

Alginate/ Polyvinyl Alcohol - Kaolin Composite for Removal of Methylene Blue from Aqueous Solution in a Batch Stirred Tank Reactor

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Abstract: The investigation of possible use of Alginate/ polyvinyl alcohol -kaolin composite instead of free kaolin in the removal of methylene blue from aqueous solutions was studied. Various experiments have been carried out using batch adsorption technique to study the effects of the process variables, which include contact time, beads diameter, beads swelling, organic-kaolin composite dosage, initial dye concentration, pH, agitation speed and solution temperature on the adsorption process. In the batch kinetic study of methylene blue, the order of the reaction, the half-life and the rate constant were determined. Numerical correlations using regression analysis for maximum percentage removal of dye with operating condition of the process were presented. The result showed that the adsorption attained to equilibrium in 360 min and the kinetics followed first order in nature. [Journal of American Science 2010; 6(5):280-292]. (ISSN: 1545-1003).

Keywords: Adsorption, Cationic dye, Isotherms, Kaolin composite, binding polymers.

1. Introduction

The effluents from textile, leather, food processing, dyeing, cosmetics, paper, and dye manufacturing industries are important sources of dye pollution [1]. Many dyes and their break down products may be toxic for living organisms [2]. Therefore, removal of dyes is important aspect of wastewater treatment before discharge. It is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from wastewater by conventional wastewater systems [3]. Adsorption of dye at the solid/liquid interface has been extensively studied the last years. Activated carbon has been successfully used in removing colored organic species with being the most widely used adsorbent due to its high capacity for the adsorption of organic materials [4–6]. However, due to its high cost and the difficulty of regeneration, a search for cheap, effective adsorbents such as bentonite clay derivatives is needed.

Clay has received particular attention as an economical adsorbent for removing heavy metals from wastewater due to its abundance and easy availability but it is still difficult to be separated from the wastewater [7]. In order to overcome the handling problem, organic binding polymers for the granulation

of kaolin have a lot of advantages such as simplicity of preparation procedure and excellent physicochemical properties [8]. Recently, Alginate, agar and carrageenan, are known as the major binding biopolymers. However, the mechanical strength of agar is rather weak, also carrageenan, has the economical disadvantage of a high removal cost for carrageenan causing the gel to become weak. Consequently, it may be impractical to apply these polymeric materials to wastewater treatment as immobilization carriers. Many studies have been carried out about the application of alginic acid to the aqueous phase separation of heavy metals, and the possibility of alginic acid for the adsorbent material has been suggested [9,10]. In such applications, alginic acid is not rigid enough to be used in a down flow packed-bed column operation and presents an unacceptable pressure drop [11]. The use of polyvinyl alcohol (PVA) as an immobilization carrier was initiated about 10 years ago [12]. PVA is a raw material of vinylon and can be produced industrially rather cheaply. PVA also offers various advantages over the conventional immobilization methods, such as low cost, high durability and chemical stability. Immobilization using PVA can be used only PVA crosslinked with boric acid [13]. But the formed beads had a strong tendency to agglomerate into a mass of polymer which was very difficult to break up. This

agglomeration problem appears to be due to the relatively slow crosslinking of the PVA by boric acid. Droplets of PVA, which have not been sufficiently crosslinked, tend to agglomerate. This problem persisted even with vigorous stirring of the boric acid solution to keep the beads suspended [14]. So, many attempts to form spherical beads, which are the preferred shape for application, from PVA took place using alginate to prevent agglomeration. Mixed solution of PVA and sodium alginate were used by few researchers. Remmers and Vorlop [15] reported that the fracture strength for alginate beads is smaller than PVA–alginate beads, in addition the PVA–alginic beads were also stable under strong acidic (below pH 1.0) and high temperature (above 170°C) conditions. On the other hand Dave and Madamwar [16] mentioned that the beads produced from mixed polymers (alginate & PVA) exhibited rubber like elastic properties, PVA contributed strength and durability to the beads, whereas calcium alginate improved the surface properties, reducing the tendency to agglomerate.

The present work deals with the preparation of organic- kaolin composite from kaolin and polymer mixture of alginate & PVA. It was also focusing on the factors that might affect the removal of cationic dye (methylene blue) using batch stirred reactor. From the present work the order of the reaction, the half-life and the rate constant of the reaction were determined. Finally, Langmuir & Freundlich isotherms were performed for interpretation of results.

2. Material and Methods

2.1. Materials

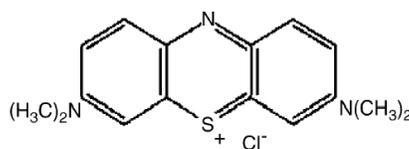
Kaolin,hydrated aluminum silicate, (SIGMA-Aldrich, Germany). Poly vinyl alcohol (PVA) (MERCK, Germany), Alginic Acid sodium salt (SIGMA, USA.), Methylene Blue (NICE CHEMICALS Pvt. Ltd., COCHIN).

2.2. Preparation of basic dye solution

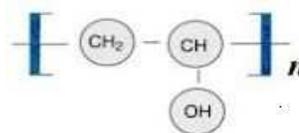
Methylene Blue, $C_{16}H_{18}N_3SCl_3 \cdot 3H_2O$, is a cationic dye. The structure of this dye is shown in Fig.1.a. The stock dye solution was prepared by dissolving 1g of methylene blue in 1000 ml distilled water. The samples were filtered and the dye concentration in the supernatant solution was estimated by measuring absorbance using UV-Vis double Beam spectrophotometer (LABOMED. Inc) using 1 cm light-path cell at λ max of 665 nm.the residual dye concentration was also determined using the same technique.

2.3. Preparation of composite Solution

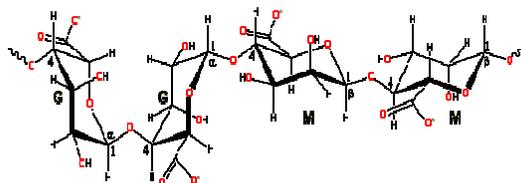
4% PVA solution was prepared by dissolving 20g of PVA (its molecular weight 72000) that has alcoholic structure as indicated in Fig.1.b. in demineralized water by heating the solution around 60°C with continuous stirring to dissolve PVA. 1% alginate solution that has linear unbranched polymers containing β -(1 \rightarrow 4)-linked D-mannuronic acid (M) and α -(1 \rightarrow 4)-linked L-guluronic acid (G) as indicated in Fig.1.C. was prepared by dissolving alginic acid sodium salt (medium viscosity ~3500cps) in water with gentle heating and stirring.



a. Structure of Methylene Blue



b. PVA structure



c. Sodium alginate structure

Fig.1. a. Structure of Methylene Blue, b. PVA structure and c. Sodium alginate structure

2.4. Preparation and characterization of Organic-Kaolin Composite

Kaolin (9g) was mixed thoroughly with an aqueous solution of 5% PVA containing 0.5% sodium alginate using the homogenizer for 5min at 14000rpm. This mixture was pumped by a peristaltic pump at 10 ml/min and then dropped into a gently stirred 6% boric acid solution containing 3% CaCl₂ to form spherical beads. In order to complete gelation inside beads, these beads were stirred gently in the boric acid-CaCl₂ solution for 24h. The beads were then removed and washed with distilled water. Finally the washed beads were dried at 40°C for 24 h. The dried composite was used for detailed studies. The prepared composite was characterized using FTIR, SEM and TGA techniques and also tested for swelling and turbidity.

2.5. Setup

The apparatus used in this study consists of a cylindrical Pyrex jacketed reactor, with outer diameter 12.3 cm, wall thickness 1.6cm and 18.2 cm in height. The mixer consists of a stainless steel shaft fitted with four blade propellers, with a diameter 5cm. The stirrer is coated with epoxy resin and is driven by a 35 watt motor which is fixed firmly against a steel frame to prevent vibrations. The rotation speed is controlled automatically by LED display. The jacketed reactor connected with water bath model-ultra term (J.P.SELECTA Co., Spain) to control the solution temperature.

2.6. Batch adsorption experiments

2.6.1. Effect of binding polymers

A sample of polymer mixture (alginate+ PVA) 3.2g compared with 4.8g sample of kaolin and 8g sample organic-kaolin composite (each 8g sample of composite contains 3.2g polymer mixture and 4.8g kaolin) with 2mm dry beads diameter was added to each 800ml of methylene blue aqueous solution having an initial concentration of 20 mg/L for investigation of the effect of binding polymer for a constant stirring speed, 500 rpm, initial pH= 9. The experiments were carried out at 22°C in the jacketed reactor. Samples at different time intervals were taken from the reactor for dye analysis using UV-Vis double Beam spectrophotometer.

2.6.2. Effect of contact time

A dry sample of organic-kaolin composite (8 g) with 2mm beads diameter was added to each 800 ml of methylene blue aqueous solution having an initial

concentration of 20 mg/L with a constant stirring speed, 500 rpm, initial pH= 9 and the experiments were carried out at 22°C in the jacketed reactor. Samples at different time intervals were taken from the reactor for dye analysis using UV-Vis double Beam spectrophotometer.

2.6.3. Effect of beads Diameter

A dry sample of organic-kaolin composite (8 g) with different diameters (0.5, 1&2mm) was added to each 800 ml of methylene blue having an initial concentration of 20 mg/L at constant stirring speed, 500 rpm, initial pH= 9 and the experiments were carried out at 22°C in the jacketed reactor. Samples at different time intervals were taken from the reactor for dye analysis using UV-Vis double Beam spectrophotometer.

2.6.4. Effect of beads swelling

A sample of either dry and swollen organic-kaolin composite (8 g) with 2mm dry beads diameter was added to each 800 ml of methylene blue aqueous solution having an initial concentration of 20 mg/L for a constant stirring speed, 500 rpm, initial pH= 9 and the experiments were carried out at 22°C in the jacketed reactor. Samples at different time intervals were taken from the reactor for dye analysis using UV-Vis double Beam spectrophotometer.

2.6.5. Effect of organic-kaolin composite dosage

Effect of organic-kaolin composite at various doses, which are 2, 4, 8, and 10g on percentage dye removal was studied. In the experiments, a 2mm dry beads diameter of composite was added to each 800 ml of methylene blue aqueous solution having an initial concentration 20 mg/L for a constant sorption time, 360 min at constant stirring speed, 500 rpm, initial pH= 9 and the experiments were carried out at 22°C in jacketed reactor.

Effect of initial dye concentration

A sample of 2mm dry organic-kaolin composite (8 g) was added to 800mL of methylene blue solution. The initial concentrations of dye solution tested were 10, 20, 125,225, and 500 mg/L and the experiments were carried out for a constant sorption time, 360 min at constant stirring speed, 500 rpm, initial pH= 9 and the experiments were carried out at 22°C in jacketed reactor.

2.6.7. Effect of pH

Effect of initial dye pH was investigated at various pH, which are 2, 7, 9, and 12. In the experiments, 8 g of 2mm dry composite was added to each 800 ml of methylene blue aqueous solution having an initial concentration 20 mg/L for a constant sorption time, 360 min and the experiments were carried out at constant stirring speed, 500 rpm, and the experiments were carried out at 22°C in jacketed reactor.

2.6.8. Effect of agitation speed

A sample of 2mm dry organic-kaolin composite (8 g) was added to 800 ml of methylene blue aqueous solution having an initial concentration of 20 mg/L for investigation of the effect of mixing rate at various stirring rate (0,100, 250, 500,750 and 1000 rpm). The experiments were carried out for a constant sorption time, 360 min at constant stirring speed, 500 rpm, initial pH= 9 and the experiments were carried out at 22°C in jacketed reactor.

2.6.9. Effect of solution temperature

A sample of 2mm dry organic-kaolin composite (8 g) was added to each 800 ml of methylene blue aqueous solution having an initial concentration 20 mg/L. The experiments were carried out at a constant temperature stirred jacketed reactor which controlled the temperature to 22, 35, 50, and 65 °C within ± 1 . The experiments were carried out for a constant sorption time, 360 min at constant stirring speed, 500 rpm, and initial pH= 9.

3. Results and discussion

3.1. Characterization of adsorbing material.

3.1.1. Fourier Transform Infrared Spectroscopy FTIR

The FTIR spectrum of Kaolin, Polymer mixture and also the prepared polymer-kaolin composite were measured using the disc technique with KBr as a matrix. And the FTIR analysis was performed using Fourier Transform Infrared Spectrophotometer FTIR-8400 Shimadzu- Japan. Fig.2. shows the pattern of Kaolin in which a broad band at 3600 cm^{-1} was which contain $\sim 14\%$ water. Also there are two bands at 1022 cm^{-1} and 465 cm^{-1} could be attributed to the stretching and bending vibrations of the SiO_2 in the structure of Kaolin. Polymer mixture pattern shows significant broad band corresponding to OH group at 3200-2500 cm^{-1} corresponding to both alcoholic and acidic groups.

Also there is a band at 2900 cm^{-1} could be attributed to CH stretching for aliphatic chain. At 1720 cm^{-1} there is a band corresponding to C=O of the carboxylic group. There is also band at 1120 cm^{-1} corresponding to C-C bond. Figure (2) also depicts the pattern of the prepared polymer- kaolin composite in which a broad band at 3400 cm^{-1} appeared and it could be assigned to the interstitial water in the Kaolin structure and also the OH group of the used polymers. Also a band at 1620 cm^{-1} was appeared and it could be attributed to the carboxylic group of Alginate [17]. the C-H stretching in PVA shows an absorption band at 1440 cm^{-1} [18] and the C-C stretching in PVA appeared at 1118 cm^{-1} [19].

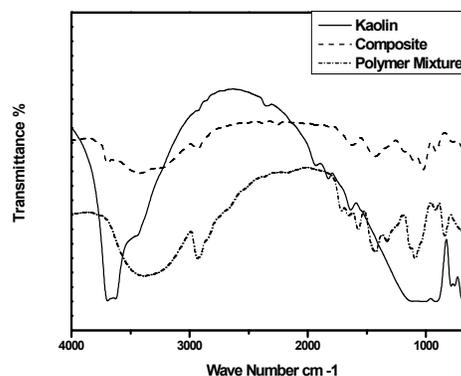


Fig.2. FTIR spectrum of (a) Kaolin and (b) Organic- Kaolin Composite

3.1.2. Thermogravimetric analysis TGA

The thermal stability of the polymer- kaolin composite was evaluated by Thermo Gravimetric Analysis TGA using Thermo Gravimetric Analyzer Shimadzu TGA-50 Japan. Fig. (3-a) shows the TGA of kaolin, the main step began at 427 °C is attributed to the loss of interstitial water in kaolin structure and the weight loss is 11.363% in accordance with the known water ratio in kaolin. Fig. (3-b) shows the TGA pattern of the prepared composite which contained three main steps. The first step began at 41 and ended at 335 °C which was explained by the removal of external water molecules together with degradation of alginate chain

and it is interpreted with second degradation temperature due to elimination of side-groups of PVA. [20].

The third step is obviously due to the complete loss of the organic components and it started at 432 °C and ended at 712 °C [21].

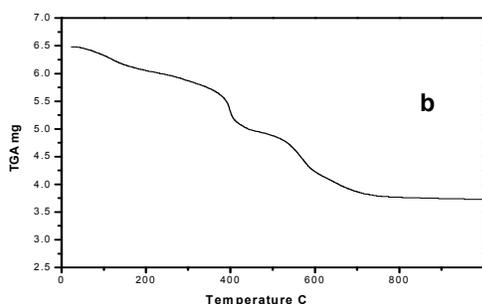
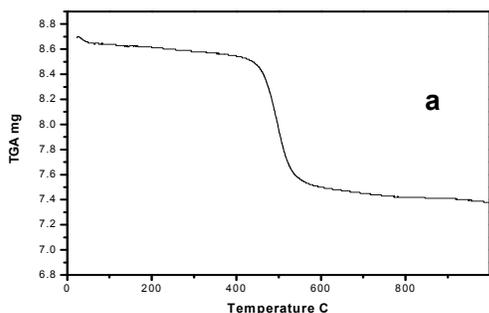


Fig.3. TGA analysis of (a) Kaolin and (b) Organic-Kaolin Composite

3.1.3. Scanning Electron Microscope SEM

The morphology of the prepared composite was investigated using Jeol JSM-6360 LA analytical Scanning Electron Microscope SEM. The samples were stocked over a holder and sprayed with gold. The sample was scanned to identify the structure and estimate the diameter. It was shown in Fig. 4. that the composite prepared from kaolin and PVA& alginate mixture has almost uniform porosity with pore diameter range 36-75 μm . The diameter of the composite beads ranged from 1.9- 2.4 mm.

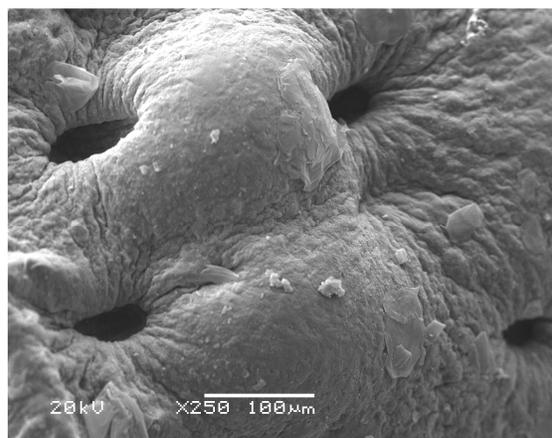
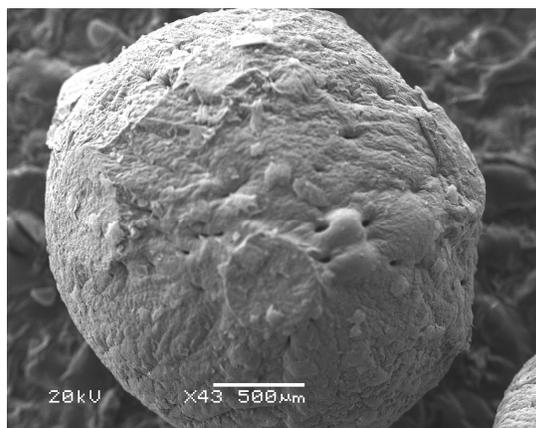


Fig.4. SEM of Organic – Kaolin composite

3.1.4. Turbidity measurements as a factor in mechanical strength

The beads produced from kaolin with mixed polymer (PVA & alginate) exhibited rubber like elastic properties, PVA contributed strength and durability to the beads whereas alginate improved the surface properties, reduced the tendency to agglomerate [16]. The mechanical properties of the composite were studied to determine its availability for the column operations. From water turbidity measurements after stirring for different time intervals, it is obvious that the beads of the prepared composite have excellent mechanical strength under stirring for 72 hours at 1000 rpm.

3.1.5. Swelling measurements

The swelling behavior of the beads was studied in order to test its suitability for column operation. It is concluded that the composite beads swelling in water increase with time till reached equilibrium after 5 hours. So the produced polymer-kaolin composite suitable to be used in column operation after being swollen in water for 5 hours to avoid column clogging during the treatment process.

3.2. Adsorption experiments

The % removal of blue dye was calculated according to the following equation:

$$\text{The removal percentage (\% removal)} = \frac{(C_0 - C)}{C_0} * 100 \quad (1)$$

Where C_0 and C (both in mg/L), are the initial concentration and the concentration at any time respectively.

% removal is defined as the ratio of difference in dye concentration before and after adsorption ($C_0 - C$) to the initial dye concentration in the aqueous solution.

The removal capacity (q)

$$q \text{ (mg/g)} = (C_0 - C) * (V/M) \quad (2)$$

Where V is the solution volume (L),

M is the adsorbent amount (g).

3.2.1. Effect of binding polymers

It was observed from Fig .5. that the alginate & PVA matrix has a small dye uptake may be due to their hydroxide groups that are suitable for cationic dyes removal. On the other hand, the presence of the polymer matrix enhance the percentage dye removal than the free kaolin due to the presence of hydroxide groups associated with the polymer matrix as indicated in Fig.1. The percentage removal increased from 70.3% to 92.7% after 360 min, upon using composite beads instead of free kaolin. However the adsorption rate decreased through the first adsorption hour may be due to the diffusion limitation of dyes through the composite beads to reach to the active adsorption sites (kaolin).

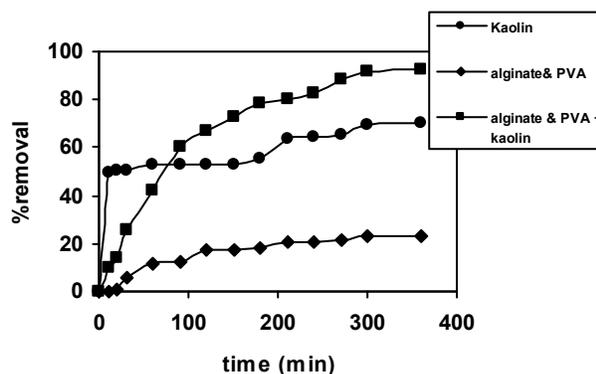


Fig.5. Effect of binding polymer on the percentage dye removal

3.2.2. Effect of contact time

The effect of contact time on the % removal of dye adsorbed was investigated as shown in Fig. 6. The % removal of Methylene Blue by organic-kaolin composite was found to increase, reach a maximum value with increase in contact time. In some cases it almost become constant with increase in contact time, after 360 min. based on these results, 360 min was taken as the equilibrium time in adsorption experiments. The removal of methylene blue from aqueous solutions by adsorption on organic-kaolin composite increases with time, till equilibrium is attained. Similar results have been reported in literature for removal of dyes [2, 22].

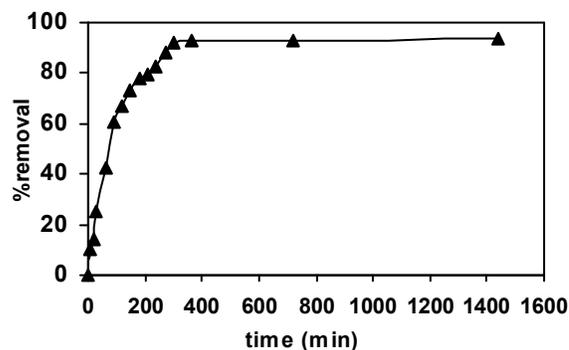


Fig.6. Effect of contact time on the percentage dye removal

In batch type adsorption process monolayer of adsorbate is generally formed on the surface of adsorbent [23] and removal rate of adsorbate species from aqueous solution is controlled especially by the transport rate of the adsorbate species from the outer sites to interior sites of the adsorbent particulars [2].

In a kinetic study of methylene blue adsorption on organic-kaolin composite was investigated, Fig.7. shows a plot of $(\ln C_0/C)$ against time (t) was applied up to 360 min. The data gave straight lines, which indicated that the reaction was classified as a first order [24]. In a first order reaction the rate is directly proportional to the concentration of the reacting substance. According to the first order equation (3) the slope of the straight line is $= K$, where K is the rate constant (min^{-1}) that equal $7.9 \times 10^{-3} \text{ min}^{-1}$.

$$\ln C_0/C = K * t \quad (3)$$

The above equation is the integrated form of the equation:

$$-V_s (dc/dt) = KC \quad (4)$$

The half time, $t_{0.5}$, for first order reaction is calculated according to the following equation [5]:

$$t_{0.5} = 0.693/K \quad (5)$$

Where, $t_{0.5}$ (min) is the time for the removal of half the amount of dye that equal 87.7min.

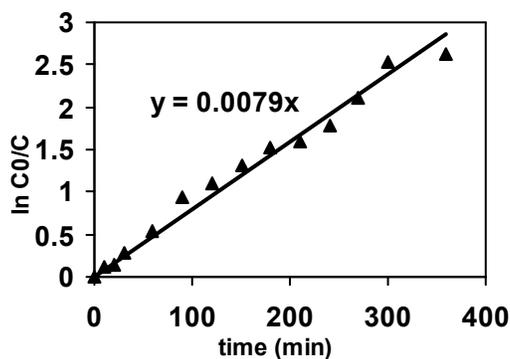


Fig.7. Plot of $\ln C_0/C$ Vs. time for methylene blue removal

3.2.3. Effect of beads Diameter

There is no significant increase in the percentage dye removal as the beads diameter increased from 0.5 mm to 2mm (Fig.8.)

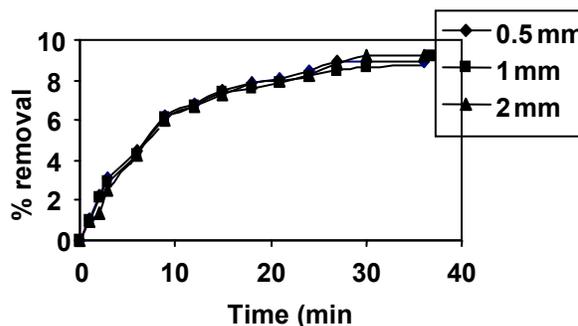


Fig.8. Effect of beads diameter on the percentage dye removal

3.2.4. Effect of beads swelling

In spite of the composite beads have swelling characteristics there is no variation on both the rate and the percentage dye removal for the swollen beads than the dry ones. Which is may be due to the effect of the other different operating variables in the batch process that eliminate the swelling effect.

3.2.5. Effect of organic-kaolin composite dosage

Fig.9. illustrates the effect organic-kaolin composite dosage that is added to methylene blue solution. It is observed that the removal of dye increases as the dosage of composite increases. For instance, the removal of dye increases from 41.8 to 95.5% on increasing the mass of composite from 2 to 10 g after 360 minutes. Increasing the adsorbent dosage at constant methylene blue concentration provided more available adsorption sites for dye and thus increased the extent of dye removal [25-26]. However the ratio of dye adsorbed to composite (mg/g) decreased with the increasing composite dosage from 3.37 to 1.53 mg/g. The relationship between % removal and the adsorbent dosage can be modeled using the following equation:

$$\text{Max. \% removal} = -1.2333 (\text{composite dosage})^2 + 21.05 (\text{composite dosage}) + 6.6333 \quad (6)$$

$$R^2 = 0.984$$

Where: $2 \leq \text{compositedosage} \leq 10$

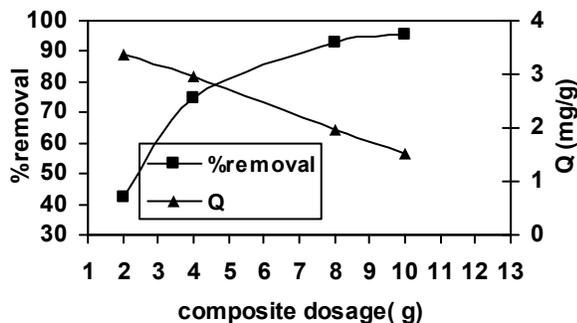


Fig.9. Effect of composite dosage on the percentage dye removal and removal capacity

3.2.6. Effect of initial dye concentration

It is observed from Fig. 10 that the % removal is inversely proportional to the initial dye solution concentration. The removal of dye decreased from 100 to 61.6% on increasing the initial dye concentration from 10 to 500 mg/L after 360 minutes.

This may be attributed to the increase of dye molecules adsorption onto the external surface of the organic-kaolin composite, increases significantly the local dye concentration, giving rise to the formation of aggregates of the dye on the composite particles. However the increase at initial dye concentration leads to an increase in the adsorption capacity. As the initial dye concentration increases from 10 to 500 mg/L, the adsorption capacity of dye onto composite changes from 1 to 30.8 mg/g. This indicates that the initial dye concentration plays an important role in the adsorption capacity of dye.

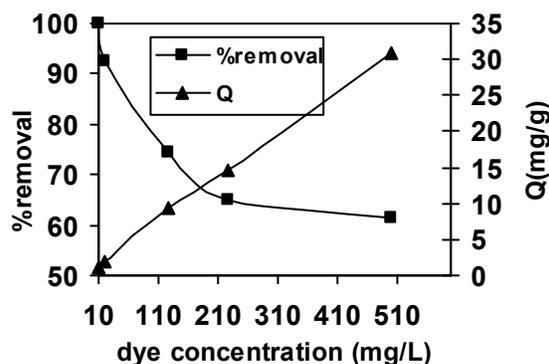


Fig.10. Effect of initial dye concentration on the percentage dye removal and removal capacity

The relationship between removal and initial dye concentration can be modeled using the following equation:

Max. % removal =

$$0.003 * (\text{conc.})^2 - 0.2288 * (\text{conc.}) + 99.53$$

(7)

$$R^2 = 0.9856$$

Where $0 \leq \text{conc.} \leq 500$

Two important physiochemical aspects for the evaluation of the adsorption process as a unit operation are the equilibrium of the adsorption and the kinetics. Equilibrium studies give the capacity of the adsorbent [27]. The equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in solution at a fixed temperature at equilibrium. There are two types of adsorption isotherms: Langmuir adsorption isotherms and Freundlich adsorption isotherms.

Analysis of equilibrium data is important for developing an equation that can be used for design purposes. Classical adsorption models, such as Langmuir and Freundlich models have been extensively used to describe the equilibrium established between the adsorbed dye on the prepared samples and the dye remaining in solution.

The Langmuir adsorption isotherm is often used for adsorption of a solute from a liquid solution. The Langmuir adsorption isotherm is perhaps the best known of all isotherms describing adsorption and is often expressed as:

$$1/q_e = 1/b + 1/abC_e \quad (8)$$

Where q_e is the mass of dye adsorbed per gram adsorbent at equilibrium, C_e is the equilibrium dye solution concentration, mg of dye/L, a is Langmuir

constant, l/mg of dye, b is the monolayer coverage, mg of dye/g of adsorbent.

A plot of $(1/q_e)$ versus $(1/C_e)$ should indicate a straight line of slope $(1/ab)$ and an intercept of $(1/b)$.

The linear Langmuir equation for Methylene Blue on organic kaolin composite was determined to be:

$$1/q_e = 0.7066/C_e + 0.0577 \quad (9)$$

The correlation coefficients R^2 value (0.9904) suggests that the Langmuir isotherm provides a good model of the sorption system. a , and b are equal to 0.0817 liter/mg of Methylene Blue and 17.33 mg of dye/g of adsorbent respectively.

The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_L), which is defined by the following relationship:

$$R_L = 1/(1+a C_e) \quad (10)$$

Calculating the dimensionless equilibrium parameter ($R_L = 0.058$) for Methylene Blue shows favorable adsorption since it is less than 1 and greater than zero [27]. Accordingly it can be concluded that the adsorption of Methylene Blue on organic kaolin composite obeys Langmuir isotherm. A similar result was reported for the adsorption of MB on hydrolyzed Oak sawdust [28].

The Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as:

$$\log q_e = \log K_f + 1/n \log C_e \quad (11)$$

Where (K_f) and (n) are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption. A plot of $(\log q_e)$ versus $(\log C_e)$ gives a straight line of slope $(1/n)$ and an intercept of $(\log K_f)$.

The linear Freundlich equation for methylene blue on organic kaolin composite was determined to be:

$$\log q_e = 0.1614 + 0.5533 \log C_e \quad (12)$$

The correlation coefficients coefficient R^2 value (0.9916) suggests that the Freundlich isotherm provides a good model of the sorption system. The related constants were K_f and n are equal to 1.45 and 1.81 respectively, also n is greater than 1 which indicates good adsorption of methylene blue on organic kaolin composite.

3.2.7. Effect of pH

The effect of pH of the dye solution on the amount of dye adsorbed was studied by varying the initial pH under constant process parameters as shown in Fig. 11. The percentage removal of methylene blue solutions after an adsorption period of 360 min was increased from 76 to 93.4% between pH values 2 to 12. The removal capacity show the same behavior, where it

increased from 1.52 to 1.87 mg/g. The lower adsorption of methylene blue at acidic pH, it could be due to the presence of excess H^+ ions that competed with the dye cation for adsorption sites. As the pH of the system increased ($pH > 8$), the number of positively charged available sites decreased while the number of the negatively charged sites increased. The negatively charged sites favored the adsorption of dye cation due to electrostatic attraction. The final pH of the solution was found to decrease only slightly (by 0.5–0.7 pH units) after adsorption of methylene blue (in cationic form) with the release of H^+ ions from the active site of the adsorbent surface. The results were in agreement with other literature reports [2, 29-30].

The relationship between % removal and pH can be modeled using the following equation:

$$\text{Max. \% Removal} = 1.8358 * (pH) + 73.781 \quad (13)$$

$$R^2 = 0.9186$$

Where: $2 \leq pH \leq 12$

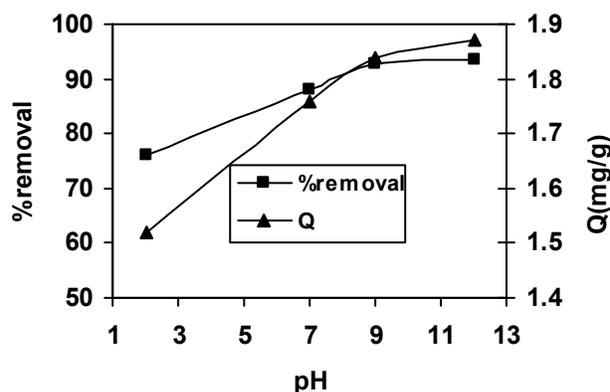


Fig.11. Effect of pH on the percentage dye removal and removal capacity

3.2.8. Effect of Agitation speed

Agitation is an important parameter in sorption phenomena, influencing the distribution of the solute in the bulk solution and the formation of the external boundary film. The effect of stirring speed (in rpm) on the %removal of the original dye concentration was investigated. Fig. 12. illustrates that the % removal seemed to be affected by the agitation speed for values between 0 and 100 rpm, thus confirming that the influence of external diffusion on the sorption kinetic control plays a significant role. In contrast, the small effect of agitation in the range of

100–750 rpm. It is clear that while increasing mixing rate from 750 to 1000 rpm, % removal decreased from 93.3 to nearly 91.1 %. The decrease may be attributed to an increase desorption tendency of dye molecules and/or having similar speed of organic-kaolin composite particles and adsorbate ions (i.e. the formation of a more stable film around the organic-kaolin composite particles). Thus, it can be conducted that the rising of mixing speed to 750 rpm may cause deformation of the stable film and so disappearance of film diffusion control resulted from the organic-kaolin composite particles and adsorbate ions that move at the same speed [31]. The results were in agreement with Batzias F.A., and D.K. Sidiras [32].

The relationship between % removal and rpm can be modeled using the following equation:

$$\text{Max. \% removal} = -1E - 05 * (\text{rpm})^2 + 0.0111 * (\text{rpm}) + 89.905 \quad (14)$$

$$R^2 = 0.871$$

Where: $100 \leq \text{rpm} \leq 1000$

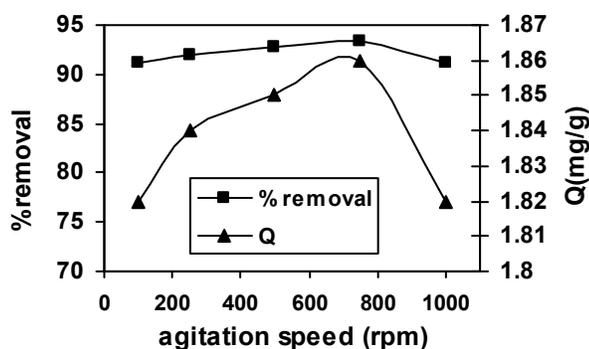


Fig.12. Effect of agitation speed on the percentage dye removal and removal capacity

3.2.9. Effect of Temperature

Temperature has important effects on the adsorption process. As the temperature increased, the rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of the adsorbent particle increased [33]. Changing the temperature will change the equilibrium capacity of the adsorbent for particular adsorbate [33-34].

Fig. 13. depicts effects of different temperatures for methylene blue adsorption on organic-kaolin composite. The % removal by adsorption on organic-kaolin composite increases from 92.7 to 99.2 % by increasing temperature of the solution from 22 to 65 °C, indicating that the process to be endothermic.

The relationship between % removal and temperature can be modeled using the following equation

$$\text{Max. \% removal} = -0.0036 * (\text{temp})^2 + 0.4613 * (\text{temp}) + 84.443 \quad (15)$$

$$R^2 = 0.9889$$

Where: $22 \leq \text{Temp.} \leq 65$

Finally the overall model that can be related to the operating condition such as agitation speed, initial dye concentration, temperature, adsorbent dose and pH of dye solution can be represented by the following equation using regression analysis:

$$\text{Max. \% removal} = 0.176 * \text{rpm} + 0.0752 * \text{conc} + 0.2681 * \text{temp} + 2.855 * \text{pH} + 7.523 * \text{amount of adsorbent} \quad (16)$$

$$R^2 = 0.99$$

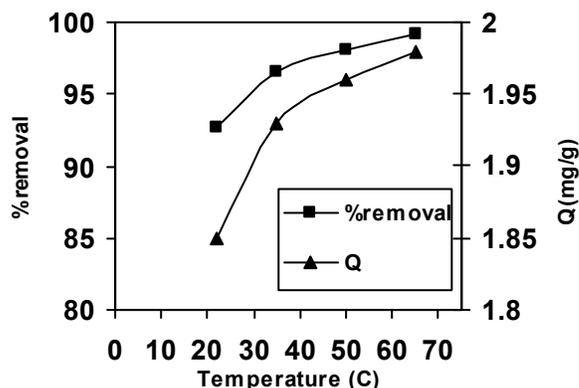


Fig.13. Effect of solution temperature on the percentage dye removal and removal capacity

4. Conclusions

With the presented results and discussions it is clear that Alginate/ polyvinyl alcohol -kaolin composite, can be successfully used as adsorbent for removal of the cationic dye, methylene blue from its aqueous solutions in a stirred tank reactor. Batch studies indicate that Alginate/ polyvinyl alcohol -kaolin composite can adsorb almost 61.6 to 100 % of the methylene blue from its aqueous solutions in the concentration range 500 to 10 mg/L, at 22°C. As the initial ion concentration increased the amount of Methylene Blue adsorbed per gram composite increased. The maximum adsorbed amount of methylene blue was 30.8mg/g organic composite. However, no significant effect was noticed on the percentage dye removal with the variations of both beads diameter and their swelling. Also from this study it was concluded that, the percentage removal of methylene blue increased with increased in the amount of composite, contact time, agitation speed up to 750rpm, initial dye pH, and temperature, which means that an endothermic process took place. Adsorption process was mainly chemisorptions, followed first order kinetics, and the half time was 87.7 min. The kinetic studies indicated that equilibrium of methylene blue adsorption on the composite was reached in 360 minute. Isothermal data of methylene blue sorption on Alginate/ polyvinyl alcohol -kaolin composite can be obeyed both Freundlich and Langmuir isotherms. Numerical correlations that can be used to predict the maximum percentage removal of dye by knowing the operating conditions were developed.

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