Chemistry Research Journal, 2018, 3(4):193-199

Available online www.chemrj.org

ISSN: 2455-8990
CODEN(USA): CRJHA5

Research Article

REMOVAL Of Cr(VI) AND Zn (II) IONS FROM AQUEOUS SOLUTION BY CARBON DERIVED FROM HENNA LEAVES

Neama A. Sobhy [1*], Rania M. Mohsen[2]

[1]Chemistry Department, Sanitary and Environmental Engineering Institute, Housing and Building National Research Center, Giza, Egypt
[2]Chemical Engineering Department, Faculty of Engineering, Cairo University, Giza, Egypt

Abstract In this study, the adsorption behavior of carbon prepared from leaves of henna, with respect to Cr(VI), and Zn(II) ions, has been studied in order to consider its application to the purification of metal finishing wastewater. The batch method was employed: parameters such as pH, contact time, adsorbent dosage and initial metal concentration were studied. The influence of the pH of the metal ion solutions on the uptake levels of the metal ions by the different adsorbents used were carried out between pH 2 and pH 10.
The highest percentage of metal removal was achieved in the adsorbent dosage of 0.7 g/l and at an initial concentration of 100 ppm metal ion. Adsorption parameters were determined using both Langmuir and Freundlich isotherms, but the experimental data were better fitted to the Langmuir equation than to Freundlich equation.
The potential of carbon prepared from henna leaves for the removal of these two solutions containing heavy metals was substantiated.

Keywords Adsorption behavior, Carbon prepared from henna leaves, Metal removal.

Introduction

Water pollution due to the disposal of heavy metals continues to be a great concern world wide. Consequently, the treatment of polluted industrial wastewater remains a topic of global concern since wastewater collected from municipalities, communities and industries must ultimately be returned to receiving waters or to the land [1].
Heavy metals pollution occurs in much industrial wastewater such as that produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the ceramic and glass industries. This wastewater commonly includes Cd, Pb, Cu, Ni and Cr [2].
Many research projects have been carried out on the treatment of heavy metals from industrial wastewater [3-7]. It uses normal materials to remove metals from different sites because it is available largely from agricultural processes and also because of their low price as adsorbent material [8].
The materials which were used from nature and of low cost included agricultural products, carbonaceous materials, waste byproducts and activated carbon [9-11] and were used as substitutes for some expensive materials. This is due to 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 [12-15].
Powdered leaves of henna is commonly used as cosmetic for staining palm, hands, hairs, and other body parts [16-17]. Henna leaves are aubsessible, elliptical, and broadly lanceolate, acuminate, having depressed veins on the

dorsal surface [18]. The leaves of this plant are used in the treatments of wounds, ulcers, cough, bronchitis, lumbago, rheumatagia, inflammations, diarrhea, dysentery, leucoderma, scabies, boils, anaemia, haemorrhages, fever, falling of hair and grayness hair [19].

This study aims at investigating the adsorption potential of carbon prepared from henna leaves for the removal of Cr(VI) and Zn(II) ions from aqueous solutions. The batch method was employed: parameters such as pH, contact time, adsorbent dose and initial metal concentration, were studied.

Materials and Methods

Preparation of Adsorbent

Leaves of henna collected from local garden in Cairo and washed with distilled water then dried at 90 ^oC for 36 hours. Dried leaves were ground in electric mixer and stored in plastic bag.

The henna leaves powder was activated by addition of concentrated sulphuric acid (1:1), then washed with double distilled water. Finally, the acid-activated carbon was kept in hot air oven at 130 ^oC for 24 hours.

Preparation of Adsorbate

The aqueous solutions of Cr(VI) and Zn(II) prepared from potassium dichromate and zinc nitrate of AR grade. Stock solutions were prepared for 1000 ppm concentration. The concentration required of aqueous solution was prepared from the stock solution. The pH of solution was adjusted by using 0.1 M HCL or 0.1 M NaOH.

Effect of Contact Time

100 ml of adsorbate solution initial concentration were measured to be 100 ppm, 0.6 g of adsorbent, with particle size 670 µm. pH of the solution was adjusted at 6. The flasks were then agitated at 200 rpm using an orbital shaker at 30 ± 2ºC. Using orbital shaker at 35 ± 2ºC, time 0- 120 min. The samples were filtered and the final adsorbate concentrations were measured by UV Spectrophotometer (ICE 3300, Thermo Scientific Ltd., UK). 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:

Metal removal % = $((C_o-C_e)/C_o) * 100$ % (1)

Adsorption capacity (mg/g) = $((C_o-C_e)*V/m)$ (2)

Effect of pH

100 ml of 100 ppm Cr(VI) and Zn(II) were used, the solution adjusted to 2-10 using 0.1 N NaOH and 0.1 N HCL. 0.6 g of adsorbent having particle size 670 mm was measured and added to each flask and agitated at 300 rpm at 30 ± 2^{o}C for 100 min. Then the samples were filtered. Finally, the final adsorbate concentrations were measured.

Effect of Adsorbent Dose

100 ml of 100 ppm Cr(VI) and Zn(II) adjusted to optimum pH 7. 0.4 to 0.8 g (increments 0.1 g) of adsorbent were measured and added to the samples., agitated at 300 rpm at 30 ± 2 ^oC for 100 min. The samples were filtered and the final adsorbate concentrations were measured.

Effect of Initial Metal Concentration

100 ml of Cr(VI) and Zn(II) were adjusted at pH 7, 50 to 100 ppm (50, 60, 70, 80, 90 and 100 ppm) of solution containing initial adsorbate concentrations were prepared. 0.6 gm of adsorbent have particle size of 670 µm was measured and added to each of the conical flasks. The flasks were agitated at 300 rpm at 30 ± 2 ^oC.

Results and Discussion

Effect of Contact Time

Figures 1(a) and 1(b) indicate the effect of contact time on removal of cation ions Cr(VI) and Zn(II). The effect of contact time was studied in the Range (0-120 min.). It was found that equilibrium time to remove the metal ions was

100 min. The results showed that the removal percentage order at equilibrium was Zn(II) > Cr(VI). As equilibrium time is one of the important parameters in adsorption.

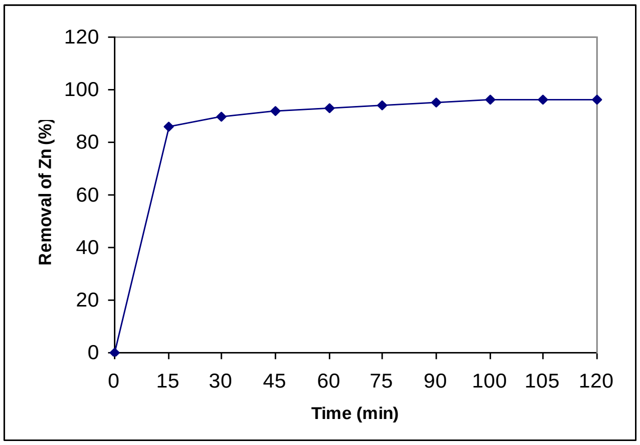

Figure (1a): Effect of contact time on the removal of Zn(II) by adsorption of the henna leaves

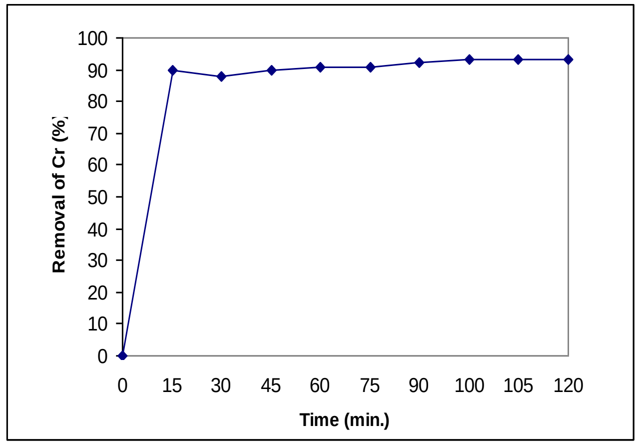

Figure (1b): Effect of contact time on the removal of Cr(VI) by adsorption of the henna leaves

Effect of pH

The pH of the solution has a significant impact on the uptake of heavy metals since it determines the surface charge of the adsorbent [20]. Effect of pH on adsorption movement on henna leaves was studied in the range from 2 to 10 as shown in Figures 2(a) and 2(b).

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 higher pH value, binding sites start deprotonating and make different functional groups available for metal binding. In general, cation binding increases as pH increases [21-23]. Maximum adsorption being observed at a pH of 4 in case of Zn(II) and 7 in case of Cr(VI). These results are in agreement with previous studies on other adsorbents [24].

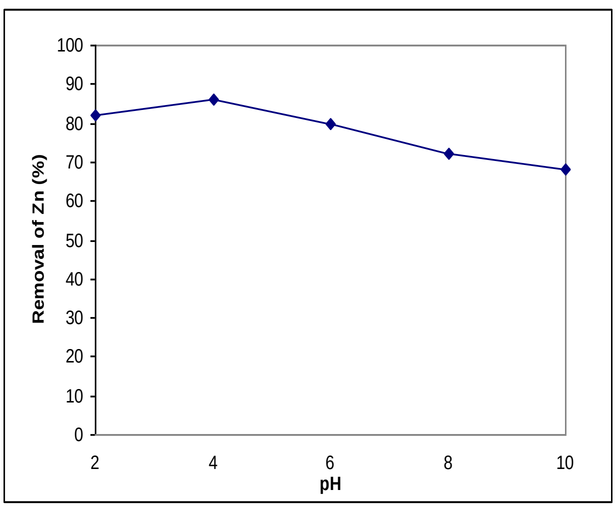

Figure (2a): Effect of pH on the removal of Zn(II) by adsorption of the henna leaves

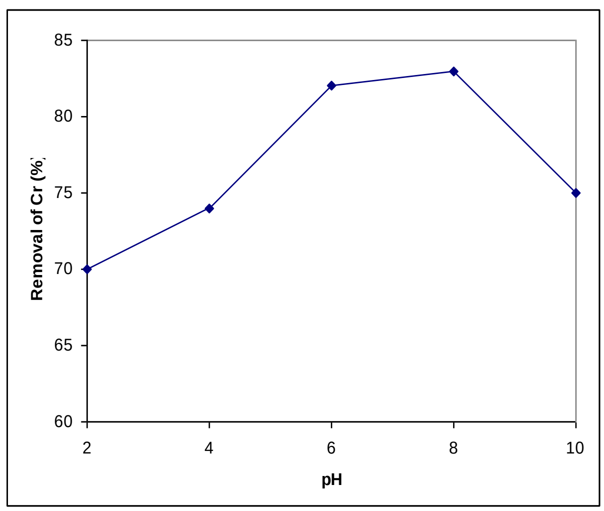

Figure (2b): Effect of pH on the removal of Cr(VI) by adsorption of the henna leaves

Effect of Adsorbent Dosage

The effect of adsorbent dosage of henna leaves with an initial concentration of 100 ppm taking the range from 0.4 g to 0.8 g was studied. It is observed that the mass of the adsorbent material increases the ability of removal as shown in figures 3(a), 3(b) which represented the amount of the adsorbent saturation stage Also, from figures 3(a), 3(b) it can be noticed that the percent removal of metal ions increases by increasing henna quantity, this is because 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 [11].

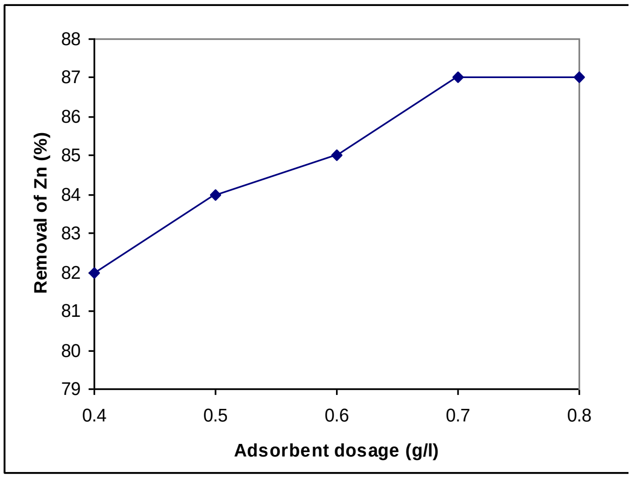

Figure (3a): Effect of adsorbent dosage on the removal of Zn(II) by adsorption of the henna leaves

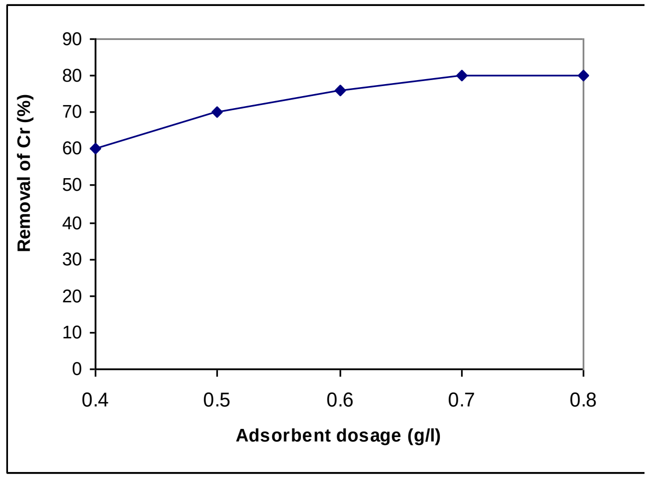

Figure (3a): Effect of adsorbent dosage on the removal of Cr(VI) by adsorption of the henna leaves

Effect of Initial Metal Concentration

The effect of initial metal ion concentration on percentage metal removal is also shown in figures 4(a) and 4(b). The concentrations in the range from 40 ppm to 100 ppm for metal ion studied. The removal of metal ions by henna leaves was increase with increase in initial metal ion concentration. This is due to the increase of metal ions concentrations which was completed in the effective site as this may be a limited active site for adsorbent material.

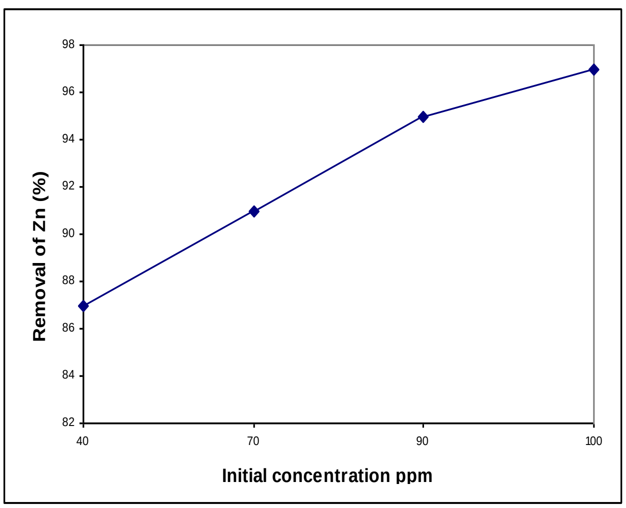

Figure (4a): Effect of initial metal concentration on the removal of Zn(II) by adsorption of the henna leaves

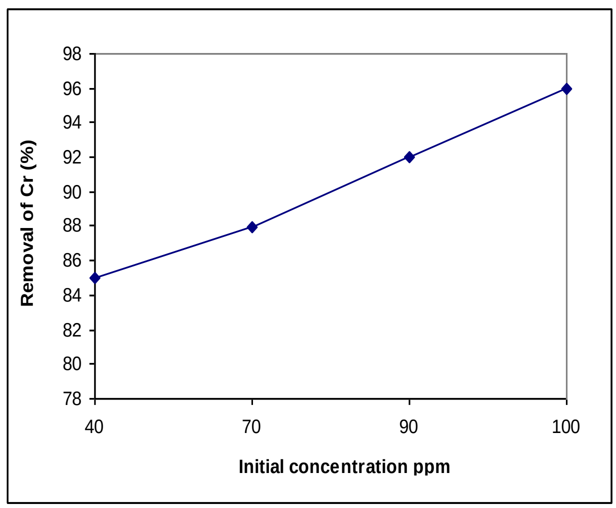

Figure (4a): Effect of initial metal concentration on the removal of Cr(VI) by adsorption of the henna leaves

Adsorption Isotherm

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase since the adsorption isotherms are important to describe how adsorbates will interact with the adsorbents so are critical for design purposes; therefore, the correlation for equilibrium data using an equation is essential for practical adsorption operation [25].

Two isotherm equations were adopted in this study as follows:

Freundlich Isotherm Equation

The Freundlich sorption isotherm, one of the most widely used mathematical descriptions, gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies.

$Qe = k. C_e^{\ 1/n}$

and in linearized form is :

$\text{Log } Q_e = \log\ k + (1/n) \log C_e$

Where ”Ce” is the equilibrium concentration in mg/l, ”Qe” amount of adsorbate adsorbed per unit weight of adsorbent (mg/g), ”k” is a parameter related to the temperature and ”n” is a characteristic constant for the adsorption system under study. The plots of log Qe against log Ce are shown in Fig. 5(a) and 5(b), the adsorption of chromium and zinc ions onto the different adsorbents give a straight line; values of “n” between 2 and 10 show good adsorption [26]. The Freundlich isotherm constants and their correlation coefficients R^2 are listed in Table (1).

Langmuir Isotherm Equation

The Langmuir equation is based on the assumptions that maximum adsorption corresponds to a saturated mono-layer of adsorbent molecules on the adsorbent surface, that the energy of adsorption is constant [27]

The Langmuir equation is defined as:

$Qe = (b.Q_m.C_e)(1+bC_e)$ (3)

And in linearized form is:

$C_e/Q_e = (C_e/Q_m) + (1/(bQ_m))$ (4)

Where “Q_m” and “b” are Langmuir constants related to the adsorption capacity and sorption energy, respectively. “Ce” is the equilibrium concentration in mg/l, and “Qe” is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). The plots C_e/Q_e against C_e are shown in Fig. 6(a) and 6(b). The adsorption of chromium and zinc ions on different adsorbents give a straight line. It is clear that the linear fit is fairly good and enables the applicability of Langmuir model. The Langmuir isotherm constants and their correlation coefficients R^2 are listed in Table (1).

As can be observed, experimental data were better fitted to Langmuir equation, and therefore it is more suitable for the analysis of kinetics.

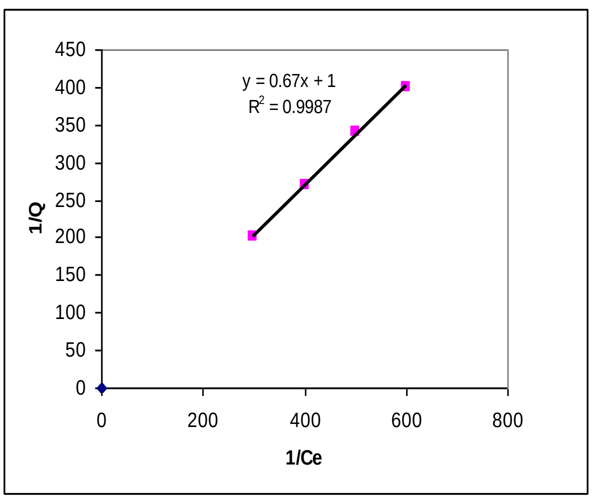

Figure (5a): Langmuir isotherm for zinc adsorption using henna leaves

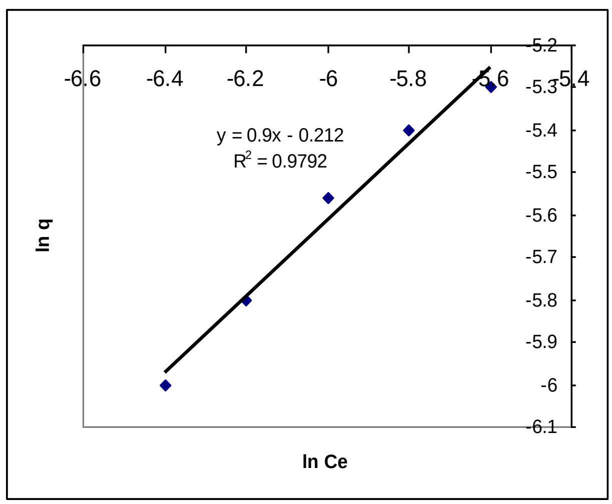

Figure (5b): Freundlich isotherm for zinc adsorption using henna leaves.

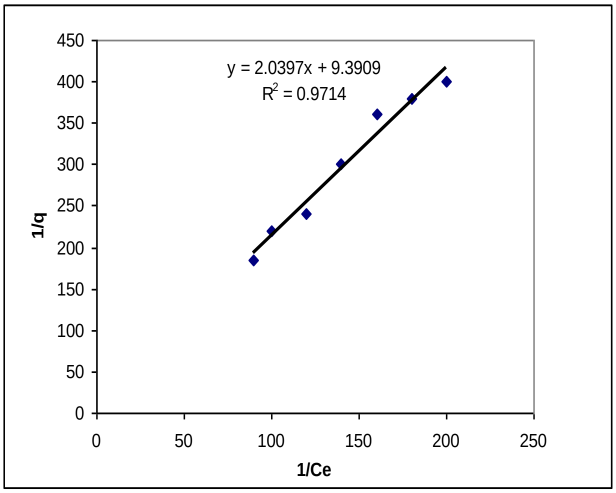

Figure (6a): Langmuir isotherm for Chromium adsorption using henna leaves.

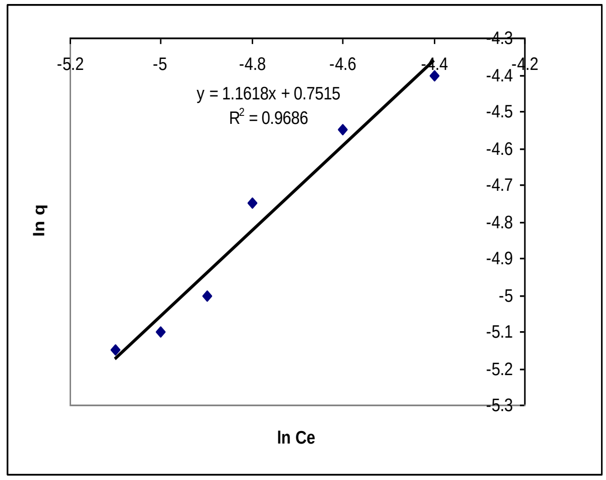

Figure (6b): Freundlich isotherm for Chromium adsorption using henna leaves.

Table 1: Langmuir and Freundlich constants for zinc and chromium adsorption using henna

No.	Metal ion	Langmuir Constants		Freundlich Constants	
		q_{max} (mg/g)	b	k	n
1	Zinc	1	1.49	0.809	1.11
2	Chromium	0.106	4.63	2.12	0.86

Conclusion

In this study, carbon was prepared from leaves of henna (Alba lam), and used to study adsorption of Cr(VI) and Zn(II) from the aqueous solutions. The batch method was employed. Parameters such as pH, contact time, adsorbent dosage and metal ion concentration were studied. The metal concentration of metal ions vary from 40 to 100 ppm. The batch adsorption results showed that the percentage of removal was higher for zinc than chromium. Also, carbon prepared by henna leaves was found to be a good adsorbent for the removal of heavy metal cations.

The Langmuir isotherm better fitted to experimental data. Since the correlation coefficient for the Langmuir isotherm was higher than that of the Freundlich for both metals.

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