

Efficacy evaluation of chromium(vi) adsorption on clay soil blended with *Azadiracta indica* (Neem) and *Moringa oleifera* (Drum stick) seed shell

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Manuscript received online 01 February 2019, accepted 25 March 2019

In the present study, the adsorptive removal efficiency of Cr^{VI} from aqueous solutions was examined by using locally available clay soil amended with *Azadiracta indica* (AI) (Neem) and *Moringa oleifera* (MO) (Drum stick trees) seed shell as adsorbent. The amended adsorbent dosage were varied 10 through 20% in clay soil to assess the maximum percentage Cr(vi) removal from the aqueous solutions at optimal pH (6.5) and equilibrium reaction time. It was observed that Cr(vi) adsorption efficiency increased with the increment of both AI and MO dosage in the soil. However, AI blended clay soil showed more promising Cr(vi) removal percentage (90%) in comparison to MO amended soil at same level of the adsorbent dosage.

Keywords: Cr(vi) removal, amended clay soil, batch adsorption study, adsorption isotherm, SEM analysis, XRD analysis.

Introduction

The presence of the heavy metals in the aquatic environment is becoming an increasing concern to the scientists and engineers because of their colossal health effects and also potential ability in causing ecological imbalance of receiving water bodies¹. Cr(vi) is a common pollutant found into the natural water bodies close to the industrial zones comprising of industries viz. steel and alloys, tanneries, chrome-plating, automobiles, paints, and ammunition¹. The unscientific and indiscriminate disposal untreated and partially treated effluents from the said industries are responsible for water quality depletion due to rise of chromium laden heavy metal pollutions.

According to USEPA, Cr(vi) being the priority toxic pollutants and intake of such contaminant by human being is a serious health concern because it possesses carcinogenic and teratogenic characteristics. The World Health Organization (WHO) and IS-10500 drinking water guidelines has set maximum permissible limit of total chromium as 0.05 mg/L².

There are several methods viz. chemical reduction and precipitation¹⁰, flocculation¹¹, electrolysis as well as electroplating method¹², nano filtration process¹³, ion exchange method¹⁴ etc. are commonly applied for the removal of chromium(vi) from contaminated waters. However, in the

present study, an attempt was made to assess the adsorptive removal of Cr(vi) from aqueous solutions by using clay soil amended with *Azadiracta indica* (AI) (Neem) and *Moringa oleifera* (MO) (Drum stick trees) seed shell.

Materials and methods:

Azadiracta indica:

Azadiracta indica is commonly known as neem or Indian Lilac³, which belongs to the mahogany family Meliaceae and mainly found in the Indian subcontinent, i.e. India, Nepal, Pakistan, Bangladesh, Sri Lanka, and Maldives⁴.

Moringa oleifera:

Moringa oleifera is the most widely cultured species in the genus *Moringa*, which is the only genus of the family Moringaceae⁵.

Preparation of the natural adsorbent:

The seed shells of the both the natural adsorbent AI and MO were collected, they are cleaned and broken into pieces, it is then cleaned by distilled water and air dried and later it is grinded to required sizes. These grinded materials were then oven dried at a temperature upto 105±5°C for 24 h. The adsorbent was then blended with the clay soil in various percentage of weight of the soil mass. The locally available clay soil of about 200 g was oven dried for 3 days at 60°C keep-

ing in mind that temperature above this would destroy biomass and minimizes volatilization of some analytes (US EPA 2002, Puget Sound). The oven dried soil samples were then pulverized by using a wooden mallet and sieved through a 425 μm sieve to form a homogenized sample as grain size plays a notable role in determining elemental concentrations in soil. Both AI and MO were mixed with soil in (10%, 15% and 20%) by the weight of the clay soil taken.

Batch adsorption:

In the batch adsorption test, a pre-determined amount of adsorbent is added with the synthetically prepared aqueous Cr solution of different concentrations in a 120 ml polyethylene bottle. The solution was stirred on a rotary shaker at a speed of 120 rpm for a fixed reaction time. The solution pH was maintained to the desired value using 0.1 mol/L HCl or 0.1 mol/L NaOH. The supernatants of the agitated samples were subsequently filtered through 0.45 μm filter paper by vacuum filtration process. The pH of the solution is maintained at 6.5 because pHzpc of clay soil was found to be 6.75. The residual chromium(vi) concentration was determined by using UV-Vis spectrometer at a wavelength of 540 nm by diphenylcarbazide the complexing agent. All the readings were noted after 5–10 min of waiting to allow the full colour development with respect to the blank sample. The absorbance were noted and the concentration of chromium(vi) were calculated from the standard calibration curve. The contact time (t) was maintained as 2, 6, 8 and 24 h. The initial concentration (C_0) of chromium(vi) was kept as 0.5, 1, 2, 4 and 5 ppm and the adsorbent dose (W) was considered as 0.1, 0.15 and 0.20 g/100 ml of the solution, the pH of the solutions were varied as 2, 5, 6, 7 and 9. The percentage of chromium(vi) removal ($R\%$) and the solute adsorption capacity (q_e) of the amended soil was estimated based on eq. (1) and eq. (2), respectively.

$$(\%) R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e (\text{mg g}^{-1}) = \frac{(C_0 - C_e) V}{M} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of the solute, respectively. All the experiments were repeated in triplicate and the average values were considered. Adsorption isotherm studies were carried out with vary-

ing initial chromium(vi) concentrations ranging from 0.5 to 5 mg/L, the adsorbent dose was maintained as 0.2 g.

Results and discussion

pH of the solution is the most important factors influencing the adsorption process. Hence it influences the ion speciation present into the solution as well the surface properties of the adsorbent. The effect of solution pH on adsorption of Cr(vi) is depicted in Fig. 1 and Fig. 2. The graph shows that there is a sharp decline in the adsorption of chromium(vi) at pH below 3, the maximum removal efficiency is shown at a pH between (6–8) maintaining over 90% and there's a abrupt decrease in adsorption above pH 11.

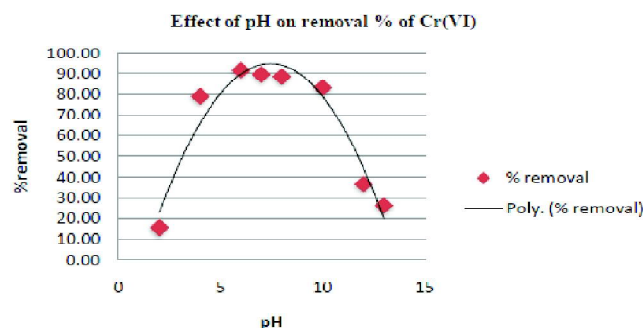


Fig. 1. Graphical representation of effect of pH on absorption of chromium(vi) with natural adsorbent as *Azadirachta indica*.

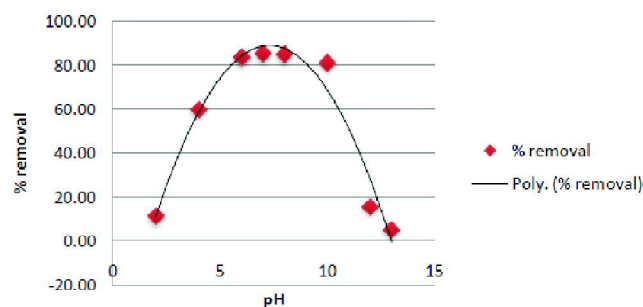


Fig. 2. Graphical representation of effect of pH on absorption of chromium(vi) with natural adsorbent as *Moringa oleifer*.

In the solution chromium(vi) subsists in the forms of H_2CrO_4 , HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ at different ratios depending on the solution pH. H_2CrO_4 preponderates at pH less than 1.0, HCrO_4^- between 1.0 and 6.5, only CrO_4^{2-} is stable at pH more about 6.5. The dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$), a dimer of HCrO_4^- , less a water molecule, forms when the chromium concentration is exceeding 1 g/L (approximately)⁹.

Comparative batch adsorption study of clay soil blended with AI and MO.

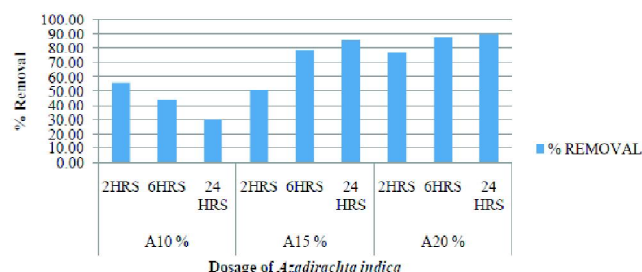


Fig. 3. Graphical representation of batch adsorption study with natural adsorbent as *Azadiracta indica*.

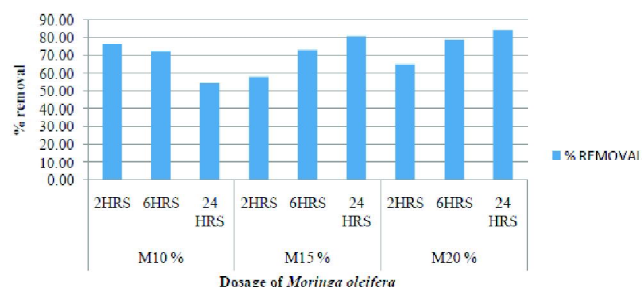


Fig. 4. Graphical representation of batch adsorption study with natural adsorbent as *Moringa oleifer*.

The Figs. 3 and 4 show that influence of contact time and varying percentage of adsorbent dosage on Cr(vi) removal from aqueous solution. Both the above graph represents that maximum removal in both the cases were achieved at 24 h contact time and the Cr(vi) removal percentage was found close to 90 and 83%, respectively when 20% (by weight) AI and MO blended with soil by weight individually and used as adsorbent. It was observed from Figs. 3 and 4 that the removal rate of chromium(vi) was rapidly increased up to 56% (approx.) during first 2 h of agitation with 10% by weight of AI and MO blended with clay soil. However, the removal percentage was gradually decreased to 30% and 55% in case of AI and MO respectively. These trend of Cr^{VI} removal were not observed when 15% and 20% by weight of AI and MO blended clay soil used as adsorbent. Increase in adsorbent percentage increased the rate of removal. Presence of more surface functional groups and surface area due to increasing percentage of adsorbent is directly proportional to Cr(vi) adsorption^{22,23} which results in higher removal of Cr(vi). However due to lower adsorbent dosage the surface area of the

adsorbent gets saturated with the Cr(vi) as a result desorption of Cr(vi) from the surface of the adsorbent tookplace and thereby increased the Cr(vi) concentration in the water.

Adsorption isotherm:

Adsorption isotherms express the relationship between the amounts of adsorbate (mg) sorbed from solution by the adsorbent (g) at specified temperature. The Langmuir and Freundlich isotherm model were considered in the present study to estimate the Cr(vi) adsorption capacity of AI and MO blended soil as shown in Table 1.

Table 1. Langmuir and Freundlich isotherms for chromium(vi) biosorption

Adsorbent	Langmuir parameters			Freundlich parameters		
	Q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_f	R^2
AI	65.789	0.0653	0.987	1.89	0.671	0.920
MO	33.44	0.05	0.992	1.12	0.446	0.896

It was found that the Langmuir Isotherm provided better fit ($R^2 = 0.987$) in comparison to Freundlich isotherm ($R^2 = 0.92$) in case of adsorption study using AI blended soil as adsorbent. Similarly in case of MO the Langmuir isotherm provided better fit ($R^2 = 0.992$). Moreover, AI blended soil showed higher potential in adsorbing Cr(vi) ($Q_{max} = 65.789$ mg/g) from aqueous solution as depicted in Table 1. A comparative study of Cr(vi) adsorption potential by different adsorbent materials along with the adsorbents used in the present study is depicted in Table 2. It clearly indicates that neem seed dust blended soil has an excellent Cr^{VI} adsorption capacity and can be considered as liner material in waste containment structures.

Table 2. Comparative study of Cr(vi) adsorption capacities of different adsorbents along with AI and MO

Adsorbent	Adsorption capacity (mg/g)
Coconut tree sawdust	3.60 ¹⁵
Beech sawdust	16.10 ¹⁶
Treated sawdust of Indian Rosewood	10.00 ¹⁷
<i>Hevea brasiliensis</i> sawdust activated carbon	44.05 ¹⁸
Treated sawdust of Sal tree	9.55 ¹⁹
Mango sawdust	37.73 ²⁰
Neem seed dust	65.789
<i>Moringa olifera</i> dust	33.44

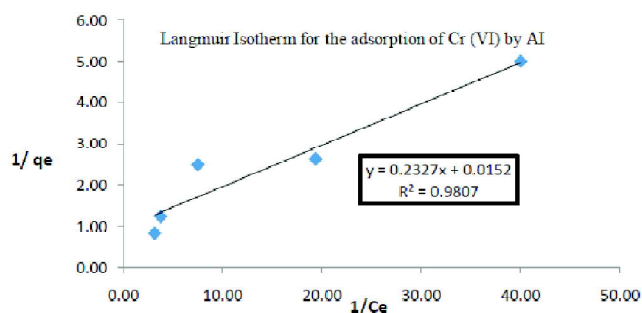


Fig. 5. Graphical representation of Langmuir adsorption isotherms for Cr(vi) adsorption by AI.

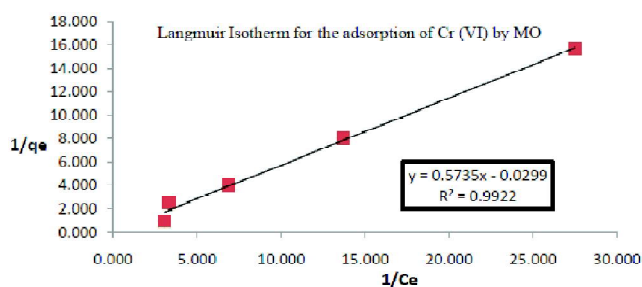


Fig. 6. Graphical representation of Langmuir adsorption isotherms for Cr(vi) adsorption by MO.

Desorption study:

For the potential practical application, it is necessary to examine the chances of desorbing Cr(vi) ions adsorbed by the AI blended with the locally available clay soil. After the batch adsorption test, the solutions were filtered to separate the Cr(vi) adsorbed soil from the solutions. The AI blended soil was then dissolved with double distilled water and pH of 6.5 was maintained. The solution is kept on the rotary shaker for a specified time at 120 rpm at room temperature. The concentration of Cr(vi) in the solution was measured after 12 h by using UV spectrophotometer. However, very less amount of Cr(vi) was detected about 30% (approx.). A SEM analysis was done to study the changes in microstructure of the soil for both raw soil and soil after the desorption study.

The above Fig. 7(c) clearly shows a change in microstructure of the clay soil blended with AI after it is blended with Cr(vi). In the Fig. 7(b) it can be seen that many irregular surface structure of soil as well as pores are present on the surface before adsorption. It can also be seen in Fig. 7(c) that lots of crystals adhere on the soil surface. This phenom-

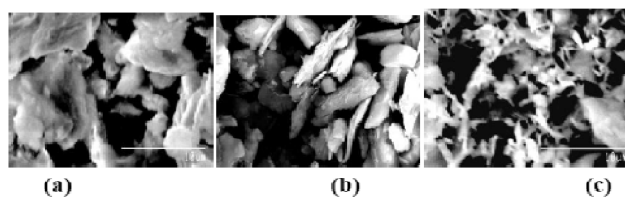


Fig. 7. SEM Images (a) raw clay soil, (b) clay soil blended with AI (20% by weight of soil) without chromium and (c) clay soil blended with AI (20% by weight of soil) with Cr(vi) after desorption study.

ena can be described as the chances of chemisorption of the Cr(vi) on the absorbent surface. To reinforce this statement the XRD test was also performed.

The XRD patterns of clay soil blended with AI before and after contaminated with Cr(vi) adsorption are illustrated in Fig. 8 and Fig. 9. From Fig. 9(b), it is very much evident that clay soil with Cr(vi) exhibits more number of fine and intense peaks. A strong peak as seen at $2\theta = 44.6^\circ$ in Fig. 9b indicates the presence of chromium in the soil.

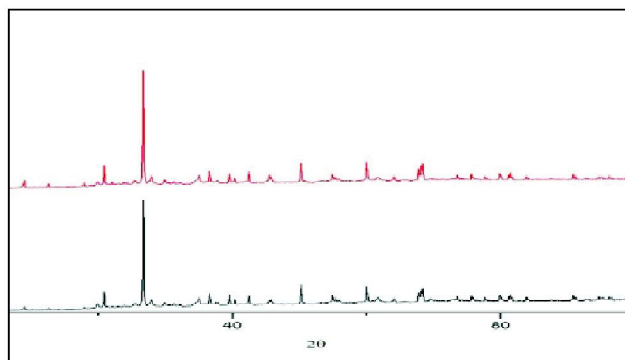


Fig. 8. XRD patterns: (a) clay soil, (b) clay soil + AI + Cr(vi).

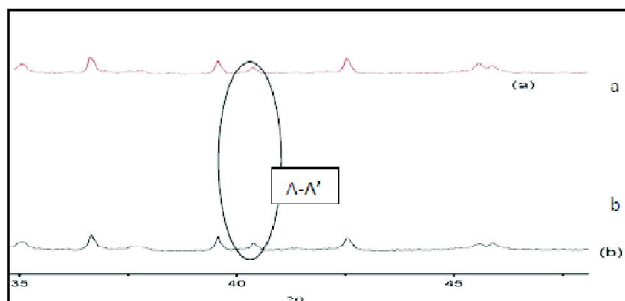


Fig. 9. Enlarged view of section A-A', XRD patterns: (a) clay soil, (b) clay soil + AI + Cr(vi).

Conclusions

Based on the above experimental study the following conclusions were drawn.

It is very much evident from the batch adsorption studies that AI and MO seeds are good adsorbent for removing Cr(vi) from aqueous solutions when mixed with clay soil. Maximum adsorption of Cr(vi) is achieved performed with AI blended with clay soil.

The excellent Cr(vi) adsorption capacity of AI blended clay soil provides an alternative solution for using the adsorbent as liner material in chromium laden waste containment structures.

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