



Adsorption Studies of Cr (VI) and Fe (II) Aqua Solutions Using Rubber Tree Leaves as an Adsorbent

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Abstract

The study on adsorption capacity of metal ions Cr (VI) and Fe (II) was carried out on rubber tree leaves (RTL). The extent of adsorption was evaluated by varying several physico-chemical parameters viz, initial concentration, contact time and pH. The variation in concentration of metal ions after adsorption was analyzed by using atomic absorption spectrophotometer (AAS). The results revealed the rubber leaves are valuable adsorbent for the removal of metal ions as the experimental data was followed by Langmuir and Freundlich models.

Keywords: Rubber tree leaves, Atomic absorption spectroscopy, Cr(VI), Fe (II), Langmuir and Freundlich model.

Introduction

The release of heavy metals by industrial activities into the environment is one of the main concerns of researchers in recent years¹. The sources of metal contamination in the environment are metal, mining, battery and alloy processing industries². The heavy metals unlike other organic pollutants are not biodegradable and result hazardous end products³. It has been reported that at lower concentrations heavy metals do not pose any threat to human health however at higher concentration they tend to get accumulated in human tissues⁴. Chromium (VI) has been considered as most toxic as compared to Chromium (III) due to its higher affinity towards cellular proteins and deoxyribonucleic acids. Chromium compounds are placed in the category of priority pollutant by US Environmental Protection Agency⁵. Environmental Protection Agency (EPA) considers chromium among top toxic pollutants, due to its two oxidation states, trivalent Cr (III) or hexavalent Cr (VI)⁶. Cr (VI) as chromate or dichromate has a property of not being well absorbed by soil with slight acidic or alkaline nature, hence making it mobile in the subsurface of soil⁷. The persons exposed to chromium dusts are prone to skin, acute breathing problems and are likely to suffer from lung cancer⁸. It has been reported that more than 0.5mg/L of chromium in industrial waste is hazardous to human health⁵. The elemental composition of various minerals and rocks suggest that they possess Iron in both 3+ as well as 2+ oxidations states. Although the presence of Iron supports many biological and enzymatic functions of plants and animals but its rapid corrosive property makes it more exposed to environment⁹. It has been reported that the concentration above 0.2 mg/L has caused a considerable damage to health of fishes due to generation of free radicals at the gill surface leading oxidation of tissue and ultimately anemia¹⁰. In Malaysia, mineral mining and textile industry activities has lead to the release of chromium and iron

to surface water bodies. Thus, the removal of such toxic metals from wastewaters before being discharged into the surrounding water bodies needs extensive attention¹¹. Therefore, herein we report the adsorption studies of chromium and iron by using rubber leaves as an adsorbent.

Material and Methods

Rubber tree leaves were collected from rubber tree farm nearby Universiti Malaysia Kelantan, Jeli Campus, Malaysia. The rubber tree leaves were extensively washed and soaked in deionized water for 24 hours. This was carried out to remove dust and any adhering particles that may affect the adsorption result. The rubber tree leaves were then dried at room temperature for 3 days and finally grinded and sieved to get the average adsorbent size of 150 μ m. The adsorbent powder was kept in the clean air tight plastic bags for further investigations.

Preparation of chromium and iron stock solutions:

Chemicals used were of analytical reagent grade. The stock solution of Fe (II) ions and Cr (VI) of concentration 1000 mg/L were prepared by dissolving appropriate amount of FeSO₄.7H₂O and K₂Cr₂O₇ in distilled water respectively. The pH of obtained solutions was adjusted by using 0.1N HCl or NaOH.

Instrumentation: Atomic Absorption Spectrometer (Perkin Erlmer, USA) was used to carry out atomic absorption studies.

Adsorption studies: Different adsorption experiments were carried out using dried rubber leaf powder and metal ion at different pH and contact time. 0.5g of rubber tree leaves with 50 mL of iron or chromium metal ion solutions under different conditions for various periods were kept in Erlenmeyer flasks at 20 \pm 0.5 $^{\circ}$ C using rotary shaker at a constant speed of 180 rpm. The percentage of residual metal ion of the supernatant was

measured by estimating remaining amount of metal ion in the sample by using AAS.

Effect of contact time: The effect of different contact time was observed by taking 0.5g of RTL with 50 ml of 200ppm of metal ions at optimal pH. The powder was left in a solution for different periods of time. The Erlenmeyer flasks were withdrawn from the rotary shaker one after the other at 40, 80, 120, 160 and 200 minutes. The mixtures were agitated at 180 rpm at temperature room. The samples were filtered by using membrane filter and filtrates containing metal ions concentration were analyzed using AAS. The removal of metal ion by the biosorbent was calculated by equation 1.

$$\text{Removal}(\%) = \frac{C_o - C_e}{C_o} \times 100\% \quad (1)$$

C_o and C_e are initial and equilibrium liquid phase metal ion concentration (mg/L) respectively. The amount of metal ion absorbed by the biosorbent was calculated by using equation 2:

$$q_e = \frac{C_o - C_e}{m} \times V \quad (2)$$

q_e (mg/g) is the amount of metal ion absorbed per unit mass of adsorbent, V is the volume of the metal ion solution, m is the mass of biosorbent and C_o and C_e are the initial equilibrium liquid phase of metal ion concentrations (mg/L) respectively.

Effect of initial concentration on adsorption: The adsorption was carried out using a concentration range of 40ppm, 80ppm, 120ppm, 160ppm and 200ppm. This was carried out by contacting 0.5g of rubber tree leaf powder with 50mL of each metal ion solutions at optimal pH in 250mL of Erlenmeyer flasks. The flasks were then agitated at 180 rpm using rotary shaker about 2 hours at room temperature. The samples were filtered and the concentration of residual metal ions in each solution was determined by AAS.

Effect of optimal pH: The effect of pH on adsorption of metal ions were carried out at pH 2- 6, the range was selected to avoid the precipitation of metal ions. 0.5g of rubber tree leaves powder with 50mL of 200 ppm metal ions solution in 250mL were taken in Erlenmeyer flask. The pH of the solution was adjusted by dropping of 0.1M of NaOH /or 0.1M of HCl. The mixture was agitated at 180 rpm using rotary for 2 hours at room temperature. The residual of metal ion of supernatant was analyzed for determining the optimum pH of biosorption.

Adsorption isotherms: The adsorption isotherm is a graphical data to represent a relationship between adsorbent and adsorbate at test equilibrium¹². The Langmuir and Freundlich models are widely used adsorption models to study even the metal uptake. Langmuir isotherm has been used to calculate and contrast the performance of various adsorbents. In our study, Langmuir and Freundlich models were used to explain the result of the

experiment. Langmuir model is designed with a hypothesis that, uptake occurs at homogenous surface by monolayer adsorption without any interaction among adsorbed molecules and is expressed as in equation 3:

$$q_e = \frac{q_{\max} b C_e}{(1 + b C_e)} \quad (3)$$

q_{\max} represents a maximum sorption uptake per unit mass of adsorbent in mg/g, C_e is the equilibrium concentration of heavy metal ions in mg/L and b is Langmuir constant of sorption and desorption rate. q_{\max} and b have been calculated from the intercept in the graph and slope of the plots as well. The Freundlich model proposes a monolayer sorption. It can be expressed equation 4:

$$q_e = k_f C_e^n \quad (4)$$

The above equation can be rearranged into a linear form as follows:

$$\log q_e = \log k_f + n \log C_e \quad (5)$$

k_f and n are the coefficients indicating the adsorption capacity intensity respectively. The Freundlich coefficient (n) has value in the range of 1 to 10 for classification as favorable adsorption.

Results and Discussion

Initial concentration and its effect on adsorption of Cr(VI) and Fe(II): The adsorption capacity of RTL powder was considerably effected by initial concentration of Cr(VI) and Fe(II) ions in aqueous solutions. Figure 1 revealed that at constant adsorbent dosage (0.5g) the percentage removal decreases from 39.45 to 9.83 and 51.88 % to 14.91 % at the same contact time (2 hr) for Fe (II) and Cr(VI), respectively. It was observed that percentage removal of Cr(VI) and Fe(II) ions decreases with increase of their concentration. Nevertheless, the decline in adsorption capacity can be attributed to saturated available adsorption sites even after using high concentration of metal ion solution¹³. Furthermore, as the concentration is increased, the electrostatic interaction is also increased between the metal ion and active sites of RTL adsorbent. This observation can be supported by the fact that with increase in metal ion concentration, the most adsorption sites are covered.

pH and its effect on adsorption of Cr(VI) and Fe(II): The pH of the solution mostly plays a crucial role in the adsorption of metal ions. Figure 2 represents the percentage removal of Cr(VI) and Fe (II) ions versus the pH range from 2- 6 at room temperature. The optimum pH for the adsorption of Cr(VI) and Fe(II) ions was found to be pH 4-6 and 4-5, respectively. It has been reported that surfaces of adsorbents are sensitive to pH of solution and plays an important role in adsorption of ions/solutes from aqueous solutions. The lower pH contributes towards the adsorption of molecular forms at surfaces, but at higher pH usually ionic species are adsorbed. At very low pH Cr(VI) has been reported to have a greater affinity towards

hydroxyl groups in the anionic form as HCrO_4^- , as surface is rich in positive charge. However tendency to cationic adsorption occurs at higher pH⁵. At low pH values, Fe (II) has to compete with the H^+ ions to bind to the adsorbent surface as at low pH iron exist as free cations¹⁴. Therefore, pH 2 was explained as the lower removal efficiency of Fe (II). As the pH exceeded pH 4, the percentage of removal began to decrease again. This can be attributed to the precipitation of metal hydroxide¹². Thus, the optimum percentage removal of Fe (II) ion was obtained to be at pH 4.

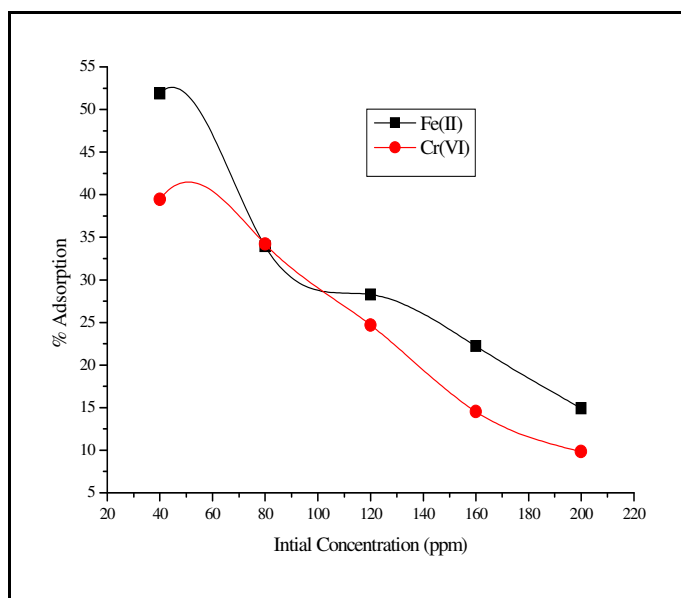


Figure-1
 Effect of initial concentration on removal of Cr (VI) and Fe (II)

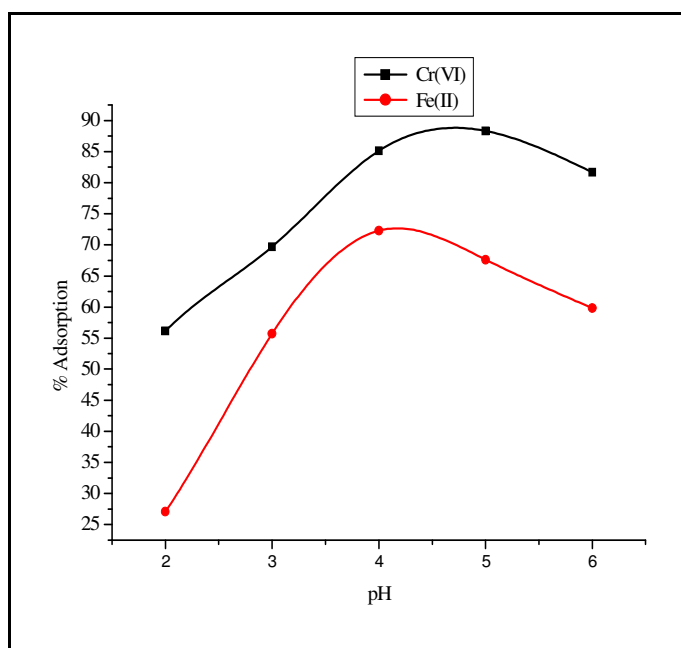


Figure-2
 Effect of pH on removal of Cr (VI) and Fe (II)

Contact time and its effect on adsorption of Fe (II) and Cr (VI): The contact time is another important factor to ascertain the effectiveness of the adsorbent to remove metal ions in aqueous solution. The adsorption of metal ions by RTL was varied from 40 minutes to 200 minutes. It was observed that the efficiency of metal ion uptake was increased with the increase of contact time. The increasing trend in adsorption was observed in both Cr(VI) and Fe(II) with increasing the contact time. The maximum adsorption was noticed at contact time of 200 minutes in both Cr(VI) and Fe(II), followed by a constant values. This type of adsorption tendency can be contributed to the nature of the adsorbent and its available adsorption sites that affect the time required to reach the equilibrium. It has been reported that adsorption sites are well exposed, thus trigger a quickly sorption¹⁴. Thus, the equilibrium time was reached in 200 minutes. This factor ascertains the effectiveness of the adsorbent to remove metal ions in aqueous solution and thus results revealed that the efficiency of metal uptake was increased with the increase of contact time.

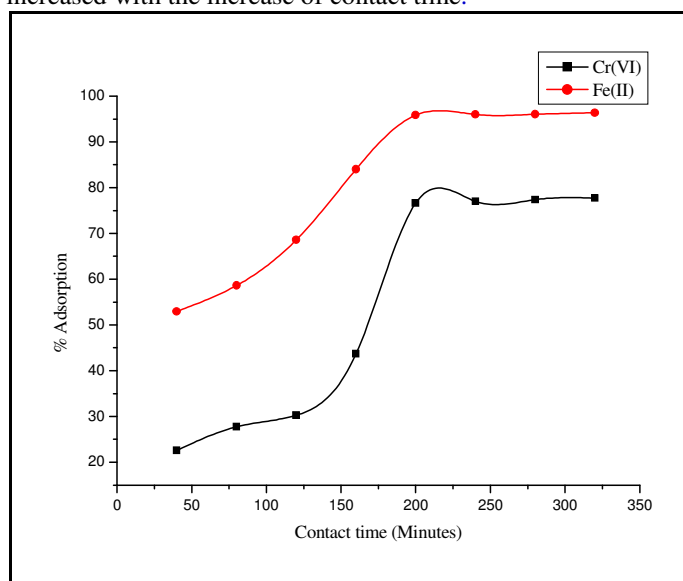


Figure-3
 Contact time on removal of Cr (VI) and Fe (II)

Adsorption isotherms: Langmuir and Freudlich models of adsorption were used to determine the extent of adsorption of Cr (VI) and Fe (II) ions (figures 4-7). The coefficients were calculated from both two models as to find out the adsorption capacity of metal ions. In table 1 and 2, $R^2 \geq 0.80$, indicated that the data are well fitted in Langmuir and Freudlich models while, the values of n which more than 1 for all adsorbents signed that the adsorption occur at low concentration of adsorbent¹⁵. It can observed from data (table 1 - 2) that, the experimental data was fitted with both model where the R^2 values are greater than 0.80. Thus, values obtained by linear regression correlation coefficient (R^2) for both Langmuir and Freudlich suggest that monolayer sorption and heterogenous surface conditions may exist under that experimental condition as well.

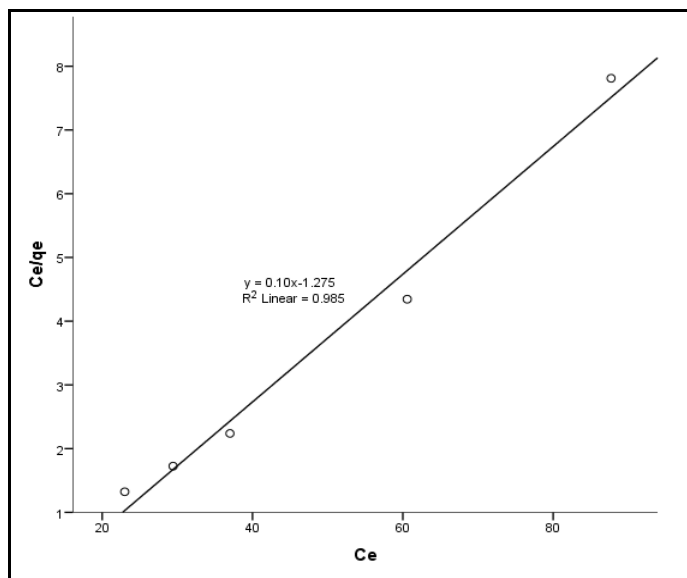


Figure-4

The Langmuir Isotherm for Cr (VI) adsorption using RTL

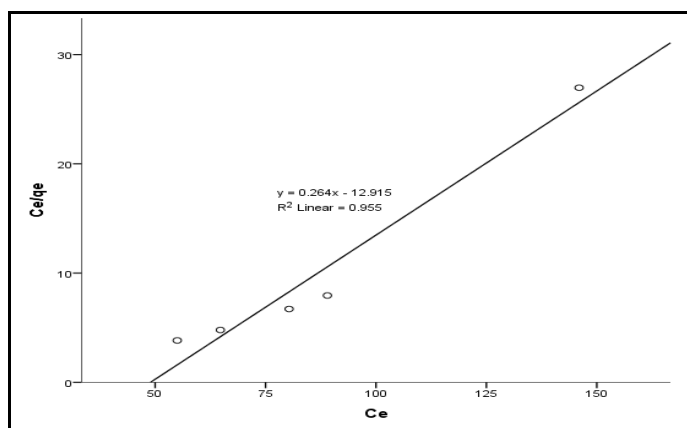


Figure-5

The Langmuir Isotherm for Fe (II) adsorption using RTL

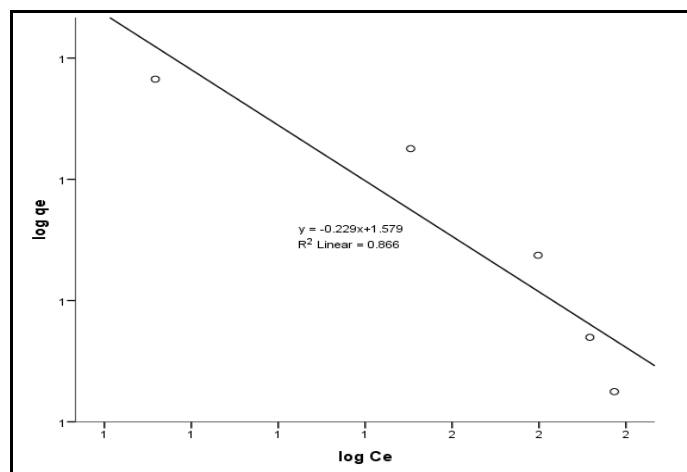


Figure-6

The Freundlich Isotherm for Cr (VI) adsorption using RTL

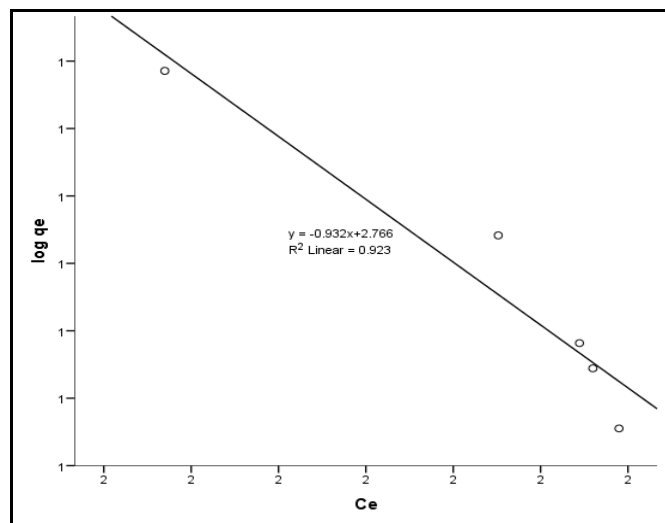


Figure-7

The Freundlich Isotherm for Fe (II) adsorption using RTL

Table-1

Langmuir isotherm models of the Cr (VI) - RTL and Fe (II) - RTL systems

Langmuir Isotherm				
Metal Ion	R ²	Q ₀ (mg g ⁻¹)	b (L mg ⁻¹)	Parameter
Cr (VI)	0.985	10.00	7.843	pH
Fe (II)	0.955	3.788	0.293	pH

Table-2

Freundlich models isotherm model of the Cr (VI)- RTL and Fe (II)- RTL system

Freundlich Isotherm				
Metal Ion	R ²	K _f (mg g ⁻¹)	n (L mg ⁻¹)	Parameter
Cr (VI)	0.866	4.850	4.367	Con. time
Fe (II)	0.923	15.895	1.073	Con. time

Conclusion

The effect of various physiochemical factors showed that the maximum uptake capacity for Cr (VI) was pH 5 and while for Fe (II) was observed at pH 4. The percentage of adsorption was found to be high for Cr (VI) as well as Fe (II) ions at initial concentrations. Similarly, the Cr (VI) and Fe (II) uptake capacity enhances with the increasing the contact time. The equilibrium showed that the systems followed both Langmuir and Freundlich model of adsorption isotherm. Since rubber tree leaves are highly abundant and show a good adsorption capacity for Cr (VI) and Fe (II) ions, RTL can be alternative low cost adsorbent to remove Cr (VI) and Fe (II) from environment.

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