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Removal of Heavy Metals Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+} and Cd^{2+} from Aqueous Solutions by Using Eichhornia Crassipes

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Abstract

The adsorption capacity of Eichhornia Crassipes towards metal ions such as Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+} and Cd^{2+}, was studied. The adsorption capacity was investigated by batch experiments. The results showed that the removal percentages increased as the weight of sorbent increased, except for Fe^{3+} and Zn^{2+}. The effect of contact time was also studied and the results showed that the removal percentages increased as the contact time increased for Cr^{3+}, Zn^{2+} and Pb^{2+}, but for Fe^{3+}, Cu^{2+} and Cd^{2+} the removal decreased. The effect of pH of the solution was also studied and the removal percentages increased as pH increased. Also the effect of the initial concentration of metal ions was studied at four different concentrations (5, 10, 30, 50 mg/L); in case of metal ions (Cu^{2+}, Zn^{2+} and Cd^{2+}) the removal percentages increased by increasing initial concentration. But, for the other metal ions it decreased by increasing initial concentration over 30 mg/L.

The order of increasing removal percentages of metal ions at pH=4.86, initial concentration of metal ions 30 mg/L, and after four hours of shaking was: $Cu^{2+} < Cr^{3+} < Cd^{2+} < Zn^{2+} < Pb^{2+} < Fe^{3+}$.

Keywords: heavy metals, eichhornia crassipes, atomic absorption, spectrophotometer.

Introduction

Activated sludge is used as bioadsorbent for Cu^{2+}, Cd^{2+} and Ni^{2+}. Pretreatment with NaOH was found to improve the adsorption capacity of the sludge, whereas treatment with HCl reduces it [1]. Anaerobic sludge supplied from a wastewater treatment plant, acts as a novel biosorbent, for Pb^{2+}, Cu^{2+}, Cd^{2+}, and Ni^{2+} removal from aqueous solutions [2]. Rice husk, a surplus agricultural byproduct, is used for the sorption of Cd^{2+} from aqueous solution. Some simple and low-cost

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chemical modifications resulted in increasing the sorption capacity of raw rice husk (RRH) have been studied [3]. Papaya wood was evaluated as a new biosorbent of heavy metal ions such as Cu^{2+}, Cd^{2+} and Zn^{2+} [4]. The sorption of lead, copper, cadmium, zinc and nickel by marine algal and characterization of biosorptive capacity were significantly affected by solution pH[5]. Coffee residues binding with clay as adsorbent (hereafter called CC-adsorbent) are utilized for removal of heavy metal ions in solution [6]. Cocoa shells (CS) have been identified as a very efficient natural sorbent to remove Pb^{2+} and other metal ions from acid soil leachates (ASL) [7]. Fungal biomass immobilized within a loofa sponge (FBILS) is used as a new biosorbent system to remove heavy metal ions such as Pb^{2+}, Cu^{2+} and $Zn^{2+}$from aqueous solution [8]. Calcined phosphate is a good adsorbent for the removal of Pb^{2+}, Cu^{2+}, and Zn^{2+} from solutions. The abundance of natural phosphate, its low price and non-aggressive nature towards the environment are advantages for its utilization in the point of view of wastewater and wastes clean up [9].

This study aims to use cheap and undesirable materials like eichhornia crassipes (which is an aquatic plant causing many problems in fresh water streams) to remove the heavy metal ions from waste water instead of the classical techniques that are difficulty controlled, and requiring mostly expensive equipments.

Experimental

Adsorbent material

The adsorbent material eichhornia crassipes was collected from fresh water streams.

The samples were collected from each location and stored in polyethylene bags and then transported to the laboratory in an icebox within the limited time.

The eichhornia crassipes plant was collected from its place within a clean plastic bag and was cut, washed with tap water followed by deionized water, dried at 65 ºC for 48 hours and ground by a mortar**.** The plant particles were sieved, and a certain size range from (0.25 – 0.75) mm was collected and stored in a plastic bag.

Chemicals

All chemicals used were high-grade chemicals from (Merck, BDH and Fisher) Companies.

1- Buffer solutions of pH equal to 4.01, 6.86 and 9.18 for calibration of the pH-meter.
2- Concentrated nitric acid 63%.
3- Individual standard solution for Fe^{3+} ion.
4- Individual standard solution for Cu^{2+} ion.
5- Individual standard solution for Zn^{2+} ion.
6- Individual standard solution for Pb^{2+} ion.
7- Individual standard solution for Cr^{3+} ion.
8- Individual standard solution for Cd^{2+} ion.
9- Sodium hydroxide pellets.

Chemical analysis

Determination of heavy metals

In flame atomic absorption a sample is aspired into a flame and atomized. A light beam is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed by the atomized element in the flame. For some metals, atomic absorption exhibits superior sensitivity over flame emission. Because each element has its own characteristic absorption wavelength, a source lamp composed of that element is used, which is called the Hollow Cathode Lamp. This makes the method relatively free from spectral or radiation interference. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range.

The instrument used in determination of heavy metals is the Atomic Absorption Spectrophotometer AA-6800 – SHIMADZU.

The method used for the determination of heavy metals was (3111B Direct Air-Acetylene Flame Method) edition 19 – 1995, Standard Method for the Examination of Water and Wastewater.

Effect of weight of eichhornia crassipes on the removal of the heavy metal ions

Multi-element standard solution containing (Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+} and Cd^{2+}) metal ions which concentration was equal to 30 mg/L, was prepared. The pH of the standard solution was adjusted to 4.86. To 50 mL of the multi-element standard, 0.1, 0.2, 0.3 and 0.4 g of the eichhornia crassipes were added in an Erlenmeyer flask, and the mixtures were shaken using a rotary shaker at about 100 rpm for 4 hours. After that the mixtures were filtered using a 0.45 µm filter paper. The filtrate and the multi-element standard were analyzed using an atomic absorption spectrophotometer.

Effect of contact time on the removal of the heavy metal ions

A multi-element standard solution was prepared. To 50 mL of each solution, 0.4 g of the eichhornia crassipes were added and the mixtures were shaken for 2, 4 and 8 hours, and analyzed using an atomic absorption spectrophotometer.

Effect of pH on the removal of the heavy metal ions

The prepared standard solutions, which had different pH values (2.06, 3.77and 4.86) were treated as previously and analyzed using atomic absorption spectrophotometer.

Effect of initial concentration of the heavy metal ions on the removal percentage

A series of multi-element standard solutions with concentrations of 5, 10, 30 and 50 mg/L were prepared. The solutions were treated as previously and analyzed using atomic absorption spectrophotometer.

Results and discussion

Effect of weight of eichhornia crassipes on the removal of heavy metal ions

The experiments were carried out with 0.1, 0.2, 0.3 and 0.4 g of the eichhornia crassipes added to a prepared standard solution (synthetic waste water); these four solutions were given the codes 1 EC, 2 EC, 3 EC and 4 EC, respectively. The effect of weight of sorbent eichhornia crassipes plant on the percent removal of Fe^{3+}, Pb^{2+}, Zn^{2+}, Cr^{3+}, Cu^{2+} and Cd^{2+} is shown graphically in Fig. 1. Inspection of the data obtained showed that:

1- Maximum percent removal was obtained for Fe^{3+} ion, which is nearly equal to 99.88%, but it decreased very slightly by increasing the weight of sorbent.

2- Minimum removal was obtained for Cu^{2+} ion, which is slightly increased by the increase in the weight of sorbent.

3- The removal of Zn^{2+} is very slightly decreased by the increase in the weight of sorbent.

4- The variation of maximum percent removal of metal ions with weight of eichhornia crassipes used as sorbent lies in the order Fe^{3+}> Pb^{2+}> Zn^{2+}>Cd^{2+}>Cr^{3+}> Cu^{2+}.

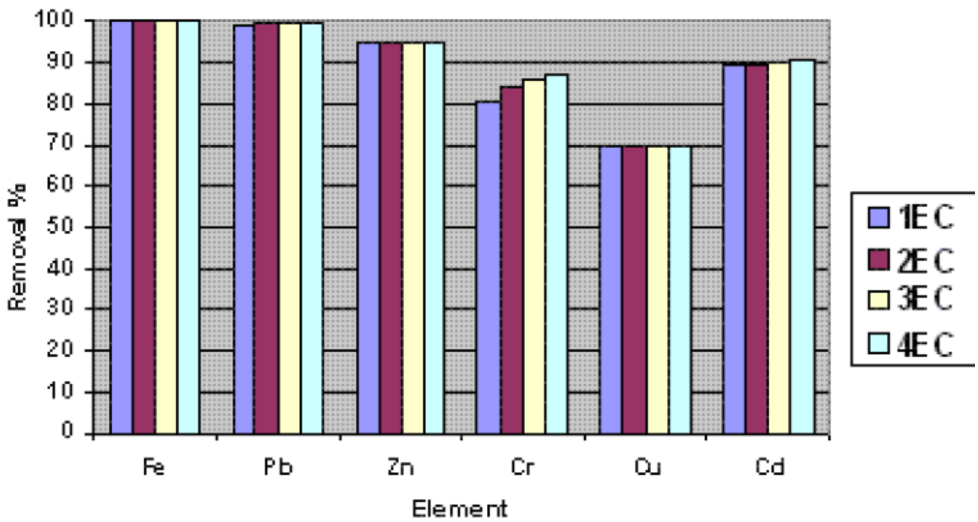

Figure 1. Effect of weight of eichhornia crassipes on the removal of heavy metal ions.

Effect of contact time on the removal of the heavy metal ions

Results of studies on the effect of contact time on the maximum removal of the metal ions under investigation, illustrated in Fig. 2, showed that there are two cases:

1-For Zn^{2+}, Pb^{2+} and Cr^{3+} the percent removal increases as the contact time of the metal ions with sorbent increases.

2-For Fe^{3+}, Cu^{2+} and Cd^{2+} the percent removal decreases as the contact time increases, being the maximum adsorption attained after 2 hours.

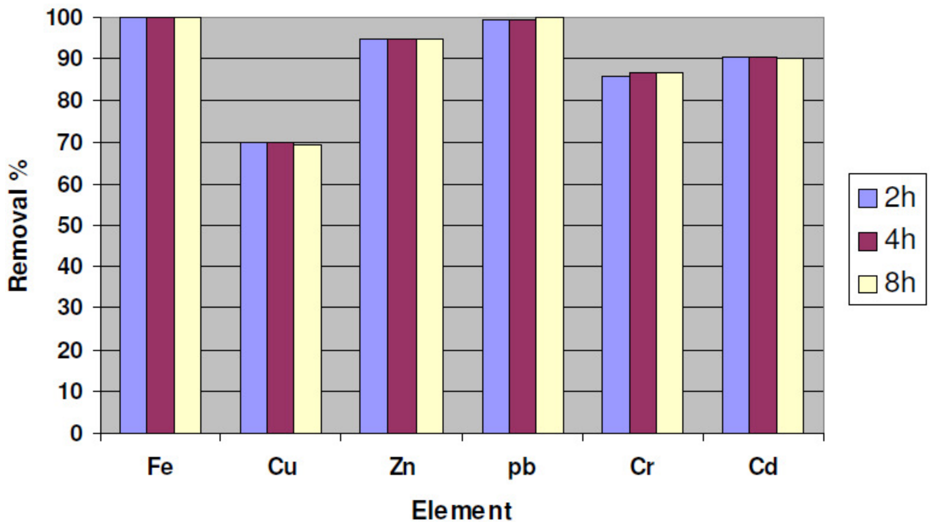

Figure 2. Effect of contact time on the removal of heavy metal ions.

Effect of pH on the removal of the heavy metal ions

Results present in Fig. 3 show that maximum removal takes place at pH 4.86, which indicates that the maximum adsorption affinities take place in moderately and slightly acidic medium.

Effect of initial concentration of the heavy metal ions on the removal percentage

The variation of percent removal with change in initial concentration of heavy metal ions showed no regular trend. For example, the percent removal of Zn^{2+}, Cu^{2+} and Cd^{2+} increases with increasing the initial concentration, and maximum adsorption is attained at the highest initial concentration (50 mg/L). On the other hand, the percent removal for Cr^{3+}, Fe^{3+} and Pb^{2+} increases with increasing the initial concentration, till reaching 30 mg/L, then decreases as the initial concentration increases up to 50 mg/L. The results are present in Fig. 4.

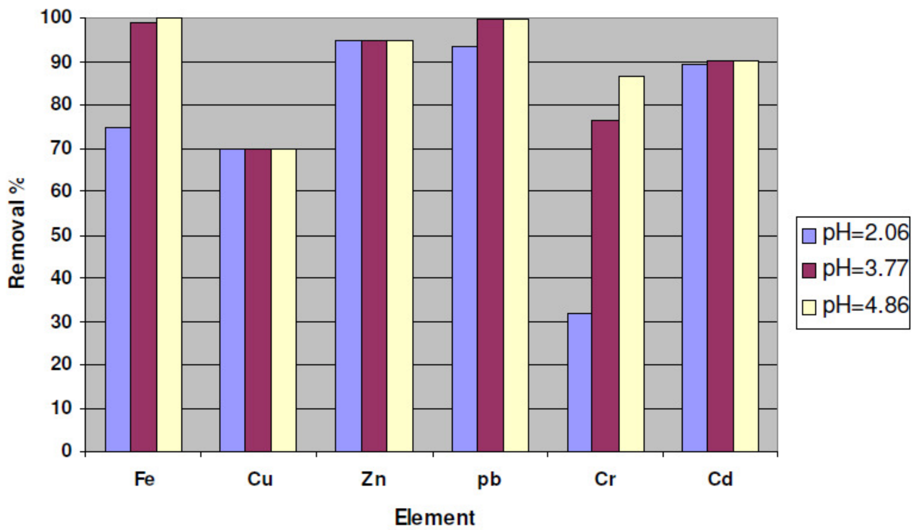

Figure 3. Effect of pH on the removal of heavy metal ions.

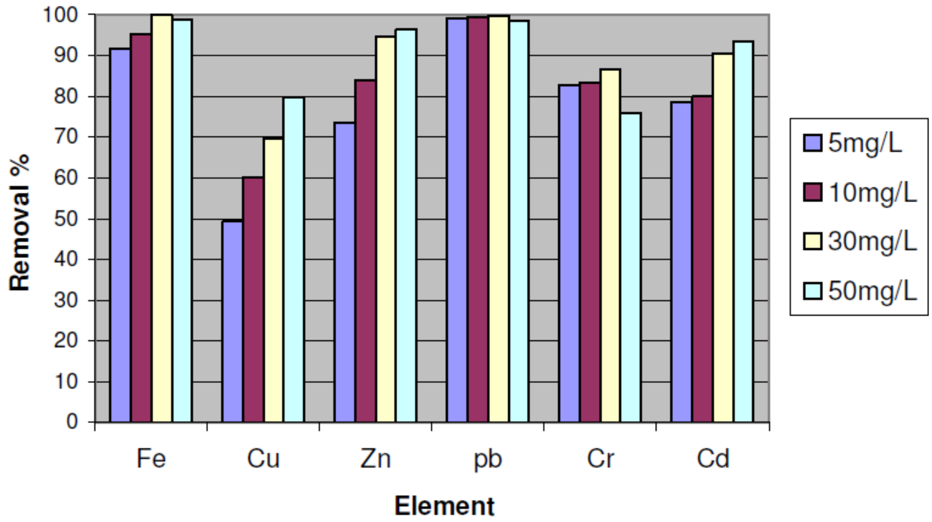

Figure 4. Effect of initial concentration of the heavy metal ions on the removal percentage.

Adsorption isotherms

Adsorption data for adsorbate concentration are most commonly described by adsorption isotherm, such as the Langmuir or Freundlish isotherms.

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. It is represented by the following equation:

$$1/q_e = 1/Q^0 + (1/b\ Q^0)\ (1/C) \qquad (1)$$

where C is the concentration of solute remaining in solution at equilibrium (mg/L), q_e is the amount of solute adsorbed per unit weight of solid adsorbent equilibrium time (mg/g) and Q^0 and b are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively. These values can be obtained from the plot of $1/q_e$ against (1/C).

The Langmuir linear relation is shown in representative examples in Fig.5 and 6.

The Freundlich adsorption isotherm was also applied for the adsorption of metal ions on eichhornia crassipes. The Freundlich equation is represented as:

$$q_e = K_f\ C\ 1/n \qquad (2)$$

or

$$\text{Log}\ q_e = \text{Log}\ K_f + 1/n\ \text{Log}\ C \qquad (3)$$

So, by plotting of Log q_e vs. Log C, the constant K_f and exponent (n) can be determined.

Freundlich linear relation is shown in representative examples in Figs.7 and 8.

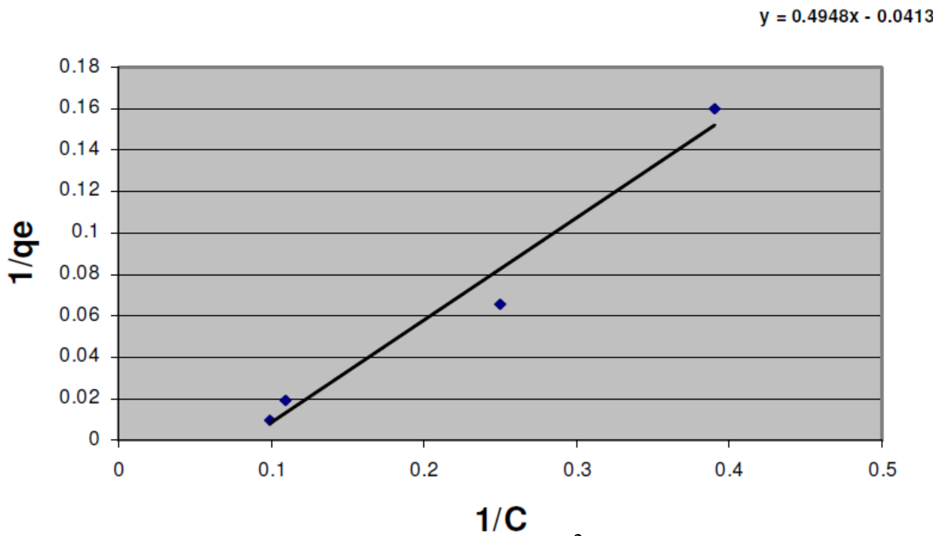

Figure 5. Langmuir curve for adsorption of Cu^{2+} ion on eichhornia crassipes.

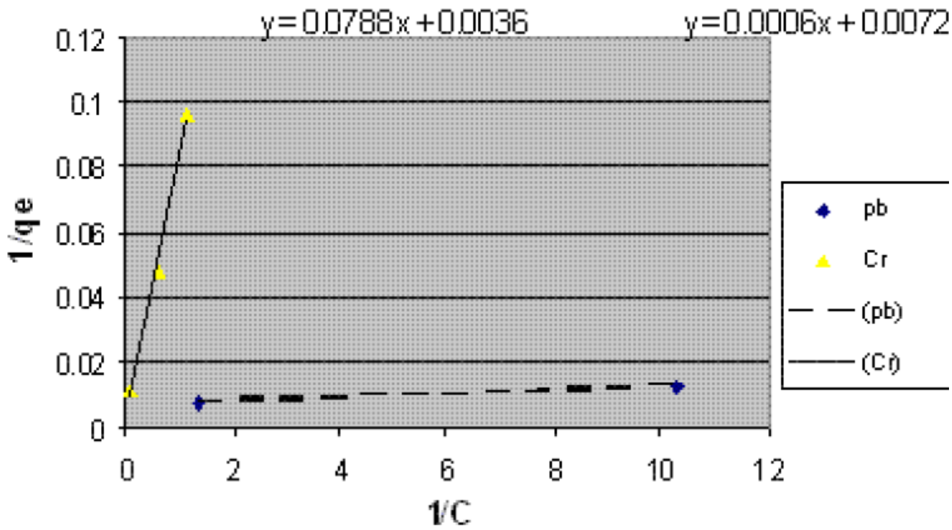

Figure 6. Langmuir curves for adsorption of Cr^{3+} and Pb^{2+} ions on eichhornia crassipes.

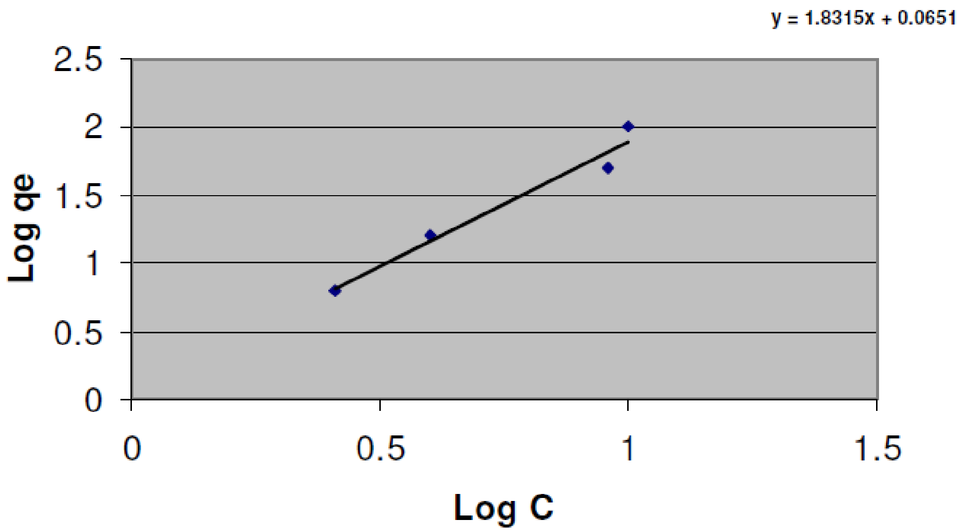

Figure 7. Freundlich curve for adsorption of Cu^{2+} ion on eichhornia crassipes.

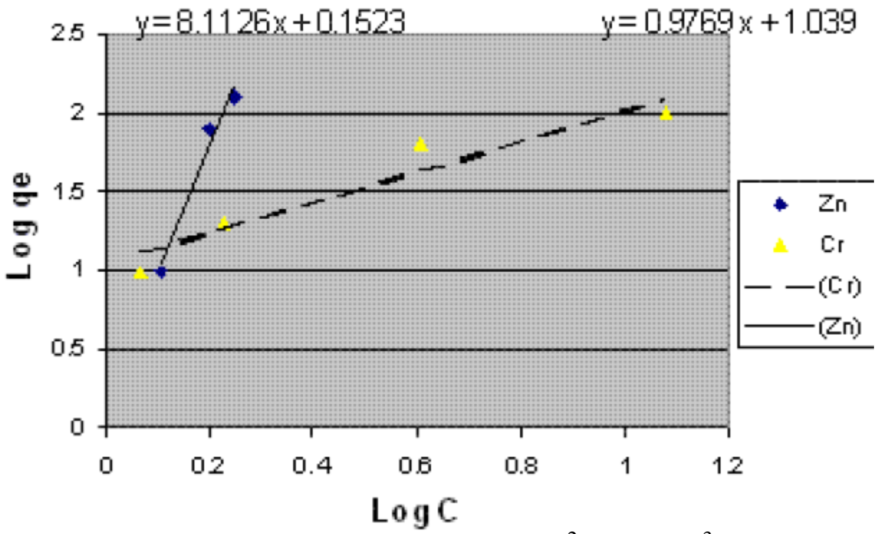

Figure 8. Freundlich curves for adsorption of Zn^{2+} and Cr^{3+} ions on eichhornia crassipes.

Conclusion

Based on the present investigation, it could be concluded that some low cost materials like eichhornia crassipes can be used efficiently in the removal of heavy metal ions (Pb^{2+}, Cu^{2+}, Cd^{2+}, Cr^{3+}, Zn^{2+} and Fe^{3+}) from aqueous solutions. The removal of heavy metal ions was pH dependent as the adsorption capacity increases with increasing the pH value of the solution, and at a particular pH the order of increasing the removal percentage was $Cu^{2+} < Cr^{3+} < Cd^{2+} < Zn^{2+} < Pb^{2+} < Fe^{3+}$.

The metal ions showed different behaviors towards adsorption on eichhornia crassipes by increasing the initial concentration of the metal ions. Adsorption of some metal ions was fitted with Langmuir isotherm, other ones with Freundlich isotherm, and the others were fitted with both the models. The experimental studies showed that eichhornia crassipes could be used as an alternative, inexpensive and effective material to remove high amounts of toxic heavy metal ions from wastewater.

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