Comparative study of adsorptive removal of oxyanion (Cr$_2$O$_4^{2-}$) from aqueous media over unmodified and magnetically modified _Melia azedarach_

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Abstract. In the present study, unmodified _Melia azedarach_ (UMA) and magnetically modified _Melia azedarach_ (MMA) were used as a low cost biosorbent for the adsorptive removal of oxyanion (chromate ion Cr$_2$O$_4^{2-}$) from aqueous solution. The UMA and MMA were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning electron microscopy (SEM). Batch biosorption process was used to check the effect of well-known process parameters including biosorbent dose, contact time and pH of solution. Experimental results revealed that MMA has more adsorption capacity as compared to UMA. Maximum % age removal (60.49%) was observed under acidic condition (pH=2) using MMA. The obtained experimental data was evaluated using Langmuir and Freundlich isotherms as well as pseudo 1st and 2nd order reaction kinetic models. Results showed that equilibrium mechanism can satisfactorily be explained by Langmuir model as depicted by the correlation factor (close to unity) and follows 2nd order reaction kinetic models.

1. Introduction

In present era, the largest component of the life affected is the water contaminated due to anthropogenic activities. As well observed, there is always increase in water demand in the agricultural and domestic sectors, hence it is of utmost importance to properly treat the industrial effluents and to remove heavy metals and other toxic chemicals before disposing into the water streams. In Pakistan, a large industrial sector consists of textile, leather, paper and pharmaceutical industry, hence releasing a large amount of heavy metals in the environment [1]. Heavy metals are major concern from the previous years because of their persistence in environment, non-biodegradable nature and toxicity. Hexavalent chromium (Cr$^{+6}$) a heavy metals is highly toxic and also categorized as a carcinogenic metals by US-EPA and many other agencies. From the various sources of Cr in the environment, tanning industries are the major source of disposal of chromium-contaminated sludge [2]. On the other hand trivalent chromium (Cr$^{+3}$) is needed by the plants and animals in trace quantity...
and act as an essential heavy metal [3,4]. The hexavalent chromium (Cr\(^{+6}\)) is a cause of sensitization and allergic reactions on the skin. Moreover the inhalation of Cr\(^{+6}\) is responsible for the absorption of chromium in the blood and serum and thus reached into the kidneys whereby producing chronic problems. It can also be absorbed by the gut and dangerous for the respiratory tract [5].

A number of physical, chemical, biological as well as physiochemical approaches have been developed to remove toxic heavy metals from industrial effluents [6]. All of these approaches have their own demerits and setbacks [7,8]. The very accurate method for removal of such heavy metals is still not known because of complexation. However, biosorption is one of the effective and efficient physical methods for the removal of such metals from the contaminated water. Different types of biosorbents have been used for the removal of chromium from water including coconut coir pith, mucor, duneliella, composite chitosan, green algae, spirogyra and so on [9-12]. It has been found from the literature that chemical or physical modification of adsorbents can enhance their adsorption capacity due to increased surface area due to the exposure of more active groups on the surface [13-15].

Thus the development of modified, more efficient, inexpensive biosorbent for waste water treatment is the subject of intensive studies. One of the biosorbent is Melia azedarach. The adsorption capacity of Melia azedarach can be enhanced by the magnetic modification because it causes ring opening of cellulose subunits that leads to the exposure and availability of more hydroxyl (-OH) groups onto the surface.

In this study unmodified and magnetically modified Melia azedarach were used for removal of oxyanion (Cr\(_2\)O\(_4^{2-}\)) from aqueous solution. Various well-established parameters including biosorbent dosage, pH, contact time and temperature were studied to explore optimum conditions. Langmuir isotherm and Freundlich isotherm were used to explain the adsorption phenomenon on the surface of adsorbate (heterogeneous surface). Date obtained from the experiments was also verified to investigate rate of adsorption and capacity by applying pseudo 1\(^{st}\) and 2\(^{nd}\) order kinetic model.

2. Materials and Method

2.1 Chemicals
Chemicals used in the current study were of analytical grade. Potassium dichromate (K\(_2\)Cr\(_2\)O\(_7\)), ferric chloride (FeCl\(_3\).6H\(_2\)O), sodium hydroxide (NaOH), hydrochloric acid (HCl), sulphuric acid (H\(_2\)SO\(_4\)) were purchased from Fluka and Sigma Aldrich. Distilled and deionized water was used to prepare the solutions.

2.2 Method

2.2.1 Preparation of Adsorbent. The branches of Melia azedarach were collected from the vicinities of University of the Punjab and were grinded by using pin mill to obtain particle size upto 60 mesh. The particles were washed and subjected to boiling for the ultimate removal of lignin and then these particles were allowed to filter. The continuous washing was continued until a clear filtrate was obtained. The residue was then dried below 80\(^{\circ}\)C.

2.2.2 Modification of Adsorbent. 25g of raw adsorbent was added in 50mL of concentrated sulphuric acid and was left for 24 hours at room temperature so that charring may proceed. Next day the charred material was washed with distilled water till the neutral pH. The material was dried below 80\(^{\circ}\)C. In this way the structure of adsorbent was modified by the ring opening of sugar molecules and thus increases the surface area (active sites) of adsorbent.

This material was then named as charred Melia azedarach. Charred Melia azedarach was poured into 0.2M solution of hydrated ferric chloride and was allowed to stir for 4 hours at 150rpm. Afterwards the mixture was decanted off and the modified adsorbent was washed with distilled water.
The adsorbent was allowed to dry and was labelled as Fe$^{3+}$ loaded charred Melia azedarach or modified Melia azedarach (MMA).

2.3 Characterization
The prepared as well as processed samples were characterized by Infrared Spectroscopy (IR), Scanning Electron Microscopy (SEM) and by Absorption spectrometer. IR spectra were recorded on Perkins Elmer FTIR (spectrum RXI) spectrometer. IR spectrographs helped to study the changes in the functional groups of unmodified and magnetically modified products.

Morphology and surface of unmodified as well as modified Melia azedarach was studied before and after modification using SEM Jeol (JSM-6390LA). The surfaces of the samples were coated with gold before the measurements. Absorption spectrometer was utilized to investigate the adsorption of chromate at various established process parameters.

Orbital Shaker (Vortex Modal-OSM-747), Vacuum Filtration Assembly, pH Meter (Jenway Modal 3320) was also used during the investigation of process parameters.

2.4 Adsorption study of Cr$_2$O$_4^{2-}$ by UMA & MMA Melia azedarach
For adsorption studies, 0.2 g of UMA and MMA Melia azedarach were added in 50ppm of chromate at pH 5.0 and the beakers were then stirred on a magnetic stirrer for 30 minutes at 150rpm, separately. Afterwards, the flasks were taken out from shaker and the contents were filtered for the removal of adsorbents. The filtrates were then subjected to atomic absorption spectrometric analysis for the concentration determination of Cr$^{6+}$ at wavelength 357.9nm. A decrease in adsorption capacity (q) was observed with the increasing amount of adsorbent (per gram). This observation is in accordance with the equation below

$$q = \frac{(C_0-C_e)V}{m}$$  \hspace{1cm} (1)

V is volume of sample, Co is initial concentration, Ce is concentration at equilibrium and m is mass of adsorbent.

To investigate the UMA as well as MMA Melia azedarach dose, the experiments were performed for 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.9g of adsorbents at temperature 25°C for 30 min at stirring speed of 150rpm. The effect of contact time was studied by varying the time at 5, 10, 15, 20, 25, 30, 35 and 40 minutes. To optimize the effect of initial pH on the adsorption of chromate onto UMA and MMA Melia Azedarach, the experiments were performed at initial pH of 1.0, 3.0, 5.0, 7.0, 9.0 and 10.0 using 0.5 g of UMA and 0.3g of MMA adsorbent at temperature 25°C and stirred for 15 min.

3. Results and Discussion

3.1 FTIR Studies
To investigate the magnetic modification of Melia azedarach FTIR studies of biosorbent was conducted before and after the modification. It can be concluded from FTIR plot that the modification of adsorbent has been done. By comparing the spectra shown in figure 1, it can be observed that there is a broad spectrum in the region of 3700-3000 cm$^{-1}$ for modified adsorbent (MMA). This shows that the modification of adsorbent has been done by the use of FeCl$_3$,6H$_2$O and H$_2$SO$_4$. By modification the binding capacity of adsorbent has been enhanced by introduction of Carboxylate, carbonyl and amino groups.
3.2 SEM Analysis
Scanning electron microscopy (SEM) was used to investigate morphology of unmodified and modified adsorbents. The operating parameters were 100mm, 8.0 kV and 200–300x magnification power. Figure 2(A) showed the SEM of unmodified *Melia azedarach* and figure 2(B) showed modified *Melia azedarach* biosorbent and reflected that the biomass consisted of heterogeneous pores, roughness and spongy surface. The adsorption capacity of biosorbent was dependent upon small pores present on heterogeneous surface. The modified *Melia azedarach* developed more porosity, roughness and spongy surface that lead to better adsorption.

![Figure 1. FTIR of UMA and MMA *Melia azedarach*](image1)

![Figure 2. SEM of UMA (A), MMA (B) *Melia azedarach*](image2)

3.3 Effect of Adsorbent dose
Figure 3A demonstrates the effect of adsorbent dose on the removal of chromate ion (CrO$_4^{2-}$) using UMA and MMA respectively. The adsorption parameter was studied by using initial concentration of 50ppm. Decrease in adsorption capacity was also found that at constant concentration of metal ion. This observation is related to the fact that with the increases in the adsorbent dose the number of binding sites is increases, in this way the chromate ions will spread on the adsorbent. Hence there is a decrease in the adsorption capacity per gram of dose. The percentage adsorption ranges from minimum percentage (5.5%) to maximum percentage (24.79%). Under these conditions, MMA showed greater q values as compared to UMA. For instance by having similar conditions (0.3g/50mL) the adsorption capacity noted to be 0.77mg/g for UMA while MMA showed 3.31mg/g for chromate ions. Hence it is proved that the modified *Melia* c is more favorable.

3.4 Effect of pH
The maximum percentage adsorption (60.49%) was observed at acidic (pH=1). The working pH range for the removal of chromate ions (CrO$_4^{2-}$) is 2-3 due to increase in the H$^+$ ions. At higher pH values, an increase in concentration of OH$^-$ (negative ions) was observed and meanwhile there was decrease in the H$^+$ ions (positive ions). The chromate ions removal would be favorable in the presence of positive species (H$^+$ ions) at low pH because of the attraction of negative ions (CrO$_4^{2-}$) towards positive ions (H$^+$).Thus the working pH for the removal of dichromate ions is acidic as shown in figure 3B.

By applying similar conditions only with the change in adsorbent dose MMA showed greater q values as compared to UMA. For instance by similar conditions at pH=3 (0.5g/50mL for UMA, 0.3g/50mL for MMA) the adsorption capacity noted to be 3.13mg/g for UMA while MMA showed 6.96mg/g for dichromate ions. Hence it is proved as demonstrated in figure 3B that the modified *Melia azedarach* is more favorable for the removal of dichromate ions as compared to unmodified *Melia azedarach*. 
3.5 Effect of Contact Time
An increase in the time results in increased adsorption capacity has been presented in figure 3C using UMA and MMA respectively. This is due the fact initially chromate ions move rapidly towards adsorbent because at this stage the biosorbent is starved for adsorbent. With the passage of time the adsorption capacity becomes constant, because at that point the amount of chromate ions being adsorbed by the adsorbent establishes a dynamic equilibrium with the amount of chromate ion desorbed from adsorbent.

By applying similar conditions, MMA showed greater q values as compared to UMA. For instance at contact time of 10 minutes (0.5g/50mL for UMA, 0.3g/50mL for MMA) the adsorption capacity noted to be 2.63mg/g for UMA while MMA showed 4.32 mg/g for chromate ions. Hence it is proved that the modified *Melia azedarach* is more favorable for the removal of chromate ions as compared to unmodified *Melia azedarach*.

3.6 Adsorbent Isotherms
Data obtained during the experimentation was analyzed by applying well established isotherm viz. Langmuir and Freundlich isotherm models.

3.6.1. Langmuir Isotherm. Langmuir isotherm is plotted according to the equation:

\[
\frac{1}{q_e} = \frac{1}{bq_{max}} \cdot \frac{1}{C_e} + \frac{1}{q_{max}}
\]

(2)
For Langmuir isotherm model the correlation coefficient values were greater and fitting best to the adsorption process ($R^2$ value for dichromate ion is 0.97 using UMA and 0.98 for MMA) thus showing that Langmuir model figure 4 is better for understanding adsorption behavior of dichromate ion than Freundlich model. Table 1 represents the slope and intercept for the derivation $q_{\text{max}}$ mg/g and constant relevant to free energy from the Langmuir plot.

MMA showed enhanced $q_{\text{max}}$ value as compared to UMA. For instance the $q_{\text{max}}$ value for unmodified adsorbent (UMA) is 5.95mg/g and $q_{\text{max}}$ value for modified adsorbent (MMA) is 16.86mg/g.

**3.6.2 Freundlich Isotherm.** Freundlich isotherm is an empirical relationship obtained by plotting graph between $\ln C_e$ on x-axis and $\ln q_e$ on y-axis.

This model assumes that adsorption of dye from liquid to liquid surfaces takes place on a heterogeneous surface which involves different sites with several adsorption energies. Freundlich isotherm is plotted according to the equation iii:

$$\log q = \log K_f + \frac{1}{n} \log C_e$$

(3)

The value of $n$ in the range of less than 1 showed average adsorption, 1-2 showed good and 2-10 showed better adsorption characteristics. The correlation coefficient value of Freundlich isotherm (Figure 5) showed that it did not fit well to the adsorption data. These values are 0.97 for UMA and 0.95 for MMA.

![Figure 4. Langmuir isotherm UMA (A), MMA (B)](image)

![Figure 5. Freundlich Isotherm UMA (A), MAA (B)](image)

**Table 1.** Langmuir and Freundlich parameters for $\text{Cr}_2\text{O}_4^{2-}$ Removal

| Adsorbent | Slope  | Intercept | $q_{\text{max}}$ (mg/g) | $b$ (dm$^3$/g) | Slope  | Intercept | n   | $K_f$  |
|-----------|--------|-----------|--------------------------|----------------|--------|-----------|-----|--------|
| UMA       | 6.69   | 0.16      | 5.948                    | 0.02           | 0.84   | -1.045    | 1.19| 0.09   |
| MMA       | 3.99   | 0.059     | 16.86                    | 0.01           | 0.704  | -0.3563   | 1.4204| 0.44   |

**3.7 Kinetic Modelling**

The pseudo 1st and 2nd order kinetic model were applied to study the rate of adsorption and capacity.
3.7.1 Pseudo 1st Order Kinetic Model. First order reaction model is plotted according to the equation:

\[ \ln (q_e-q_t) = \ln q_e - k_1 t \]  

(4)

A graphical representation of Pseudo 1st order kinetic model for (Cr\(_2\)O\(_7\)^{-2} \)) removal using MMA is shown in figure 6.

The value of linear correlation coefficient \( R^2 \) for pseudo 1st order is less as compared to pseudo 2nd order model. For the prediction of mechanism involved Lagergren’s pseudo 1st order kinetic model is usually applied.

By using *Melia azedarach* for chromate ion adsorption a pseudo 1st order kinetic model was obtained by plotting a graph between time and \( \ln(q_e-q_t) \).

The \( R^2 \) value for UMA was 0.97 and that for MMA was 0.94 as shown in table 2 and didn’t explain well to the adsorption kinetic.

3.7.2 Pseudo 2nd Order Kinetic Model. Second order reaction model is plotted (Figure 7) according to the equation:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + t/q_e \]  

(5)

By using UMA and MMA for the adsorption of chromate ion, the pseudo 2nd order model is represented in Fig. 7 and parameters for pseudo 2nd order are demonstrated in table 2. The value of correlation factor (\( R^2 = 0.99 \)) value for UMA and MMA depicted that the pseudo 2nd order model was fitted better to the data. In a comparative analysis to the pseudo 1st order kinetic model, the \( q_e \) value derived for 2nd order kinetic model very appreciable related to the experimental value for UMA and MMA showing that pseudo 2nd order kinetic mechanism is best for the adsorptive removal of chromate ions by *Melia azedarach*.

![Figure 6. Pseudo 1st order kinetic model](image)

![Figure 7. Pseudo second order model](image)
Table 2. Pseudo 1st and Pseudo 2nd order order kinetic parameters for Cr₂O₇²⁻ Removal

| Adsorbent | k₁ | R²  | qₑ   | qₑ(experimental) | k₂   | R²  | qₑ   | qₑ(experimental) |
|-----------|----|-----|------|-------------------|------|-----|------|-------------------|
| For UMA   | 0.142 | 0.97 | 0.99 | 2.91 | 2.98 | 0.99 | 4.103 | 2.91 |
| For MMA   | 0.150 | 0.94 | 0.60 | 4.32 | 6.53 | 0.99 | 5.88  | 6.37 |

4. Conclusion
In the present study cost effective and readily available *Melia azedarach* was applied as a adsorbents for the removal of dichromate ions from water bodies. *Melia azedarach* was magnetically modified to increase the efficiency for oxyanions uptake. FTIR characterization revealed that various functional groups are observed on the surface of UMA that can be responsible for chromate ions removal. Modification improves the surface morphology by ring opening of cellulose and producing free hydroxyl group (-OH) in MMA which is shown by the high uptake capacity of MMA as compared to UMA. Optimum pH for the maximum percentage adsorption removal (60.49%) of chromate ions were found in acidic medium (pH=2-3). Batch biosorption experiments showed that removal efficiency of chromate ions using MMA was better as compared with UMA. Equilibrium data was found better fit to Langmuir equilibrium model. The maximum Adsorption was observed i.e. 2.63mg/g for UMA while MMA showed 4.32 mg/g for chromate ions. Kinetic data was observed to follow pseudo 2nd order mechanism. Hence it can be concluded that MMA can be used for treatment of wastewater in terms of oxyanions removal in an effective and economical way.

5. References
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