at 2θ=35.56°. The broadening of such peak indicates a large number of generated surface defects with high specific surface area and particles distortions which contribute to such diffraction broadening. The morphology of natural bentonite and Fe_3O_4 /bentonite composites was studied by SEM (Figures 2a-2c). Very fine micro particles can be observed with diameter 0.2-0.8 μm in the SEM of Fe_3O_4 /bentonite nano composites. Presence of these fine particles leads to increase the porosity and the surface area of the modified clay. This was confirmed by the measured surface area obtained for modified bentonite (98 m²/g).

Effect of pH values on adsorption

In order to understand the effect of pH on the adsorption process, the point of zero charge (pHPZC) of the normal bentonite and Fe_3O_4 /bentonite nano composites was determined by the solid addition

method [27]. It was 2.6 and 3.2 for the normal bentonite and Fe_3O_4 /bentonite nano composites respectively. This indicates that the presences of nanoparticles on bentonite surface did not change its charge properties rather than its surface morphology. Adsorption of

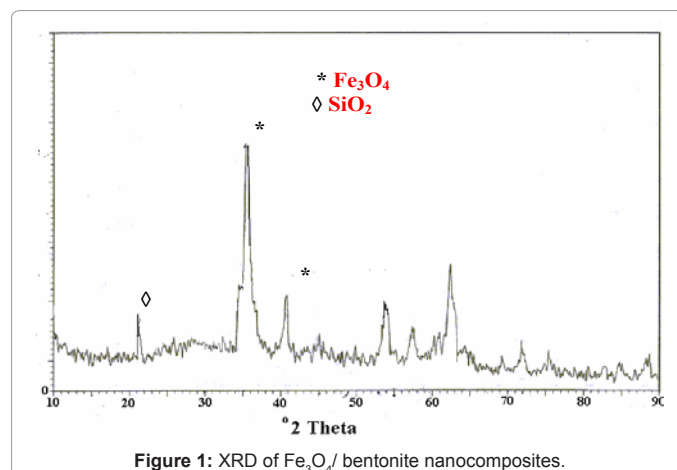
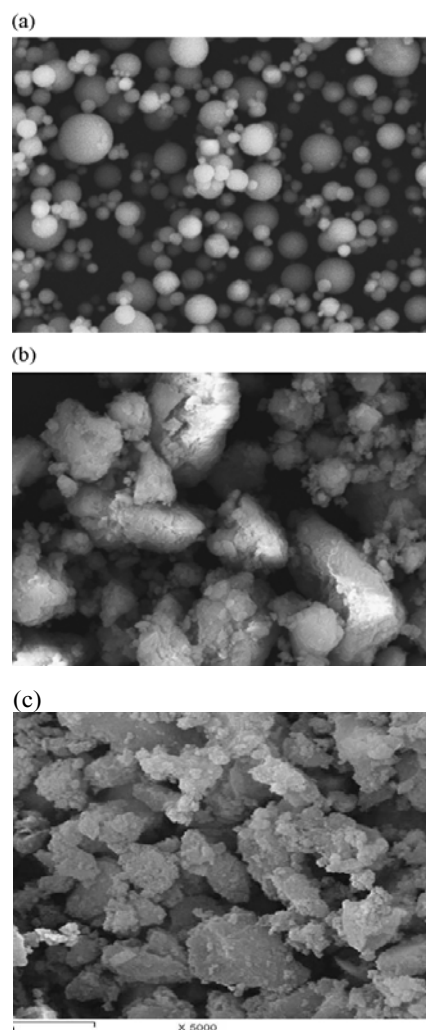


Figure 1: XRD of Fe_3O_4 /bentonite nanocomposites.



(a) nano Fe_3O_4 (b) bentonite (c) Fe_3O_4 /bentonite nanocomposite

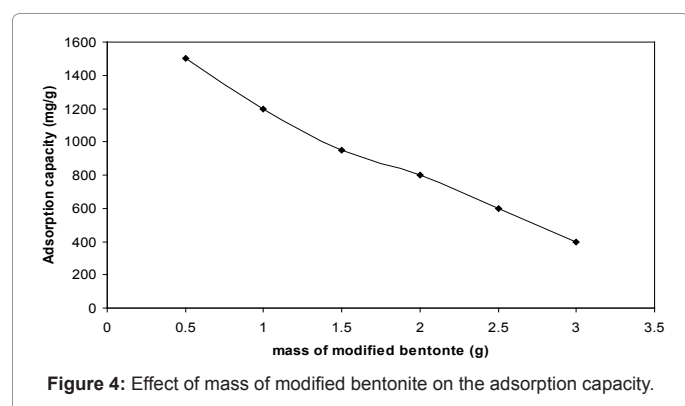
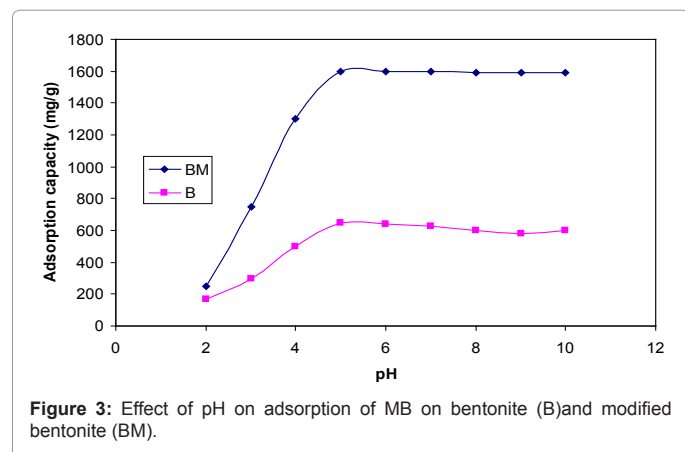
Figure 2: SEM of Bentonite and modified bentonite.

the cations is favored at $\text{pH} > \text{pHPZC}$, while the adsorption of the anions is favored at $\text{pH} < \text{pHPZC}$.

Figure 3 shows the effect of the initial pH of MB solution on the adsorption capacity of the bentonite and Fe_3O_4 /bentonite nanocomposites. The adsorption of MB on modified bentonite was higher than normal bentonite at all the pH range studied. The adsorption capacity ranged between 2-3 fold for modified bentonite compared to non modified one which related to increase in surface area and surface roughness caused by nano particles. However, the adsorption of MB on modified bentonite is highly pH dependent. The adsorption capacity increased continuously in the pH 2- 5 and reached 1600 mg/g at $\text{pH} = 5$. In the pH range 5 - 10 the adsorption capacity nearly unchanged or slightly decreased. At low pH values, the number of negatively charged adsorbent sites decreased and the number of positively charged sites increased, which did not favor the adsorption of positively charged dye cations like methylene blue due to electrostatic repulsion. In addition, lower adsorption of methylene blue at acidic pH might be due to the presence of excess H^+ ions competing with MB cations for the available adsorption sites which reduce the adsorbed amount. Increasing the pH values from 2-5 leads to deprotonation of the acid sites on the clay surface which becomes negatively charged with high attractive properties. This leads to increase in the surface diffusion of the dye molecules due to high the electrostatic interactions between MB and modified bentonite [17]. At higher pH values (>5) no further adsorption occurred which may be related to the complete coverage of the surface by methylene blue molecules.

Effect of adsorbent mass

Figure 4 shows the amount adsorbed of MB (mg/g) with change



in the mass of Fe_3O_4 /bentonite nanocomposite. It was noted that the amount adsorbed of MB per gram of adsorbent decreases with the increase the mass of the modified bentonite. So that 6-fold increase in modified mass resulted in 400% decrease in the adsorption capacity. Such result has been obtained by other authors [28-31] and has many explanations. Increasing the adsorbent amount reduces the unsaturation of the adsorption sites and correspondingly, the number of such sites per unit mass comes down resulting in comparatively less adsorption. Also this decreases the driving forces for adsorption (Conc. of dye molecules/ conc. of adsorption sites) which decrease the dye diffusion from solution into the adsorbent platelets. In addition, overlapping of adsorption sites as a result of over-crowding of adsorbent particles may be another explanation [32].

Effect of contact time

Figure 5 shows the effect of contact time on the adsorption capacity of MB by the modified bentonite. It can be seen from figure 5 that the adsorption process could be divided into three steps. In the first step, the adsorption rate was fast and 82% of the adsorption capacity was achieved within the first 40 min of the adsorption process. This is followed by second step represents a gradual adsorption stage from 40 to 60 minutes of the adsorption process. In the third step the rate of adsorption of MB on modified bentonite was slow and reached equilibrium at about 150 min. The quick adsorption in the first 40 minutes of the adsorption process indicates the high diffusion of the dye molecules into the external surface of the modified bentonite or the boundary diffusion layer of the solute molecules. This is followed by a slow diffusion to the internal surface and pore matrix in which intra-particles diffusion is the rate limiting. At later times the available adsorption sites became fewer which decrease the rate of adsorption and an equilibrium state was attained.

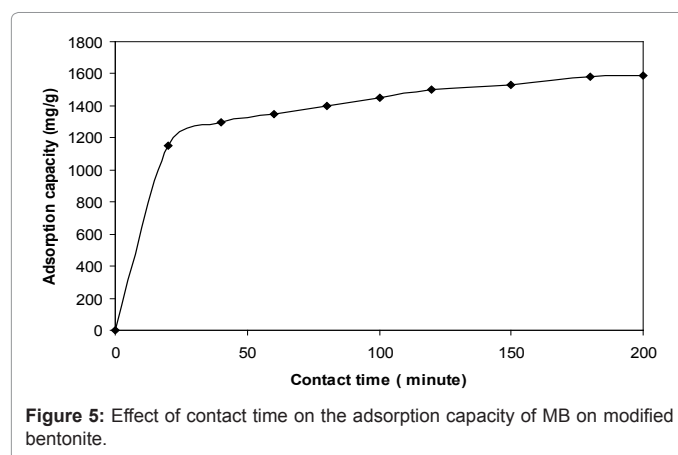
Adsorption kinetics

In order to understand the process of adsorption, three kinetic models were applied to the experimental data.

The linear form of pseudo first-order kinetic model is expressed as Equation (2):

$$\ln(q_e - q_t) = \ln q_e - k t \quad (2)$$

Where; q_e : the concentration of MB adsorbed after equilibrium, q_t : the concentration of MB adsorbed in time t , k (min^{-1}) is pseudo 1st order rate constant.



Pseudo 2nd order rate equation in the linear form is expressed as:

$$t/q_t = 1/kq_e^2 + t/q_e \quad (3)$$

Where; k (g/mg. min) is the pseudo 2nd order rate constant which can be calculated from the intercept of the straight line obtained from plotting t/q_t vs. t.

Intra-particle diffusion model is an empirical model assuming that the adsorption capacity varies with $t^{1/2}$ [33] (Equation (4)):

$$q_t = K_d t^{1/2} + C \quad (4)$$

Where; K_d (mg/g t^{1/2}) is the intra-particle diffusion rate parameter and C is a constant. Plotting q_t versus $t^{1/2}$ should give a straight line if the diffusion model is valid. K_d and C are calculated from the slop and intercept of the line and the value of C indicates the thickness of boundary layer, and with the larger value of C the contribution of the surface sorption is greater in the rate limiting step.

The three models are tested for MB on Fe₃O₄/bentonite nanocomposite. The best-fit model was determined depending on the linear correlation coefficient R². The results are shown in table 1. The

Model	Parameters
Pesdo 1 st order rate equation	R ² =0.886 k=0.0034
Pseudo 2 nd order rate equation	R ² =0.998 k=0.001 q _e , cal.=1666.7 (mg/g) q _e , exp.=1600 (mg/g)
Intra-particle diffusion model	R ² =0.974 K _d =43.67 C=999.64

Table 1: kinetic parameters for three model of adsorption of MB on modified bentonite.

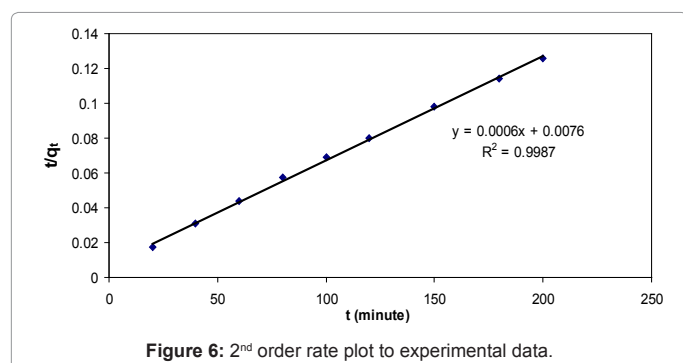


Figure 6: 2nd order rate plot to experimental data.

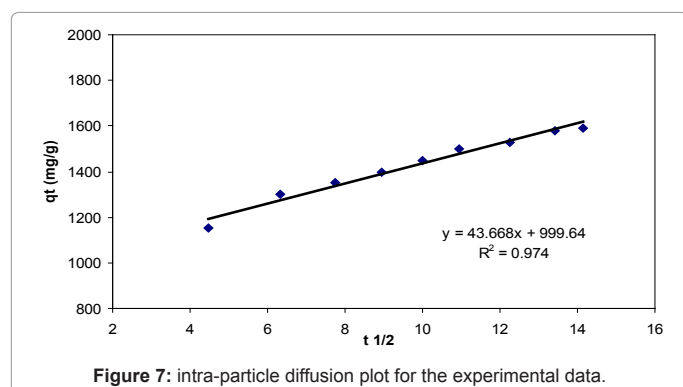


Figure 7: intra-particle diffusion plot for the experimental data.

pseudo 2nd plot was represented in figure 6. According to the value of the correlation coefficient, the pseudo 2nd order rate equation (R²=0.999) showed more fitting to the experimental data than the 1st order rate equation (R²=0.886). In addition the experimental q_e value (q_e , exp) and the calculated q_e value (q_e , cal) calculated from the pseudo-second order kinetics model are very close to each other. The intra-particle diffusion model showed also good fitting to the experimental data (R²=0.974), see figure 7. This indicates the adsorption of MB on the modified bentonite followed the 2nd order rate equation and controlled by diffusion of MB molecules from the bulk of the solution to the external surface and pore structure of the modified bentonite.

Adsorption isotherm

In order to study how the molecules of MB interact with the adsorbent surface the adsorption isotherms are used to analyze the experimental data. The most widely used isotherm equations are Langmuir and Freundlich equations.

In the langmuir model there is an activate point on the surface of the adsorbent is able to adsorb one molecule, indicating the adsorbed layer is one molecule thick. It is expressed as the following Equation (5).

$$C_e/q_e = 1/bq_m + C_e/q_m \quad (5)$$

Where; C_e (mg/l) is the equilibrium concentration, q_e (mg/g) is the amount adsorbed, q_m (mg/g) is the complete monolayer adsorption capacity, and b (L/mg) is the Langmuir constant.

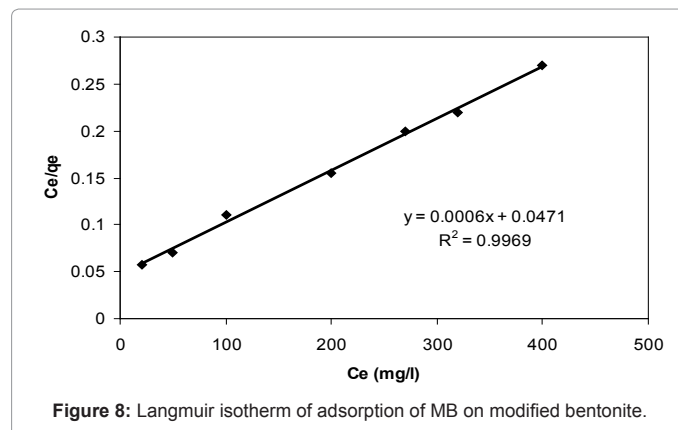


Figure 8: Langmuir isotherm of adsorption of MB on modified bentonite.

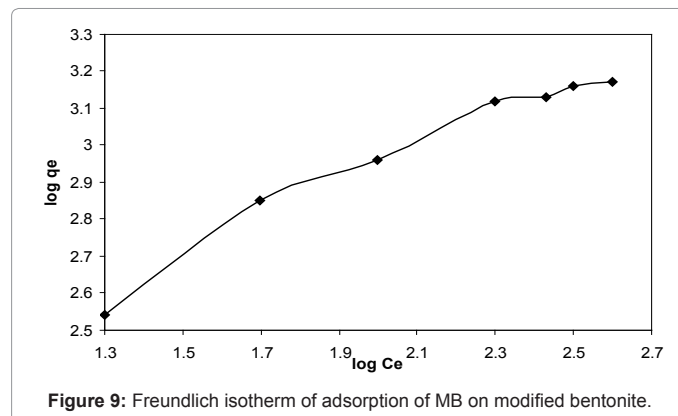


Figure 9: Freundlich isotherm of adsorption of MB on modified bentonite.

Isotherm	Constants
Langmuir	R ² = 0.996 q _m =1660 (mg/g) q _e =1600 (mg/g) b=0.013 R ² =0.96
Freundlich	1/n=0.473 k=1.987

Table 2: Isotherm constants for MB adsorption on modified bentonite.

Freundlich isotherm is valid for non-ideal adsorption on heterogeneous surface, suggesting multilayer adsorption on adsorbent surface. Freundlich equation is presented as following:

$$q_e = k C_e^{1/n} \quad (6)$$

Where: k and n are Freundlich constants. The value 1/n is a measure of adsorption intensity or surface heterogeneity, which may become more heterogeneous when 1/n close to zero [34]. The value of 1/n below one suggests a normal Langmuir isotherm while 1/n above one is indicative of cooperative adsorption [35].

The two adsorption isotherms are constructed by plotting Ce/qe versus Ce for Langmuir and log qe versus log Ce for Freundlich. Figures 8 and 9 showed the two isotherms and table 2 showed the Langmuir and Freundlich parameters. The correlation coefficients (R²) determine the most related model to the adsorption process. The values of R² for Langmuir and Freundlich models are 0.99 and 0.96 respectively. Also the calculated value of qm for adsorption obtained from Langmuir model are 1660 mg/g which close to the experimental value 1600 mg/g indicating there is only one layer of the dye molecules was formed on the surface of the adsorbent. In addition, according to the value of 1/n calculated from Freundlich plot (1/n = 0.47) which less than one means a surface homogeneity. This indicates the Langmuir isotherm describes the adsorption of MB on the modified bentonite very well and there is a monolayer coverage of the dye on the nanocomposite surface.

Conclusion

1- Introduce of magnetic nano particles of Fe₃O₄ into the surface of bentonite generates a porous surface with high surface area which is suitable for the adsorption of basic dyes like methylene blue.

2- The results of batch experiments for removal of MB showed that the adsorption capacity increased with increasing the contact time and the initial pH of MB solutions with maximum adsorption capacity at pH 5. However the adsorption capacity decreased with increasing the mass of the adsorbent.

3- Kinetic data of adsorption are well fitted by the pseudo 2nd order kinetic model with a good agreement with the intra-particle diffusion model.

4- The equilibrium experimental data fits perfectly the Langmuir isotherm which implies the monolayer formation on the surface of the modified bentonite. The maximum adsorption capacity was 1600 mg/g.

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