

Research Article

Removal of Cr(VI) and Cu(II) Ions from Aqueous Solution by Carbon Prepared from Henna Leaves

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Carbon prepared from leaves of henna (*Lawsonia inermis*) was used to study the adsorption of Cr(VI) and Cu(II) ions from their aqueous solutions. The experimental conditions which include pH, contact time, initial concentration, and adsorbent dosage on the metal removal were investigated. The capacity of adsorption depends on pH value; it increases with an increase in pH value from 1 to 7 and then decreases. The highest percentage of metal removal was achieved in the adsorbent dosage of 0.7 g and at an initial concentration of 100 ppm metal ion. The adsorption isotherm studies revealed that data was confirmed with both the Langmuir and Freundlich isotherm models. The removal percentage was found to be higher for Cu(II) when compared with Cr(VI). The potential of carbon prepared from henna leaves for the removal of these two solutions containing heavy metals was substantiated.

1. Introduction

Nowadays the awareness of increasing water pollution and its studies concerning water treatment and the use of removal of heavy metals from industrial wastewater are of primary importance. The use of natural materials for the removal of heavy metal has become a concern in all countries. Natural materials that are available in large quantities or certain waste from agricultural processes may have the potential to use as low-cost adsorbents, as they represent unused resources, widely available and environmentally friendly [1]. Many research projects have been carried out on the treatment of heavy metals from industrial wastewater [2–6]. It uses normal material to remove metals from different sites because it is available largely from agriculture processes and also because of their low price as adsorbent materials [7]. The materials which were used from nature and of low cost included carbonaceous materials, agricultural products, activated carbon and waste byproducts [8–10] and they were used as substitutes for some expensive materials. This is because of the technicalities and the cost involved in the process of precipitation, ion exchange, solvent extraction,

liquid membrane, and others to remove heavy metals from industrial wastewater [11–15]. Therefore, materials of biological origin were used to remove these metals [16]. All these sources had their limitations and were able to remove only one or two materials.

Henna, a tall shrub or small tree, is glabrous multi-branched with spine-tipped branchlets. Leaves are opposite, subsessile, elliptical, and broadly lanceolate, acuminate, having depressed veins on the dorsal surface. This study aims at investigating the adsorption potential of carbon prepared from henna leaves for the removal of Cr(VI) and Cu(II) ions from aqueous solutions.

2. Materials and Methods

2.1. Preparation of Adsorbent. Leaves of henna were collected from nearby agricultural field in Salem District, Tamil Nadu. Leaves of Henna were washed thoroughly with double distilled water and then dried at 80°C for about 36 h. Finally, the dried leaves were ground in clean electric mixer and stored in a clean plastic bag. Then the henna leaves powder was activated by the addition of concentrated sulphuric acid (1 : 1)

and the excess acid was removed by washing with double-distilled water. Finally, acid activated-carbon was kept in hot-air oven at 110°C for 24 h.

2.2. Preparation of Adsorbate. The aqueous solutions of Cr(VI) and Cu(II), prepared from potassium dichromate and copper nitrate of AR grade, respectively, were procured from Nice Chemicals Private Limited, Kochi, Kerala, India. Stock solutions were prepared for 1000 ppm concentration. The required concentration of aqueous solution was prepared from the stock solution. The pH of the aqueous solution was adjusted by using 0.1 M HCl or 0.1 M NaOH. The concentration of Cr(VI) was determined by diphenylcarbazide method [17]. The concentration of Cu(II) was determined by 8-hydroxyl quinoline method [18].

2.3. Effect of Contact Time. 250 mL Erlenmeyer flasks with 100 mL of adsorbate solution were prepared. Initial concentrations of samples were measured to be 50 ppm. 0.3 g of adsorbent, having a particle size of 630 μm , was measured and added to each of the conical flasks. pH of the solution was adjusted at 6. The flasks were then agitated at 250 rpm using an orbital shaker at $35 \pm 2^\circ\text{C}$. They were removed from the shaker for the determination of residual adsorbate concentration one after the other at 10, 20, 30, 40, 50, 60, 90, and 120 min. The samples were filtered and the final adsorbate concentrations were measured by UV-V spectrophotometer (Elico SL 159). The experiments were repeated three times, and the results given were their average. The percentage removal of metal ions by Henna leaves was calculated by the following equation:

$$\text{Metal Removal \%} = \left\{ \frac{(C_0 - C_e)}{C_0} \right\} \times 100\%, \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations (ppm) of metal ions in solution, respectively.

The adsorption capacity of metal ions by henna leaves was calculated by the following equation:

$$\text{Adsorption capacity } q \left(\frac{\text{mg}}{\text{g}} \right) = \left\{ (C_0 - C_e) \times \frac{V}{m} \right\}, \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations (ppm) of metal ions in solution respectively, V is the volume of solution and m is the quantity of adsorbent.

2.4. Effect of Initial Metal Concentration. 250 mL Erlenmeyer flasks with 100 mL of Cr(VI) and Cu(II) solutions were arranged. All samples were adjusted to the pH value of 6. 50 to 100 ppm (50, 60, 70, 80, 90 and 100 ppm) of solution containing initial adsorbate concentrations were prepared and numbered. 0.3 g of adsorbent, having a particle size of 630 μm , was measured and added to each of the conical flasks. The conical flasks were agitated at 350 rpm at $35 \pm 2^\circ\text{C}$ for 90 min. The samples were filtered and the final adsorbate concentrations were measured.

2.5. Effect of pH. 250 mL Erlenmeyer flasks with 100 mL of 100 ppm Cr(VI) and Cu(II) solutions were used. The samples

were adjusted to pH 1–9 by using 0.1 N sodium hydroxide (NaOH) or 0.1 N hydrochloric acid (HCl). 0.3 g of adsorbent, having a particle size of 630 μm , was measured and added in each flask. The flasks were agitated at 350 rpm at $35 \pm 2^\circ\text{C}$ for 90 min. Then the samples were filtered and the final adsorbate concentrations were measured.

2.6. Effect of Adsorbent Dose. 250 mL Erlenmeyer flasks with 100 mL of 100 ppm Cr(VI) and Cu(II) solutions were arranged. All samples were adjusted to an optimum pH value of 6. 0.3 to 0.7 g (in increments of 0.1 g) of adsorbent and were measured and added to the samples. The particle size of adsorbent was 630 μm . The conical flasks were agitated at 350 rpm at $35 \pm 2^\circ\text{C}$ for 90 min. The samples were filtered and the final adsorbate concentrations were measured.

3. Results and Discussion

3.1. Effect of Contact Time. Figures 1(a) and 1(b) indicate the effect of contact time on removal of cation ions Cr(VI) and Cu(II). The effect of contact time was studied in the range of 10, 20, 30, 40, 50, 60, 90, and 120 min. It was found that equilibrium time to remove these metal ions was 90 min. The results showed that the removal percentage order at equilibrium was Cu(II) > Cr(VI). These results are important, as equilibrium time is one of the important parameters in adsorption, and the time consumed for industrial wastewater disposal should be considered.

3.2. Effect of Initial Metal Ion Concentration. The effect of initial metal ion concentration on percentage metal removal is also shown in Figures 1(a) and 1(b). The concentrations in the range from 50 ppm to 100 ppm for the metal ions have been studied. The removal of metal ions by henna leaves was found to increase with increase in initial metal concentration. This was due to the increase of metal ions concentration which was completed on the effective site as this may be a limited active site for adsorbent material. Therefore, more metal ions were left unabsorbed in solution at higher concentration levels.

3.3. Effect of pH. Effect of pH on process of adsorption movement on henna leaves was studied in the range from 1 to 9 (Figures 2(a) and 2(b)). It was noticed that the ability of removing chromium and copper by adsorbent depends on pH of solution and this depends on the ion state and nature of material. In low pH value, binding sites are generally protonated or positively charged (by the hydronium ions). Thus, repulsion occurs between the metal cation and the adsorbent at a higher pH value; binding sites start deprotonating and make different functional groups available for metal binding. In general, cation binding increases as pH increases [17, 19]. The biosorption of Cr(VI) was found to depend on the pH of the metal solution. Biosorption capacity was found to decrease with an increase in the pH, maximum adsorption being observed at a pH of 7 [19]. It is well known that the dominant form of Cr(VI) at this pH is HCrO_4^{4-} . Increasing the pH will shift the concentration of HCrO_4^{4-} to other forms,

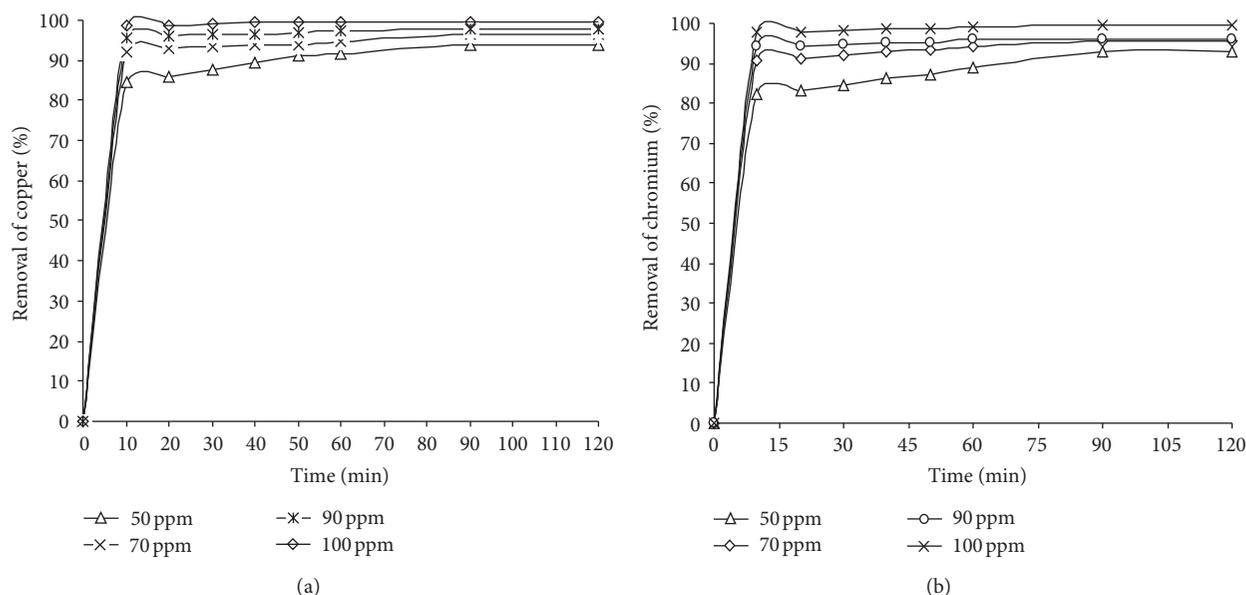


FIGURE 1: (a) Effect of contact time on the removal of copper by adsorption of the henna leaves at initial concentrations of 50 ppm, 70 ppm, 90 ppm, and 100 ppm, pH 7, and 1 g adsorbent dose. (b) Effect of contact time on the removal of chromium by adsorption of the henna leaves at initial concentrations of 50 ppm, 70 ppm, 90 ppm, and 100 ppm, pH 7, and 1 g adsorbent dose.

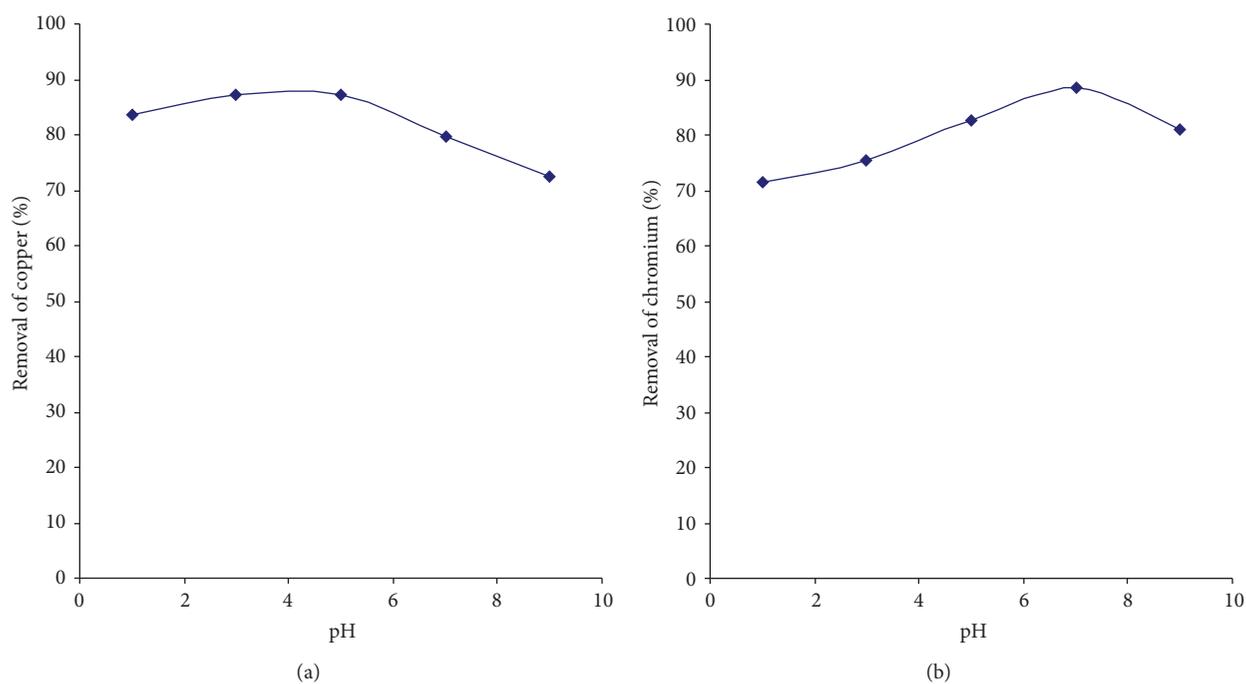


FIGURE 2: (a) Effect of pH on copper adsorption by henna leaves at an initial concentration of 100 ppm, 90 min, and 1 g adsorbent dose. (b) Effect of pH on chromium adsorption by henna leaves at an initial concentration of 100 ppm, 90 min, and 1 g adsorbent dose.

CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$. It can be concluded that the active form of Cr(VI) that can be absorbed by henna leaves is HCrO_4^- .

The experiments were carried out at different pH shows that there was a change in the quantity of adsorbed copper ions on the solid phase of henna leaves over the entire pH range from 1 to 9 as shown in Figures 2(a) and 2(b). This

indicates the strong force of interaction between the copper ions and the henna leaves powder that H^+ ion could influence the adsorption capacity. Here the interaction is more at pH 7 due to the competence of acidic H^+ ion with metal cation for the sorption sites. The adsorption of metal ions on the henna leaves powder involves ion exchange mechanism [17].

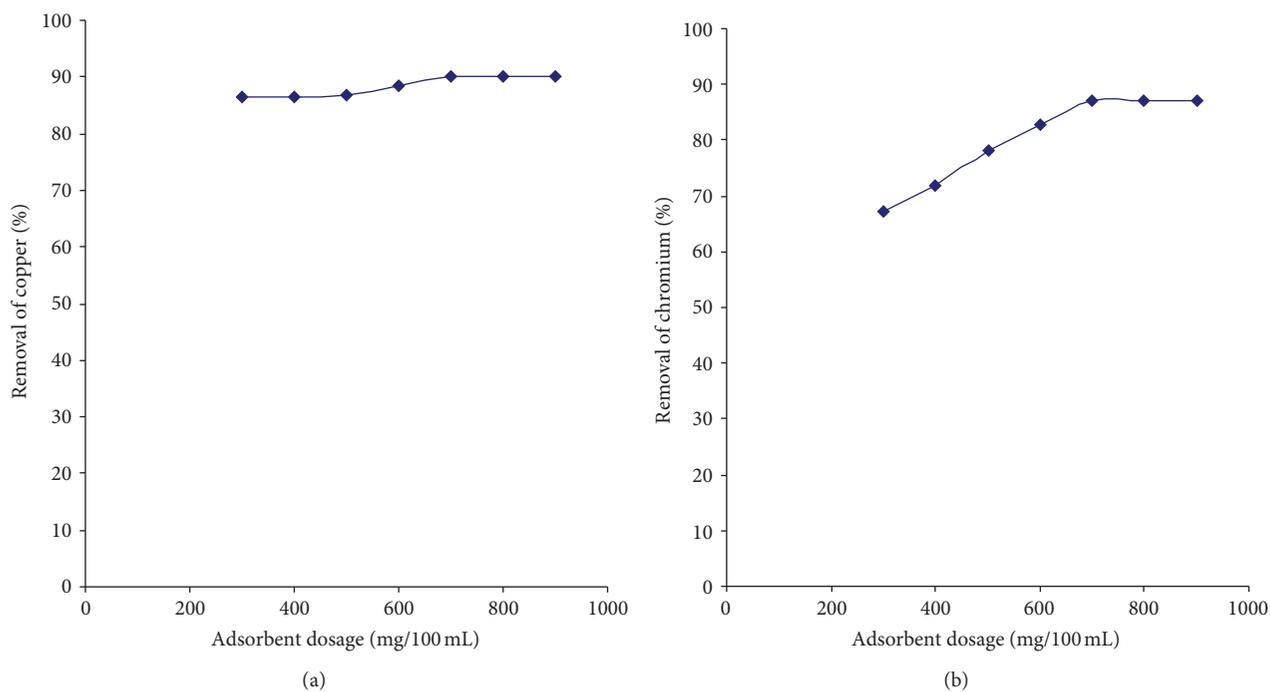


FIGURE 3: (a) The effect of variation of adsorbent dosage on copper adsorption by henna leaves an initial concentration of 100 ppm, 90 min, and pH 7. (b) The effect of variation of adsorbent dosage on chromium adsorption by henna leaves an initial concentration of 100 ppm, 90 min, and pH 7.

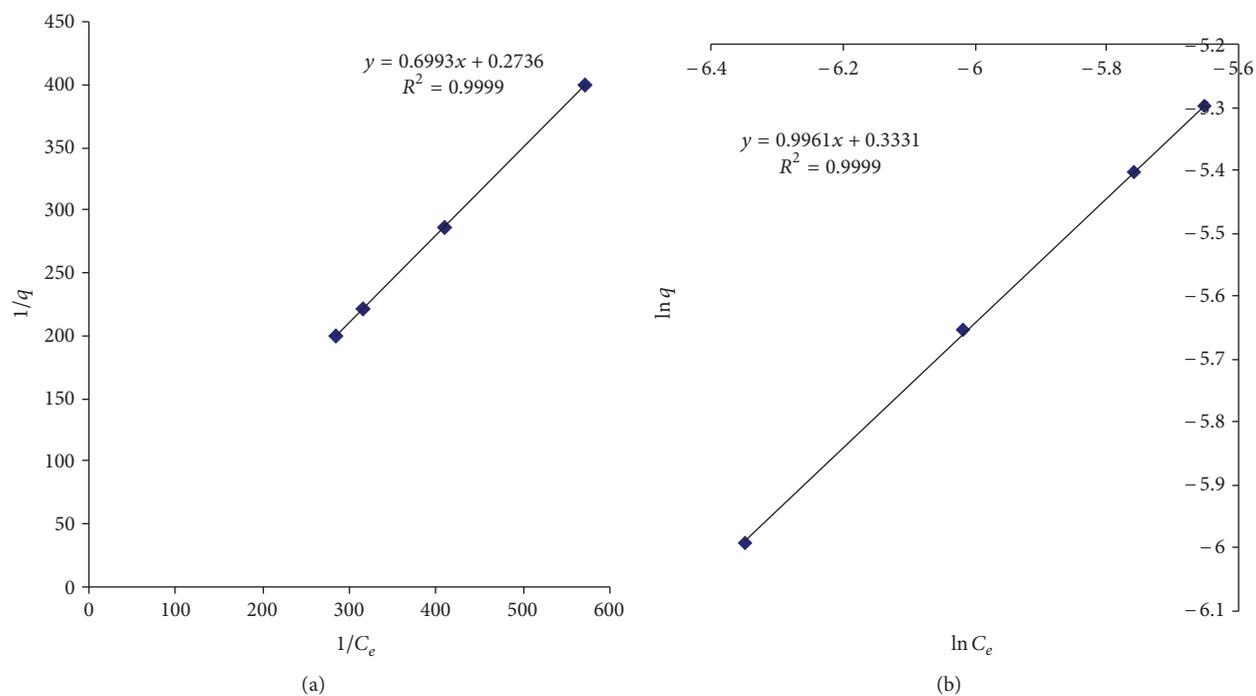


FIGURE 4: (a) Langmuir isotherm for copper adsorption using henna leaves. (b) Freundlich isotherm for copper adsorption using Henna leaves.

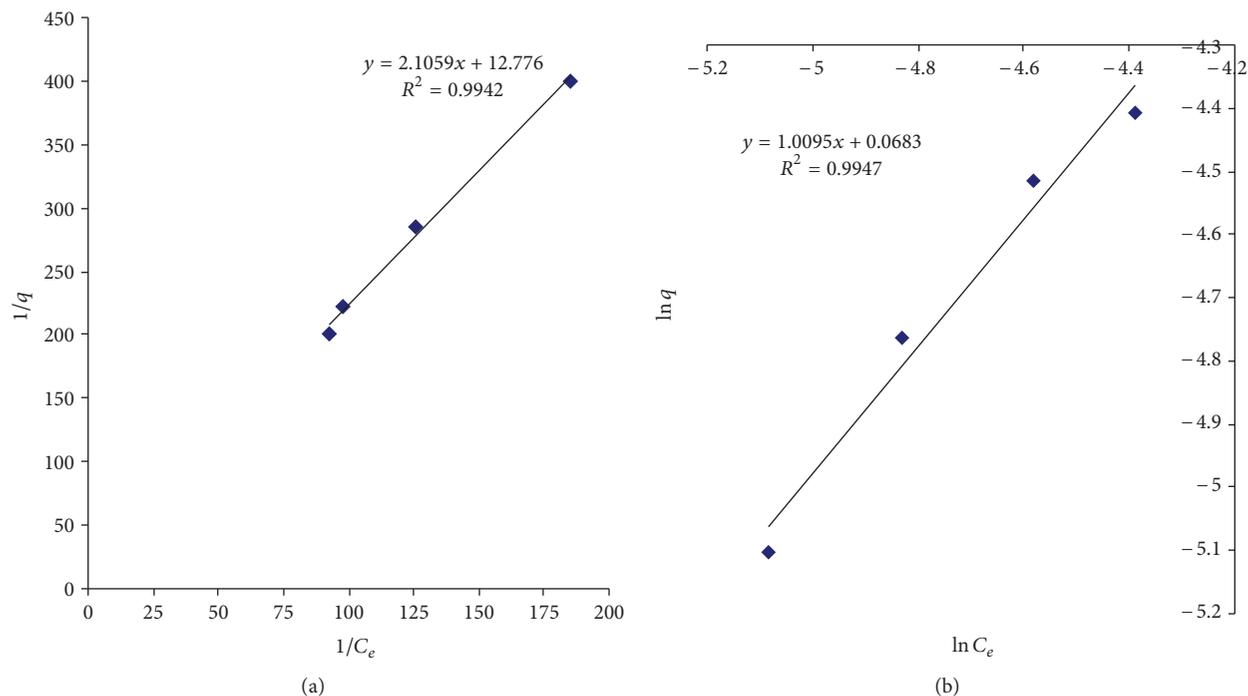


FIGURE 5: (a) Langmuir isotherm for chromium adsorption using henna leaves. (b) Freundlich isotherm for chromium adsorption using henna leaves.

3.4. Effect of Adsorbent Dosage. The effect of adsorbent dosage of henna leaves with an initial concentration of 100 ppm taking the range from 0.3 g to 0.7 g was studied. It was noticed that the mass of the adsorbent material increases the ability of removal as in Figures 3(a) and 3(b) which represented the amount of the adsorbent at saturation stage and also depends on the physical properties of the henna leaves like surface area and iodine number, in general. Also, from Figures 3(a) and 3(b), it can easily be inferred that the percent removal of metal ions increases with the increasing quantity of henna. This is due to the greater availability of the exchangeable sites or surface area at higher dose of the adsorbent. These results are in agreement with previous studies on many other adsorbents [9, 18].

3.5. Adsorption Isotherms. Among various plots employed for analyzing the nature of adsorbate-adsorbent interaction, adsorption isotherm is the most significant. The results of adsorption studies of Cr(VI) and Cu(II) at different concentrations ranging from 50 to 100 ppm on a fixed amount of adsorbent are expressed by two of the most popular isotherm theories, namely, Freundlich and Langmuir isotherms.

Freundlich equation is given by

$$q = K_f C_e^{1/n}, \quad (3)$$

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

TABLE 1: Langmuir and Freundlich constants for copper and chromium adsorption using henna.

S. no.	Metal ion	Langmuir constants		Freundlich constants	
		q_{\max} (mg/g)	b	K_f	$1/n$
(1)	Copper	3.650	0.391	2.684	1.004
(2)	Chromium	0.078	6.070	1.099	1.009

Langmuir equation is given by

$$q = q_{\max} \frac{bC_e}{1 + bC_e}, \quad (4)$$

$$\frac{1}{q} = \frac{1}{q_{\max}} bC_e + \frac{1}{q_{\max}},$$

where q is adsorbent capacity (mg/g), C_e is equilibrium concentration of adsorbate in solution (ppm), q_{\max} , b , K_f , and n are constants. In the above equations, the values of constants in the Freundlich equation, obtained by least squares fitting of the data on $\ln q$ and $\ln C_e$ (Figures 4(b) and 5(b)) are tabulated in Table 1. The values of the parameters, evaluated by the least square fitting of the data on $1/q$ versus $1/C_e$ (Figures 4(a) and 5(a)), are tabulated in Table 1.

4. Conclusions

The result of batch adsorption clarifies the percentage of removal of metal ions from their wastewater solution. The

initial concentration of metal ions vary from 50 ppm to 100 ppm with experimental conditions at time of contact, pH, initial concentration, and the weight of loading material. The batch adsorption result showed that removal percentage was higher for Cu(II) than Cr(VI). Also, carbon prepared from Henna leaves was found to be a promising adsorbent for the removal of metal cations from mixed metal ions solution, representing an effective and clean environment.

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