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Research Article

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Adsorption studies of Cr(VI) and Mn(II) in solution on a synthesized melamine formaldehyde supported Attapulgite clay

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ABSTRACT

In this study, a new type of composites namely attapulgite-melamine formaldehyde (AMF 5%) was prepared using poly-condensation polymerization of melamine with the formaldehyde in the presence of attapulgite as essential supported material. The prepared composite was used to remove both, Cr^{+6} and Mn^{+2} ions using adsorption process at variable conditions of pH, contact time, ion concentration and temperature. The adsorption characteristics of the new formed composite toward the two metal ions in dilute aqueous solutions were followed spectrophoto-matrically. The sorbed amount of the two metal ions under study appeared to closely follow Freundlich isotherm, with sorption process showing exothermic behavior. The kinetic of the sorption was analyzed using the pseudo- first order and pseudo- second order kinetic models. These studies indicate that attapulgite clay is a valuable support for the simple adsorption of (AMF 5%).

INTRODUCTION

Attapulgite is clay consists of two double chains of the pyroxene-type $(SiO_3)^{-2}$ like amphibole $(Si_4O_{11})_n^{-6n}$ running parallel to the chain axis. Attapulgite units are connected to one another by shared oxygen atoms and the interstices between the chains are filled with water molecules^(1, 2).

Attapulgite has very good colloidal properties such as: specific features in dispersion, high temperature endurance salt and alkali resistance, and also high adsorbing and de-coloring capabilities ⁽³⁾.

The issue of heavy metals such as Cr^{+6} and Mn^{+2} in aquatic systems is of considerable interest because of their cumulative toxicity to aquatic organisms. These problems are increasingly felt by nations as the number of industrial establishments increase rapidly. Industries as well as agricultural and municipal sectors are directly affected by any discharge of these heavy metals into their water sources. A number of methods can be used to remove the heavy metals. Among these chemical precipitations, are membrane filtration, ion exchange, and adsorption ^(3,4). In industries, attaplugite clay, with relatively large surface area and good adsorption capability, is used in the treatment system employing simultaneous adsorption and biodegradation process.

In the present study we evaluated the capacity of a new formed composite resin (AMF 5%) to remove Cr^{+6} and Mn^{+2} . Batch studies are carried out involving process parameters such as the initial ion concentration, solution temperature, pH and contact time.

Equilibrium and kinetic analysis were conducted to understanding sorption process and optimization of various parameters in metal ion recovery.

It was, therefore, through worthwhile to study the ability of attapulgite to support polymers without covalent attachment, taking advantage of its adsorption.

EXPERIMENTAL SECTION

Materials:

The main constituents of the moulding compounds are described in the following:

Melamine-Formaldehyde (MF)

Polymers of melamine (2,4,6-triamino-1,3,5-triazine) with M.wt=126.1 g/mol, (BDH chemicals, England) and formaldehyde (CH₂) M.wt=30.03g/mol, (Fluka. Riedel-DE Haen, Germany) form an important class of amino resins. MF is one of the hardest and stiffest isotropic polymeric systems that exist. It has outstanding scratch resistance and surface gloss. Also, advantageous, are temperature resistance, flammability and environmental characteristics. MF is used, for example, in laminates, moulding compounds, coatings and as adhesives. The unique properties of MF make it an interesting case as a matrix for composites $^{(5, 6)}$.

Attapulgite (A)

Is a purified native Aluminum Magnesium Silicate $[(OH_2)_4 (Mg, Al)_5 (OH)_2 Si_8O_{20}].4H_2O$. it is a light cream or buff colored, very fine powder, free or almost free from gritty particales. It may be used to adsorb some alkaloids, bacteria, odours, toxins, heavy metals and viruses ⁽⁷⁾.

Procedures

1. Attapulgite Processing: Preparation of Clay:

The kaolin clay was supplied in the powder form , (100) gm from the clay was washed with several washing with distilled water, and then activated through adding a mixture of diluted solutions from nitric acid and hydrochloric acid. The mixture was left with a continuous stirring for (72 hrs.) with continuous stirring using a magnetic stirrer to remove all the soluble materials. The clay was washed with excessive amounts of distilled water and then dried in an oven at $(160^{\circ}C)$ for 3hrs., and then cooled down to room temperature and kept in airtight containers. The clay was ground and sieved and using a test sieves.

2. Preparation of Melamine-Formaldehyde Polymer MF:

Melamine-Formaldehyde polymer MF was prepared by adding formaldehyde to the amino groups in melamine by weighting (27.75)g, which equalize (75)ml of formaldehyde (37%) (Fluka, Riedel-DE Haen, Germany), at (pH 8) and by using NaOH (10%) and using pH meter. Aweight of (31.5g) from melamine ((97.5%), BDH Chemicals, England) was added to formaldehyde boiling solution at (100-180°C) with continuous stirring for (30min) until reaction completed and having a solid yield. After that the formed polymer was washed several washings and dried in an oven at (75-100°C), then the (MF) polymer cooled at room temperature and ground to different sizes and kept

in an air tight container ⁽⁸⁾. The partial size of 75 µm was used in all experiments of this study.

3. Preparation of Attapulgite-Melamine-Formaldehyde Composite (AMF 5%):

MF was synthesized via an in additional of formaldehyde to the amino groups in melamine (27.75 g), which equalizes (75ml) from the formaldehyde (37% concentration) after equalizing the pH value to (8) by using NaOH (10%), and then (31.5 g) of melamine was weighted and added to the formaldehyde boiling solution at (80-100)°C with a continuous stirring for (30 min.) until the melamine was completely dissolved. When the reaction was completed, a solid precipitate resulting from the polymerization reaction was filtered and washed with distilled water. The precipitate was then dried in a thermal oven at (75-100)°C. After that the formed polymer was cooled at room temperature and then ground and sieved and kept in well closed containers ⁽¹⁶⁾.

4. Reagents and Instrumentation:

All reagents were of analytical reagent grade. The aqueous stock solutions were prepared as follows:

• Chromium (Cr^{+6}) (1000mgL⁻¹): (3.73)g of Potassium Chromate (K₂CrO₄, BDH Chemicals, England) was dissolved in distilled water and made up to 1000ml. it was stored and used to prepare a dilute solutions by taking a suitable volume from the concentrated solution and diluted with distilled water according to dilution law for measurement purpose.

• Hydrochloric Acid (HCl) (BDH Chemicals, England) (1M) of concentrated (37%), and from that solution, a serial of dolutied solutions were made.

• Sodium hydrochloride (NaOH) (BDH Chemicals, England) (1M): (4g) of NaOH was dissolved in 100ml of distilled water. More dilute working solution of NaOH was prepared as required.

• Manganese Chloride ((98%), BDH Chemicals, England) was used to prepare (1L) of stock solution.

All spectrophotometric measurements were made with (100% conc. VARIAN, USA), double beam in range of (200-900nm) UV-Vis spectrophotometer equipped with 1.0cm quartz cells. Measurements of pH were made with (pHm

84, research pH meter Radiometer, Cobenhagen, Denmark), using a combined glass electrode. The new laboratorysynthesized composite was characterized by FT-IR spectrophotometer using (Shimadzu 8400 FT-IR, Japan) instrument. Also, a thermal laboratory oven with a (GAllen Kamp Vacuum Drying Oven, Dp61 Yamato HITEC, Japan) (25-630)°C. A thermo stated water path shaker was used in all adsorption experiments in type of (BS-11 digital, JEIO TECH, Korea), (20-185)rpm, (0-120)°C. The sieves used to separate particles were (200-mesh) sieve (Test sieves, RetschGmb. Co. KG, Germany) and particle size of both the clay and the new synthesized composite

was of 7 µm.

5. Adsorption Studies:

Solutions of different concentrations for each metal ion were prepared by serial dilutions. Absorbance values of these solutions were measured at the selected λ_{max} value for each metal ion and plotted against the concentration values, and the calibration curves in the concentration range that falls in the region of applicability of Beer-Lambert's law were employed.

6. Equilibrium Studies:

In order to optimize the time that is sufficient for the adsorption process to reach equilibrium at certain temperature and pH, an initially fixed concentration $(5x10^{-4}M)$ of each metal ions solution and (1g) from the new composite were transferred into nine volumetric flasks of (50ml), and the shaking time recording was started.

The concentrations of the metal ion solutions were determined spectrophotometrically at 5, 10, 20, 30, 40, 60, 90, 120 min).

For selecting the optimal pH of adsorption systems (Cr^{+6} -AMF 5%) and (Mn^{+2} -AMF 5%), a fixed concentration of each metal ion solutions in different pH: 2, 3, 4, 5 and 7 was determined. The pH of suspensions at the commencement of the adsorption was measured as well as after filtration at the end of the experiment using pH meter.

In order to observe the dependence of the adsorption process of the (metal ion-AMF 5%) systems on temperature, the adsorption experiments was repeated in the same manner at temperature of 25, 35 and 45 to estimate the basic thermodynamic functions. The temperature of solutions was controlled with a thermostated shaker bath.

7. Adsorption Isotherm:

Solutions of each metal ion (50ml) of known concentrations ((50 ppm for Cr^{+6} ion) and (100ppm for Mn^{+2} ion)) at 25°C and fixed pH value were added to stoppered flasks containing (1g) of (AMF 5%) composite. The flasks were shaken in a thermostatically controlled shaker water bath, till equilibrium is attained.

After the equilibrium time elapsed, the rotation was stopped and the solution was filtered by using double filter paper (Whatman, size 42). The clear supernatants were assayed for metal ion $(Cr^{+6}, and Mn^{+2})$, spectrophotometrically after the appropriate dilution. The adsorbed amount of the metal ion was calculated from the concentration in solutions before and after adsorption according to the equation:

$Q_e = (C_o - C_e).V/W \dots \dots \dots \dots (1)$

Where C_o and C_g are the initial and equilibrium liquid-phase concentrations of metal ion solutions (mg/L), respectively, Q_g is the equilibrium metal ion concentration are adsorbent (mol/g), V is the volume of metal ion solution (L), and W is the mass of (AMF 5%) composite sample used (g).

The efficiency of (Cr^{+6}) and (Mn^{+2}) removal was calculated according to equation (2):

Removal Efficiency (P) =
$$\frac{C_o - C_s}{C_o} 100 \dots \dots \dots (2)$$

RESULTS AND DISCUSSION

Characterization of Adsorbent:

FTIR Spectral characterization of AMF5% at 190 $^{\circ}$ shows several distinct peaks.as shown in Figure 1, the band of N-H stretching appeared in the region 3416 cm⁻¹ along with other peaks in the region (1476cm⁻¹)and (1557 cm⁻¹) of -NH groups (N-H bend).There is a band at 1625 cm⁻¹ for C=N. The range of bands in the region 1353-1013 cm⁻¹ due to C-N stretching .And there happen a creation of new strong peak at 2360 cm⁻¹ that corresponds to the stretching vibration of bridged CH₂ group which gave a strong evidence for methylene bridge formation. And also there is a decrease in the intensity of the peaks that corresponds to the methylene bending vibrations from 1565 cm⁻¹ and 1492 cm⁻¹ to 1557 cm⁻¹ and 1476 cm⁻¹ respectively on comparison with spectrum of MF This decrease in intensity may possibly due to the extent of crosslinking. Bending vibration of triazine ring was found at 813 cm⁻¹. For comparison, FTIR spectrum of MF is also shown in Figure 2.However, all the peaks of (AMF 5%) composite show similar characteristics compared to pure MF polymer even if the clay loading is increased. This shows that there are weak bonds between clay and polymer matrix due to agglomeration or lower dispersion of clay. From this FTIR interpretation, it was confirmed that the melamine has reacted and cross linked during the thermal curing process.



Adsorption Studies: pH Dependent:

The adsorption of the metal ions Cr^{+6} and Mn^{+2} on the surface of (AMF 5%) composite due to the electrostatic attraction between the negative ions under study as it is present in solution as $(Cr_2O_7^{-2})$ and (MnO_2^{-2}) respectively with the positive charges of the functional Amino groups which are presented on the adsorbent surface as a protonated formula and this result has been approved with several researchers ^(10, 11), structure 1.



Structure 1: Suggested Mechanism for the Adsorption of Cr⁺⁶ and Mn⁺² on (AMF 5%) Composite

The adsorption characteristics of the two metal ions (Cr^{+6} and Mn^{+2}) by (AMF 5%) composite were studied at varying pH ranging from 2 to 7. The profile (Figure 3) concerning pH shows that in the observed pH range the adsorption capacity was much pronounced at lower pH 2, while as the pH increases adsorption decrease.

As such all subsequent studies were performed at pH, which is the optimum value for the adsorption.



Figure 3: Effect of pH on Uptake of a) (Cr⁺⁶) and b) (Mn⁺²) by AMF 5%, 25°C

Temperature Dependent:

The adsorption of (Cr^{+6}) was also recorded in the concentration range from (10-50ppm; pH of 2) and for (Mn^{+2}) was (30-150 ppm; pH of 3) at temperatures 25, 35 and 45°C (Figure 4) and (Figure 5).

These figures indicate that the adsorption of these two metal ions by (AMF 5%) increases with increasing in temperature, indicating thereby the process to be endothermic in nature. It is also observed that the initial removal of these ions is fast and with the rising in concentration the percentage uptake gradually decreases.

Variable temperature study will help in evaluating the basic thermodynamic functions (ΔH° , ΔG° , ΔS°) of the adsorption processes. And these parameters were evaluated to confirm the adsorption nature of the present study. Based on the following literature equations ⁽⁹⁾:

$$\Delta G^{o} = -RT \ Ink \qquad \dots \dots \dots \dots (3)$$

$$InX_{m} = \frac{\Delta H^{o}}{RT} + constant \qquad \dots \dots \dots \dots (4)$$

$$\Delta S^{o} = \Delta H^{o} - \Delta G^{o}/T \qquad \dots \dots \dots \dots (5)$$

Where R is the ideal gas constant (8.314 J/mol.k), T is the absolute temperature, k is the equilibrium constant for the adsorption process at each temperature, X_m is the maximum uptake of adsorption at certain value of equilibrium concentration C_o that was fixed for all temperatures of study[12].

Evaluated thermodynamic parameters are presented in Table (1). Negative values of ΔG° establish the feasibility of adsorption process. Furthermore, the decrease in the values of ΔG° with the increasing temperature indicates the spontaneity of the process at higher temperatures.

Thermodynamic quantities of (Cr^{+6} -AMF 5%) and (Mn^{+2} -AMF 5%) systems exhibited endothermic heat of adsorption, while the entropy is positive. This can be explained by the hydrophobic bonding with the orderly iceberg structure of water molecules originally surrounding both the metal ions and the active sites being disrupted, and showing increase in randomness.

Table 1: Thermodynamic Parameters for the Adsorption of Metal Ions on (AFM 5%)

Metal Ions	∆H [©] KJ.Mol ⁻¹	ΔG^{o} KJ.Mol ⁻¹	∆ S⁰ KJ.Mol ⁻¹
Cr ⁺⁶	+7.823	-1.152	+0.030
Mn ⁺²	+28.843	-3.590	+0.108



Figure 4: The effect of temperature on the adsorption of $(Cr^{\scriptscriptstyle +6})$ on (AMF 5%)



Figure 5: The effect of temperature on the adsorption of (Mn⁺²) on (AMF 5%)

Adsorption Isotherm:

Isotherms are the equilibrium relation between the concentration of the adsorbate on the solid phase and in the liquid phase. Two isotherms, as described below in equations (6 and 7) (13, 14), were used to fit the experimental data obtained at $(25^{\circ}C)$ and at pH=2.

Freundlich equation $logQ_e = logK_f + \frac{1}{n}logC_e \dots \dots \dots \dots (6)$ Langmuir equation $\frac{C_e}{Q_e} = \frac{1}{Q_mK_L} + \frac{C_e}{Q_m} \dots \dots \dots \dots (7)$

Where Q_{e} is the quantity adsorbed per gram of adsorbent (mg/g.), C_{e} is the equilibrium adsorbate concentration in solution (mg/L), Q_{m} is the monolayer capacity of the adsorbate (mol.g⁻¹), K_{f} parameter is relative to the adsorption capacity and n is a measure of adsorption intensity; a favorable adsorption correspond to a value of 1 < n < 10.

The Langmuir constant, K_L is related to energy of the adsorption. The estimated model parameters with correlation coefficient (R^2) for the different models are shown in, Table (2).



Figure 6: Freundlich isotherm plots for adsorption of (Cr⁺⁶) and (Mn⁺²) onto (AMF 5%) at 25°C and pH 2



Figure 7: Langmuir isotherm plots for adsorption of (Cr⁺⁶) and (Mn⁺²) onto (AMF 5%) at 25°C and pH 2

Table 2: Estimated isotherm parameters of (Cr⁺⁶) and (Mn⁺²) adsorption Ions at Fixed pH and Temperature on (AMF 5%)

	Isotherm models				
Metal ions	Freundlich isotherm			Langmuir	
	\mathbf{R}^2	K _f	n	\mathbf{R}^2	KL
Cr ⁺⁶	0.928	0.291	1.362	0.385	0.032
Mn ⁺²	0.831	1.073	1.412	0.708	0.0364

The constant (n) in Freundlich equation indicates affinity or interaction energy between the adsorbent and adsorbate. The value of 1/n also indicates the preference of the adsorption process. If 1/n<1, the rate of change of concentration of adsorbed substance is smaller than the rate of change in solution. Such an adsorption is favorable ^(15, 16).

Here the applicability of the two parameters isotherm models for the present data follows the order: Freundlich (Figure 6)>Langmuir (Figure 7)

Effect of Contact Time:

Effect of contact time on removal of Cr^{+6} and Mn^{+2} from two solutions of different initial concentrations on (AMF 5%) composite is showed in Figure (8). It was found that Cr^{+6} and Mn^{+2} adsorption percentage increased with increasing contact time. Above 50% of these two heavy metals (Cr^{+6} and Mn^{+2}) adsorption occurred in the first 15 to 20mints., and thereafter the rate of adsorption of the adsorbate species onto the adsorbent was found to be slow.

However, the contact time required for maximum Cr^{+6} adsorption onto (AMF 5%) was found to be nearly 80 mints., while (60 mints.) were enough to reach the equilibrium for the the adsorption process of (Mn⁺²-AMF 5%) adsorption system, which is independent of both sorbate concentration

Our time dependent experimental adsorption data (Figure 8) are used for kinetic modeling to model equation used for fitting the data are:

1. Lagergren equation.

2. 2nd order equation



The two heavy metals under study (Cr^{+6} and Mn^{+2})sorption data of (AMF 5%) at 25°C and a fixed pH value are tested for kinetic modelling by linear regression plots. The estimated model and the related statistic parametersare reported in Figure (9) and Table (3). Based on linear regression (R^2 >0.90) values. The results clearly indicate that the 2nd order equation model progressively fits the two adsorption systems under study.

The two metal ions under study are tested for kinetic modeling by liner regression plots. The estimated model and the related statistic parameters are reported in Table (3). Based on linear regression ($R^2>0.9$) values, the results clearly indicate that the 2^{nd} order equation model progressively fits the two adsorption systems under study.



Figure 9: The applicability of a) the lagergrem equation, and b) pseudo second order of Cr⁺⁶ and Mn⁺² sorption on (AMF 5%) composite surface

Table 3: Kinetic Models and Other Statistical Parameters at Fixed Temperature and pH

Kinotia Madal	Domomotors	Metal Ions	
Kinetic Woder	rarameters	Cr ⁺⁶	Mn ⁺²
Lagergren equation	\mathbb{R}^2	0.963	0.920
$log(q_e - q) = log(q_e - \left(\frac{K_1}{2.303}\right)t$	Kı	0.027	0.129
2 nd order equation	\mathbb{R}^2	0.998	0.999
$1/C-1/C_0 = K_2 t$	K_2	0.006	0.005

Comparison study was carried on between natural attapulgite clay only and the new prepared composite resin.

In order to evaluate the additional process of attapulgite to melamine formaldehyde to form the attapulgite-melamine formaldehyde (AMF 5%) composite, a fixed initial concentration from each metal ion (in a separate way) was added to (20 g) of adsorbent at a fixed temperature, pH and fixed equilibrium time needed for each metal ion adsorption. The results are given in Table (4). As can be seen the new synthesized (AMF 5%) composite surface appeared of highest activity in the adsorption form solution for the two heavy metals under study than that for the attapulgite

clay only. In addition, the order of adsorption of the two metal ions on the two different adsorbent are in the order of:

$Mn^{+2} > Cr^{+6}$

Table 4: Percent removal (R%) results removal of Cr^{+6} and Mn^{+2} from aqueous solution onto natural attapulgite clay alone and (AMF 5%) composite resin

Metal ions	Co (ppm) of metal ions	Ce (ppm) of metal ions	R% from the natural kaolin clayalone	Ce (ppm) of metal ions	R% from the new synthesized composite
Cr ⁺⁶	50	44.116	5.884	18.990	62.020
Mn ⁺²	100	89.436	10.564	1.850	98.146

CONCLUSION

- Optimum pH for heist Cr^{+6} sorption is $\cong 2.0$ while for Mn^{+2} is $\cong 3$.

- The determination free energy change (ΔG^0) indicate the spontaneous and endothermic nature of the adsorption process.

- The adsorption isotherms of (Cr^{+6}) and (Mn^{+2}) on (AMF 5%) composite surface obeyed Freundlich isotherm according to the R^2 values, known as goodness of fit criterion.

- At constant temperature, the adsorption of the two metal ions on the (AMF 5%) composite surface has increased as the pH pf solution decreased.

- Kinetic experiments were conducted in order to determine the equilibrium contact time and use it in the isotherm experiments. This time was found to be (90 min) in the case of aqueous solution of Cr^{+6} and (60 min) in the case of the Mn^{+2} .

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