Preparation and Characterization of Kaolin/Melamine Formaldehyde Composite for the Removal of Some Heavy Metals from Aqueous Solution

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ABSTRACT- Kaolin melamine formaldehyde (KMF 5%) composite was synthesized in laboratory and its systematic Cr(VI) and Mn(II) adsorption behaviour was studied by means of batch experiments. With the aim to evaluate the efficiency of the new resin to remove the two metal ions studies on the variable parameters viz the effect of concentration of metal ions, temperature, pH and time of contact … etc are here reported. The equilibrium sorption isotherms have been analyzed by the Langmuir and Freundlich models. The Freundlich isotherms have the highest correlation coefficients. The results indicate that (KMF 5%) could be successfully employed as a good and useful adsorbent in wastewater treatment for the removal of heavy metal ions.

KEY WORDS-Adsorption from solution, melamine from aldehyde, heavy metal ions Cr\(^{\text{VI}}\), Mn\(^{\text{II}}\), Adsorption isotherms, Adsorption kinetics

INTRODUCTION

Polymers of melamine and formaldehyde form an important class of amino resins, which have been commercially used for more than 60 years. Melamine formaldehyde polymer MF is one of the hardest and stiffest isotropic polymeric systems that exist. A flexural modulus as high as 9Gpa has been reported neat MF\(^1,2\). It has outstanding search resistance and surface gloss. Also, advantages, temperature resistance, flammability and environmental characteristics.

MF is used in laminates, molding compounds, coating and as adhesives. The unique properties of MF make it an interesting case as a matrix for composites.

Kaolin is a clay mineral, part of the group of industrial mineral with the chemical composition Al\(_2\)Si\(_2\)O\(_5\)(OH)\(_4\). It is a layered silicate mineral, with one tetrahedral sheet linked through oxygen atoms to one octahedralsheet of alumina octahedral. The kaolinitic type clay minerals have relatively low cation exchange capacities, while much of the surface charge can be attributed to the amphoteric dissociation on the particle\(^3,4\).

Environmental contamination by metals is a widespread problem, with sources of pollution arising from industrial activities. Many toxic metal ions that are highly toxic for human being and other organisms have been discharged into the environment as industrial wastes, causing serious soil and water pollution\(^5,6\). Chromium and Manganese exist in the aqueous environment mainly in (VI) and (II) states for Cr and Mn respectively. Cr(VI) is a powerful epithelial irritant and confirmed human carcinogen\(^6\). Additionally, Cr(VI) and Mn(II) are toxic to many plants, aquatic animals and bacteria. Various physicochemical and biological techniques can be employed to remove heavy metals from wastewater. They include the membrane filtration coagulation flocculation\(^7,8\), adsorption\(^9\), ion exchange\(^10\), advanced oxidation (chlorination, ozonation)\(^11\),
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chemical reduction\(^\text{(12)}\), etc. In comparison with other techniques adsorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substance. This technique uses a large number of suitable sorbents as activated carbon\(^\text{(13)}\), polymeric resins\(^\text{(14)}\), clays\(^\text{(15)}\).

There are two forms of manganese in the environment. Inorganic manganese compounds are used in the production of steel, batteries and dietary supplements. Manganese compounds can be present as dust particles in the air and dissolved in ground water or drinking water\(^\text{(16)}\).

The primary targets of Mn toxicity are the brain and central nervous system. Mn has been shown to be deposited in certain regions of brain, and exposure to higher concentration in occupational studies was associated with permanent damage, with symptoms of impaired neurological and neuromuscular control. Muscle stiffness, lack of coordination, tremors, difficulties with breathing or swallowing and other neuromuscular problems\(^\text{(16)}\).

This study reports and for the first time on line the synthesis and characterization of a new composite (KMF 5%), which has a special properties differs from the original materials properties that made from through the development of MF polymer characteristic in the presence of kaolin as essential supported material. Batch studies are carried out involving process parameters such as the initial metal ions concentration, solution temperature, pH effect and contact time. Equilibrium and kinetic analysis were conducted to understand sorption process and optimization of various parameters in metal ions recovery.

**EXPERIMENTAL**

1. **Reagent:**
   Manganese Chloride (98%) and Potassium Chromate (99%) was used for preparation of (1L) of stock Mn(II) and Cr(VI) solutions (1000 mg/L) in distilled water respectively (in separate way). For pH adjustment throughout the experiment, hydrochloric acid (37%) and/or sodium hydroxide (96%) solutions were used as necessary. All these reagents were from (BDH Chemicals, England). Nitric acid (65%) was used in the preparation of the clay and it was from (BDH Chemicals, England).

2. **Instrumentation:**
   Fourier Transform Infrared Spectrophotometer (FTIR Shimadzu 8400, Japan) was used to determine the functional groups in (KMF 5%) composite using KBr pellets. The pellets were analyzed with FTIR spectrophotometer in transmittance (%) mode in the range 4000-400 cm\(^{-1}\). X-ray Diffraction pattern was measured (XRD6000 Shimadzu, Japan X-ray diffractometer).

   The concentration of metal ion solutions were determined spectrophotometrically in range of (900-200nm) by using (100conc. VARIAN, USA) double beam spectrophotometer. The pH value of the solutions were determined with (pHm 84, Research pH meter Radiometer, Copenhagen, Denmark). Thermostatic Waterpath shaker (BS.11 digital, JEIO TECH, Korea, (20-185 rpm) was used in batch adsorption experiments.

   A thermal laboratory oven (Gallen Kamp Vacuum Drying Oven, DP6T Yamato HITEC, Japan (25-360°C)) was used in this study. The new formed composite have been ground and sieved (Electrical sieve, RetsohGmb and Co-KG, German) and the partical size of (75 µm) was obtained.

3. **Materials:**
   Melamine (2,4,6-triamino-1,3,5-triazine) of a molecular weight equal to (126.1) g/mol and has a purity of (97%) was from (BDH Chemicals England). Formaldehyde (CH\(_2\)O) has a molecular weight equal to (30.03) g/mol was from (Fluka Riedel-DE Hean, Germany). The natural kaolin is from (Dwaikhla) opened mine (North of Rutba) in the western desert. The main chemical components of kaolin are the following:

   \[\text{SiO}_2: 54.68\%, \text{Al}_2\text{O}_3: 30.19\%, \text{Fe}_2\text{O}_3: 1.02\%, \text{TiO}_2: 1\%.\]
4. Preparation of Clay:
The kaolin clay was supplied in the powder form, (100) gm from the clay was washed several washings with distilled water, and then activated through adding a mixture from 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°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.

5. Synthesis of Melamine-Formaldehyde Polymer MF:
(MF) polymer was synthesized via anlinadditional 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 react ion 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.

6. Preparation of (KMF 5%) Composite:
A weight of (2.8 g) from the purified activated kao lin clay was mixed well with (25.2g) from the melamine and mixture formed was added to (60ml) of formalydesolution at (pH 8) with a continuous heating and stirring till the composite was formed. The resulting composite was cooled at room temperature and the ground and sieved and a practical size (75 μm) was obtained. The sample was kept in a well closed containerand to be used in the batch adsorption experiments of this work. The prepared composite was identified by using FTIR, DSC and X-ray diffraction spectrophotometries.

7. Calibration Curves:
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. The calibration curves in the concentration range that falls in the region of applicability of Beer-Lamber’s law were employed.

8. Determination of the Adsorption Equilibrium Time and Adsorption Isotherm:
Effect of contact time was determined by the “limited bath” technique. A (0.2 g) sample of composite was added to 20 ml volume metal ion solutions, with initial metal ion concentration (10-50g/L) for Cr^{6+} and (30-150g/L) for Mn^{2+}, under stirring. The temperature of solution was held constant at (25°C) with a thermostatic bath. After various time intervals (10-120mints), volume of (1ml) supernatant was taken for spectrophotomet-rically measurements of metal ion content, and it was found that the required time for Cr^{6+} adsorption system was 90 min., while for the Mn^{2+} system was 60 min.

9. Adsorption Isotherm:
Solutions of each metal ion (20 ml) of well-known concentrations (10-50) ppm for Cr^{6+} and (30-150) ppm for Mn^{2+} in aqueous solutions were added to stoppered flasks containing (0.2 g) of composite. The flasks were shaken in a thermostatically controlled water bath at a speed of 60 cycle/min at (25°C) till equilibrium is attained. After the equilibrium time elapsed (90 min. for Cr^{6+} adsorption system), and (60 min. for Mn^{2+} adsorption system), the suspensions were filtered using double filter paper (42 whatman). The clear supernatants were assayed for metal ions, after
Comparing the experimental data with the calibration curve. Equilibrium concentrations were obtained by appropriate dilution, spectrophotometrically. The adsorbed amounts at each metal ion were calculated according to the equation (1)\(^{(18)}\).

\[ Q_e = \frac{(C_o - C_f)}{m} V \]  

(1)

Where \( Q_e \) is the equilibrium metal ion concentration on adsorbent surface (mol g\(^{-1}\)), \( C_o \) and \( C_f \) are the initial and equilibrium liquied-phase concentrations (mg/l), respectively, \( V \) is the volume of solution (L), and \( m \) is the mass of surface sample used (g).

The efficiency of metal ions removal (p) was calculated by equation (2).

\[ \text{Removal efficiency} (p) = \frac{C_o - C_f}{C_o} \times 100 \]  

(2)

10. Effect of Temperature:

Adsorption experiment was repeated in the same manner at temperatures of 25, 35 and 45 °C to estimate the basic thermodynamic functions.

11. Effect of pH:

Adsorption experiment was carried out as a function at pH using a fixed concentration of the metal ion in different pH, ranging from 2 to 7. The pH at the suspensions at the commentement of the adsorption was measured as well as after filtration at the end of the experiment using pH-meter.

RESULTS AND DISCUSSION

The results and discussion in this paper were organized as follows: Section I contains the diagnostic and spectroscopic studies of the (KMF 5%) composite. In Section II we briefly the chromatographic application for the new formed (KMF 5%) composite.

Section I

FT-IR Spectral characterization of KMF shows several distinct peaks, as shown in Figures (1) and (2), the band of N-H stretching appeared in the region 3416 cm\(^{-1}\) along with other peaks in the region (1476, and 1557) cm\(^{-1}\) of –NH groups (N-H band). There is a band at 1625 cm\(^{-1}\) for C=\( \equiv \)N. the range of bands in the region 1353-1013 cm\(^{-1}\) due to C-N stretching strong peak at 2360 cm\(^{-1}\) that corresponds to the stretching vibration of bridged CH\(_2\) group, which gave a strong evidence for methylene bridge formation. The methylene bending vibrations from 1565 cm\(^{-1}\) and 1492 to 1557 cm\(^{-1}\) and 1476 cm\(^{-1}\) respectively due to the extent of crosslinking. Bending vibration of triazine ring was fond at 813 cm\(^{-1}\).

XRD spectra of kaolin and KMF composite are presented in Figures (3) and (4), the crystalline peak of kaolin at \( 2\theta = 26.682, 36.580 \), and 20.902 are also found in kaolin composite with very small shifting in \( 2\theta \) this may be due to binding of kaolin with resin this indicated that there was small marked change in the peak structure of their composite formation and confirmed that the crystal structure of kaolin is retained in composite.
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Section II

A serial experiments have been made to evaluate the best conditions for the removal Cr(VI) and Mn(II) from the prepared solutions. These ions were chosen because of their presence in low concentration in waste water that could be removed by adsorption process (19, 20).

The adsorption of the metal ions Cr$^{6+}$ and Mn$^{2+}$ on the surface of (KMF 5%) composite due to the electrostatic attraction between the negative ions under study as it is present in solution as (Cr$_2$O$_7^{2-}$) 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 (21, 22), structure 1.

Structure 1: Suggested Mechanism for the Adsorption of Cr$^{6+}$ and Mn$^{2+}$ on (KMF 5%) Composite Surface

Isotherm Analysis

The purpose of the adsorption isotherms is to relate the adsorbent concentration in the bulk and the adsorbed amount at the interface (23). The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used to design process (24). Several isotherm equations are available. Two of them have been selected in this study, namely Langmuir and Freundlich equation isotherms (25-26).

The Langmuir equation is given by:

$$
\frac{C}{Q} = \frac{1}{Q_mk} + \frac{C}{Q_m}
$$

where:
- $C$ is the concentration of the adsorbate in the bulk phase (M)
- $Q$ is the amount of adsorbate adsorbed on the adsorbent (M/g)
- $Q_m$ is the maximum amount of adsorbate that can be adsorbed (M/g)
- $k$ is the Langmuir constant (M/L)

This equation describes the adsorption process at monolayer coverage and assumes that the adsorption sites are homogeneous and of equal energy.
Freundlich equation:

\[ q_e = \frac{1}{n} K_f + \frac{1}{n} q_m C_e \quad \ldots \ldots \ldots (4) \]

Where \( C_e \) is the equilibrium concentration of the adsorbate in solution (mg l\(^{-1}\)), \( (Q_e) \) is the amount of adsorbate which adsorbed per unit of sorbent (mg g\(^{-1}\)), \( (Q_m) \) is the monolayer capacity of the adsorbate (mol g\(^{-1}\)) and \( k \) is the adsorption constant (L mol\(^{-1}\)). A value of \((1/n)\) below one indicates a normal Langmuir isotherm, while \((1/n)\) above one is indicative for a cooperative sorption \((27)\). In order to decide the isotherm type, which best fits the sorption experimental data, we plotted \((C_e/Q_e)\) versus \((C_e)\) for Langmuir equation to get straight line with a slope \((1/Q_m)\) and intercept \((1/Q_mk)\). If equation (4) applies, a plot of \((l_n Q_e)\) against \((l_n C_e)\) will give a straight line of slope \((1/n)\) and intercept \(l m (K_f)\). The best fit isotherm parameters are summarized in Table (1). The isotherm data were calculated from the least square method and the related correlation coefficients \((R \text{ values})\) are given in the same table.

As seen from Figure (5), Table (1), the Freundlich equation represents the adsorption process very well; the \((R \text{ values})\) were almost higher than \((0.95)\), indicating a very good mathematical fit.

![Figure 5: Linear Forms of: a) Freundlich Isotherm, b) Langmuir (KMf 5\%)
Composite](image)
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Table 1: Best Fit Isotherm Parameters for Adsorption of Cr(VI) and Mn(II) Aqueous Solutions on (KMF %) Composite Surface

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temp. °C</th>
<th>pH</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ce/Qm</td>
<td>l/Qmk</td>
<td>$R^2$</td>
<td>l/n</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>25</td>
<td>2</td>
<td>0.126</td>
<td>3.277</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>25</td>
<td>3</td>
<td>0.091</td>
<td>7.034</td>
</tr>
</tbody>
</table>

Effect of Temperature and Thermodynamic Parameters

The adsorption isotherms at different temperatures are shown in Figure (6). It is found that the adsorption capacity of Cr(VI) and Mn(II) on (KMF 5%) composite surface increases with decreasing temperature, showing the exothermic nature of the process.

This result agrees with general principles of the adsorption process\(^{[28]}\). Variable temperatures will help evaluating the basic thermodynamical functions ($\Delta H$, $\Delta S$, $\Delta G$) of the adsorption process based on the following literature available equations (Eq 5-7).

\[
\Delta G = -RT \ln K \quad \ldots \ldots \ldots (5)
\]

\[
l_nX_m = \frac{-\Delta H}{RT} + \text{Constant} \quad \ldots \ldots \ldots (6)
\]

\[
\Delta G = \Delta H - T\Delta S \quad \ldots \ldots \ldots (7)
\]

($X_m$) is the maximum uptake of adsorption at a certain value of equilibrium concentration ($C_e$) that was fixed for all temperatures of study\(^{[29]}\), (R) is the gas constant, (T) is the absolute temperature and (K) is the equilibrium constant for the adsorption at a certain value of equilibrium\(^{[30]}\).

The basic thermodynamic quantities of adsorption of Cr\(^{6+}\) and Mn\(^{2+}\) on the (KMF 5%) composite surface were estimated through calculating $X_m$ values at different temperatures. Figure (7) demonstrate these calculations.

Table (2) shows the basic thermodynamic functions of the two metal ions under study on the (KMF 5%) surface. The process of adsorption appeared exothermic, this could be interpreted as a result of weakening of attractive forces between the adsorbent and the solid surface with increasing temperature\(^{[31]}\). The exothermality for the adsorption of the two metal ions-(KMF 5%) system was in conjunction with a decrease in entropy, and this result could be explained through the fact that ($\Delta S$) of the ordered constrained adsorbed layer is always less than dissolved solutes one \(^{[31]}\). The change in the free energy ($\Delta G$) for both adsorption systems possesses negative values indicating a spontaneous adsorption process.

Figure 6: The Effect of Temperature on the Adsorption of: a) (Cr(VI)), and b) (Mn(II)) on (KMF 5%)
Table 2: Calculated Thermodynamic Parameters of Metal Ions Adsorption on (KMF 5%)

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>$\Delta H$ KJ.mol$^{-1}$</th>
<th>$\Delta G$ KJ.mol$^{-1}$</th>
<th>$\Delta S$ J.mol$^{-1}$.K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI)</td>
<td>-17.140</td>
<td>-2.331</td>
<td>-49.69</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>-18.373</td>
<td>-2.051</td>
<td>-54.77</td>
</tr>
</tbody>
</table>

Figure 7: Plot of $\ln K$ against Reciprocal Absolute Temperature for Adsorption of Cr$^{6+}$ and Mn$^{2+}$ on the (KMF 5%) Composite Surface

Effect of Contact Times and Kinetic Studies:

Percent removal of the examined metal ions by (KMF 5%) composite as a function of contact time are shown in Figure (8). Under the conditions of the experiments, different shaking times (ranging from 10 to 120 mints.) were studied, the (Cr-KMF 5%) system approached equilibrium within (90 mints.) of contact time, while it reached equilibrium within (60 mints.) of shaking time for (Mn-KMF 5%). The increasing of initial metal ions concentrations has a favorable effect on the rate of adsorption by increasing of concentration gradient between the solution and porous sorbent.

The Kinetic of metal ions (Cr(VI) and Mn(II)) sorption onto (KMF 5%) was investigated using two different models: the Pseudo- first order and Pseudo- second order kinetics.

The Pseudo-first order Lagergeren model, traditionally used for describing sorption kinetics, is generally expressed by equation (8).

\[
\text{Lagergeren equatio: } \log(q_0 - q_t) = \log q_0 - K_1 t \quad \ldots \ldots \ldots (8)
\]

Where $K_1$ (g/g.mn) is the Lagergeren constant of the first order sorption evaluated from the slope of the plot $\log (q_0 - q_t)$ versus $t$ \(^{32,33}\). While the Pseudo- second order model is described by equation (9), where $K_2$ is the rate constant of second order sorption (g/mg.min) and $K_2 = \frac{q_0}{h}$ is the initial sorption rate (mg/g.min) \(^{34}\). A straight line could be obtained by plotting $\frac{t}{q_t}$ versus $t$, and $q_t$, $K_2$, and $h$ can be calculated, as follows:

\[
\frac{t}{q_t} = \frac{1}{K_2 q_0^2} + \frac{t}{q_0} \quad \ldots \ldots \ldots (9)
\]
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The experimental kinetic data are adjusted according to the indicated models, Figure (8), and the coefficients of correlation as well as the kinetic parameters of metal ions on composite surface are given in Table (4).

![Figure 8: Effect of Shaking Time on the Adsorption of Cr(VI) and Mn(II)](image)

**Table 3: The Kinetics Parameters of Adsorption Process of Cr(VI) and Mn(II) onto (KMF 5%)**

<table>
<thead>
<tr>
<th>Co of Metal Ion (mg/l)</th>
<th>t_{1/2} (min)</th>
<th>Lagergren kinetic model</th>
<th>Pseudo-second kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K_1 (mg/g.min)</td>
<td>R^2</td>
<td>K_2 (g/mg.min)</td>
</tr>
<tr>
<td>Cr(VI) 50</td>
<td>31.357</td>
<td>0.0221</td>
<td>0.980</td>
</tr>
<tr>
<td>Mn(II) 100</td>
<td>16.618</td>
<td>0.0417</td>
<td>0.978</td>
</tr>
</tbody>
</table>

The results shown in Table (3) indicate that the second order equation model provided best correlation with experimental results; this fact indicates that the adsorption of both two metal ions on composite surface follows the Pseudo-second order kinetic model.

**Effect of pH:**

The results of the two metal ions adsorption on the (KMF 5%) composite surface with increasing pH from 2 to 7 are shown in Figure (10), and Table (4). The amount of Cr(VI) and Mn(II) adsorption on the surface under study was found to decrease as the pH value of adsorption.
solution increased. This result may be related to the chemical nature of the (KMF 5%) surface at different pH values. The attraction between the composite surface and the metal ions at low pH values may be specific and stronger than the attraction between solvent-solute leading to an increase in the quantity adsorbed \(^{(35)}\).

Table (4) shows the data concerning the amount of the removal efficiencies (P) of the two metal ions under study according to equation (2) on the (KMF 5%) composite at different pH values.

Table 4: Removal Efficiency Values of Cr(VI) and Mn(II) at 25°C for Different pH Values

<table>
<thead>
<tr>
<th>pH</th>
<th>Cr(VI) %P</th>
<th>Mn(II) %P</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>58.22</td>
<td>78.22</td>
</tr>
<tr>
<td>3</td>
<td>66.35</td>
<td>47.40</td>
</tr>
<tr>
<td>4</td>
<td>39.52</td>
<td>30.89</td>
</tr>
<tr>
<td>5</td>
<td>30.57</td>
<td>13.07</td>
</tr>
<tr>
<td>7</td>
<td>16.49</td>
<td>8.72</td>
</tr>
</tbody>
</table>

Comparison Study between Natural Kaolin Uptake Clay and the Synthesized Composite

In order to evaluate the additional process of kaolin to melamine formaldehyde to form the kaolin-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 kaolin clay only. In addition, the order of adsorption of the two metal ions on the two different adsorbent are in the order of:

\[
\text{Mn}^{2+} > \text{Cr}^{6+}
\]

Table 5: Percent Removal (R%) Results Related to Cr(VI) and Mn(II) from Aqueous Solution onto Natural Kaolin Clay and (KMF 5%) Composite Resin

<table>
<thead>
<tr>
<th>Co (ppm) of metal ions</th>
<th>Ce (ppm) of metal ions</th>
<th>R% from the natural kaolin clay alone</th>
<th>Ce (ppm) of metal ions</th>
<th>R% from the synthesized composite (KMF 5%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(VI)50</td>
<td>43.830</td>
<td>6.16</td>
<td>19.392</td>
<td>64.20</td>
</tr>
<tr>
<td>Mn(II)100</td>
<td>74.302</td>
<td>25.70</td>
<td>21.771</td>
<td>78.22</td>
</tr>
</tbody>
</table>
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As shown from Table (5), the new synthesized (KMF 5%) composite surface appeared of highest activity in the adsorption from solution of heavy metal ions than that for the kaolin clay. In addition, the order of adsorption of heavy metal ions on the two different adsorbent are in the order of Mn(II)>Cr(VI).

Separation of Cr(VI), Cr(III), and MnO4- with Mn²⁺ Mixtures:
The prepared composite was used to remove and separate both of Cr(VI) and MnO4- from Cr(III) and Mn(II) ions, respectively, it will be of great importance to study the competition of surface binding sites among various anions.

The adsorption of mixtures of Cr(VI) with Cr(III) and MnO4- with Mn(II) mixtures ions was studied at the (KMF) composite, when 1g of KMF composite were mixed with a solution of mixture ions of Cr(VI) with Cr(III) and MnO4- with Mn(II) mixtures ions respectively under optimized conditions. The pH was adjusted at pH 2.0 and the suspension allowed to equilibrate further for 60 mints. The separation of Cr(VI) from Cr(III) and MnO4- from Mn(II) could be recognized. The electrostatic interaction between Cr(VI) ions and the composite was attractive. The composite reacts with Cr(III), a chelated complex was formed by coordination, but for Cr(VI) exists mainly as CrO₄²⁻ and MnO4-, which have negative charges. Amiongroups on composite react with H⁺, producing –NH₃⁺ groups, which adsorb Cr(VI) and MnO4- anion strongly through electrostatic attraction was thus the attachment of Cr(III) and Mn(II) species on the composite needed to overcome the unfavorable electrostatic repulsion to take place.

CONCLUSION
- It is worth pointing out that the composite (KMF 5%) has the more selectivety and high performance to separations Cr(VI) with Cr(III) and MnO4- with Mn(VI) mixture.
- The results of this study showed that the new formed powered (KMF 5%) composite using kaolin clay as a supportive surface has a limited capacity for heavy metal ions [Cr(VI) and Mn(II)] uptake.
- The (KMF 5%) composite showed non-swelling in cold or hot aqueous solutions.
- The results showed additional kaolin clay, which could provide the elasticity of MF resin.
- The results obtained are well fitted in linear form of Freundlich adsorption isotherm.
- The calculated values of different thermodynamic parameters clearly indicate that the ingoing adsorption process exothermic and spontaneous in nature, and the adsorption of the system under study takes place through electrostatic interaction between adsorbent surface and sorbate species in solution. This is supported by the calculated negative entropy thermodynamic parameter.
- The kinetic sorption data fitted well to the second order kinetic model in the concentration range studies, indicating an intra-particle diffusion mechanism.
- The contact time for the maximum adsorption of the Cr(VI) and Mn(II) on the (KMF 5%) required is 60mints and 90 mints, respectively.
- At fixed temperature and pH, the activity of the studied surface in adsorbing the two metal ions was found to follow the order.

Mn(II)>Cr(VI)

It can be concluded that it is necessary for various adsorbents to be tested because of their different surface properties in the determination of optimum conditions in terms of adsorbents for removal of the heavy metals by adsorption from aqueous solution in same conditions. The reason for this is that a substance, which is a good adsorbent for one adsorbate may not be good adsorbent for another.

REFERENCES
Preparation and Characterization of Kaolin/Melamine Formaldehyde Composite for the Removal of Some Heavy Metals from Aqueous Solution