Removal of Heavy Metals Fe3+, Mn2+, Zn2+, Pb2+ and Cd2+ from Wastewater by Using Rice Straw as Low Cost Adsorbent

Nagwa Nawar

*Department of Chemistry, Faculty of Science,
El-Mansoura University, Egypt*

Mohamed Ebrahim

*Water and Wastewater Company,
Dakahlia, Egypt*

Eslam Sami

*Water and Wastewater Company,
Dakahlia, Egypt*

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Abstract

The adsorption of some heavy metals from wastewater by rice straw was investigated. The adsorption capacity was investigated by batch experiments. The effect of weight of rice straw, contact time, initial metal ion concentration and pH on metal ions removal have been studied. The results showed that the removal percentages increased as the weight of sorbent increased, except for iron. The effect of contact time showed that the removal percentages increased as the contact time increased for all metals expect for iron the removal was decreased. The effect of pH showed that removal percentages increased as pH increased for all metals. In case of initial concentration changing for metal ions (Mn^{2+} and Cd^{2+}) the removal percentages decreased by increasing initial concentration but for Zn^{2+} it increased by increasing initial concentration until 40 mg/L then decreased. In case of Pb^{2+} the removal efficiency was constant until 40 mg/L then decreased by increasing initial concentration and for Fe^{3+} it was decreased until 60 mg/ L then increased. The adsorption data of metal ions have been described by the Freundlich and Langmuir isotherm models. The order of increasing efficiency of metal ions was Pb(II) > Cd(II) >Mn (II) > Zn(II) > Fe(III).

Keywords: *heavy metals, rice straw, wastewater, low cost adsorbent, Langmuir isotherm model.*

1. Introduction

Heavy metals are often discharged by a number of industries, such as metal plating facilities, mining operations and tanneries, this can lead into the contamination of freshwater and marine environment (Low and Lee, 2000; Bailey, Olin, Bricka and et al., 1999). Heavy metals are not biodegradable, often toxic at a certain concentration, and they tend to accumulate along the food chain, where human being is the last in the link, causing various diseases and disorders (Bailey et al., 1999). Lead and cadmium are deemed the most toxic heavy metals. Their poisoning in humans causes severe damage to the kidney, nervous system, bones and brain (ATSDR, 2007; WHO, 1992). Zinc and copper are essential elements for good health, but like all heavy metals, an excess of the metals can be harmful. For example, Zn excess can cause nausea, vomiting and hematemesis (Yamataka, Pringle, Wyeth, 1998).

There are so many methods available for the removal of metal ions from effluents. The technologies are divided into three categories, biological, chemical and physical.

Chemical methods involved coagulation combined with flotation and filtration, electro flotation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents, irradiation and electro chemical processes. These chemical technologies are very expensive have disposal problems. Physical methods are membrane filtration and adsorption. Membrane filtration processes are nanofiltration, reverse osmosis, electro dialysis etc. The major disadvantage of this membrane filtration is limited life time before membrane fouling occurs (Yadla, Sridevi1 and Lakshmi, 2012). Disadvantage of the biological method is requires large area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals and less flexibility in design and operation (Miyaji, Masuda and Suyama, 2010; Ajmal, Rao and Ahmad, 2011). The use of activated carbon and Ion exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated. The use of activated carbon and ion exchange resins is not suitable for developing countries due to their high capital and operational costs (Raji and Anirudhan, 1997). This has encouraged research into discovering materials that are both efficient and cheap as a replacement for costly current methods.

Adsorption is one of the most popular methods for the removal of pollutants from effluents since proper design of the adsorption process will produce high quality treated effluents. Adsorption is a separation process in which certain components of the fluid phase are transferred to the surface of the solid adsorbents. Most adsorbents are highly porous materials, and adsorption takes place primarily on the walls of the pores or at the specific sites inside the particle. Separation occurs because differences in molecular weight, shape, or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules (Yadla, Sridevi1 and Lakshmi, 2012).In general, a adsorbent can be assumed as “low cost” if it requires little processing, is abundant in nature, or is a by-product or waste material from (Bailey, Olin, Bricka and et al, 1999). Agricultural waste materials have carboxyl, hydroxyl, sulfate, phosphate, and amino groups that can bind metal ions. The adsorption of heavy metals by these materials might be attributed to their proteins, carbohydrates, and phenolic compounds (Bulut and Tez, 2007).

Agricultural waste materials such as polymerized onion skin (Kumar and Dara, 1981), rice husks (Khalid and Ahmad, 1999), some simple and low-cost chemical modifications resulted in increasing the sorption capacity of raw rice husk (RRH) have been studied (Kumar and Bandyopadhyay, 2006). Sawdust (Doris, Zhang, Shukla and et al, 2000; Ajmal, Khan and Ahmad, 1998), wheat bran (Bulut and Baysal, 2006) have been studied to investigate their affectivities in binding heavy metal ions.Papaya wood was evaluated as a new biosorbent of heavy metal ions such as Cu2+, Cd2+ and Zn2+ (Saeed, Akhter and Iqbal, 2005). Coffee residues binding with clay as adsorbent (hereafter called CC-adsorbent) are utilized for removal of heavy metal ions in solution (Boonamnuayvitaya, Chaiya, Tanthapanichakoon and Jarudilokkul, 2004). Cocoa shells (CS) have been identified as a very efficient natural sorbent to remove Pb2+ and other metal ions from acid soil leachates (ASL) (Meunier, Blais and Tyagi, 2004).Eichhornia Crassipes (which is an aquatic plant causing many problems in fresh water streams) was used to remove the heavy metal ions from wastewater (Shama, Moustafa and Gad, 2010). Fly ash a waste product from thermal power plants has some adsorption capabilities for Cr (VI) (Grover and Narayanaswamy, 1982). Chitin is second only to cellulose in terms of abundance in nature and is found in the exoskeletons of crabs and other arthropods and in the cell walls of some fungi (Berkeley, 1979; Rorrer et al., 1993). This study depend on using low cost material as rice straw which production annually is about 4.7 ton in Egypt to remove the heavy metal ions having the majority in wastewater.

2. Experimental and Chemicals

2.1 Adsorbent Material

Rice straw was washed several times with de-ionized water to remove all dirt followed by filtration and were dried at 100°C. The cleaned and dried rice straw was oven dried at 500°C for 3 hours without any other further treatment to form what is called Carbonized Rice Straw (CRS).

2.2 Chemicals

All chemicals are analytical grade.

1. Sodium hydroxide from POCH.
2. Concentrated nitric acid 63% from POCH.
3. Stock solutions of (Fe^{3+}, Mn^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+}) ions 1000 mg/L from MERCK.

2.3 Determination Of Heavy Metals

The instrument used in determination of heavy metals is the Atomic Absorption Spectrophotometer AAS-Vario 6 – Analytik Jena AG.

The method used for the determination of heavy metals was (3111B Direct Air- Acetylene Flame Method), Standard Method for the Examination of Water and Wastewater 20th Edition. Each element has its own characteristic absorption wavelength; a source lamp composed of that element is used, which is called the Hollow Cathode Lamp. 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.

2.4 Effect Of Contact Time On The Removal Of The Heavy Metal Ions

Single element standard solutions of (Fe^{3+}, Pb^{2+}, Zn^{2+}, Mn^{2+} or Cd^{2+}) which concentration were equal to 100 mg/L, were prepared. To 20 ml of each element solution known weights of CRS were added in 250 ml beakers for a contact time (5, 10, 15, 30, 45, 60, 90, and 120) min. After that the mixtures were filtered and the clear supernatant solutions were analyzed with atomic adsorption spectrophotometer to determine the equilibrium concentrations.

2.5 Effect Of Weight of (CRS) On The Removal Of The Heavy Metal Ions

Weights of (0.1, 0.3, 0.5, 0.7, 1, 1.5 and 2) gm CRS were added to 20 ml of each single element standard solution in 250 ml beakers till equilibrium was reached.
After that the mixtures were filtered and the clear supernatant solutions were analyzed with atomic adsorption spectrophotometer to determine the equilibrium concentrations.

2.6 Effect Of pH On The Removal of The Heavy Metal Ions

20 ml of prepared standard solutions, which had different pH values (1, 3, 5, 7and 9) were added with respective optimum conditions of weights of CRS and contact time of each metal in 250 ml beakers. Then were treated and analyzed as previously.

2.7 Effect Of Initial Concentration Of Metal Ions On The Removal Percentage

20 ml of prepared standard solutions, which had different concentration ranging from (20, 40, 60, 80, 100) mg/L, were added with respective optimum conditions of weights of CRS and contact time of each metal in 250 ml beakers. Then were treated and analyzed as previously.

2.8 Adsorption Isotherm

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:

$$1/qe = 1/Q0 + (1/b\ Q0)\ (1/C)$$

where C is the concentration of solute remaining in solution at equilibrium (mg/L), qe is the amount of solute adsorbed per unit weight of solid adsorbent equilibrium time (mg/g) and Q0 and b are Langmuir constants related to the adsorption capacity and energy of adsorption, respectively.

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

$$\text{Log } qe = \text{Log } Kf + 1/n \text{ Log } C$$

Where Kf is the adsorption capacity and n is the adsorption intensity.

2.9 Effect Of Competition Among Metal Ions On The Removal Efficiency

4 ml of each metal ion (100mg/L) solutions were mixed in 250 ml beaker. Addition of 1 gm CRS with contact time 30 and 60 min at pH =1**.** Then were treated and analyzed as previously

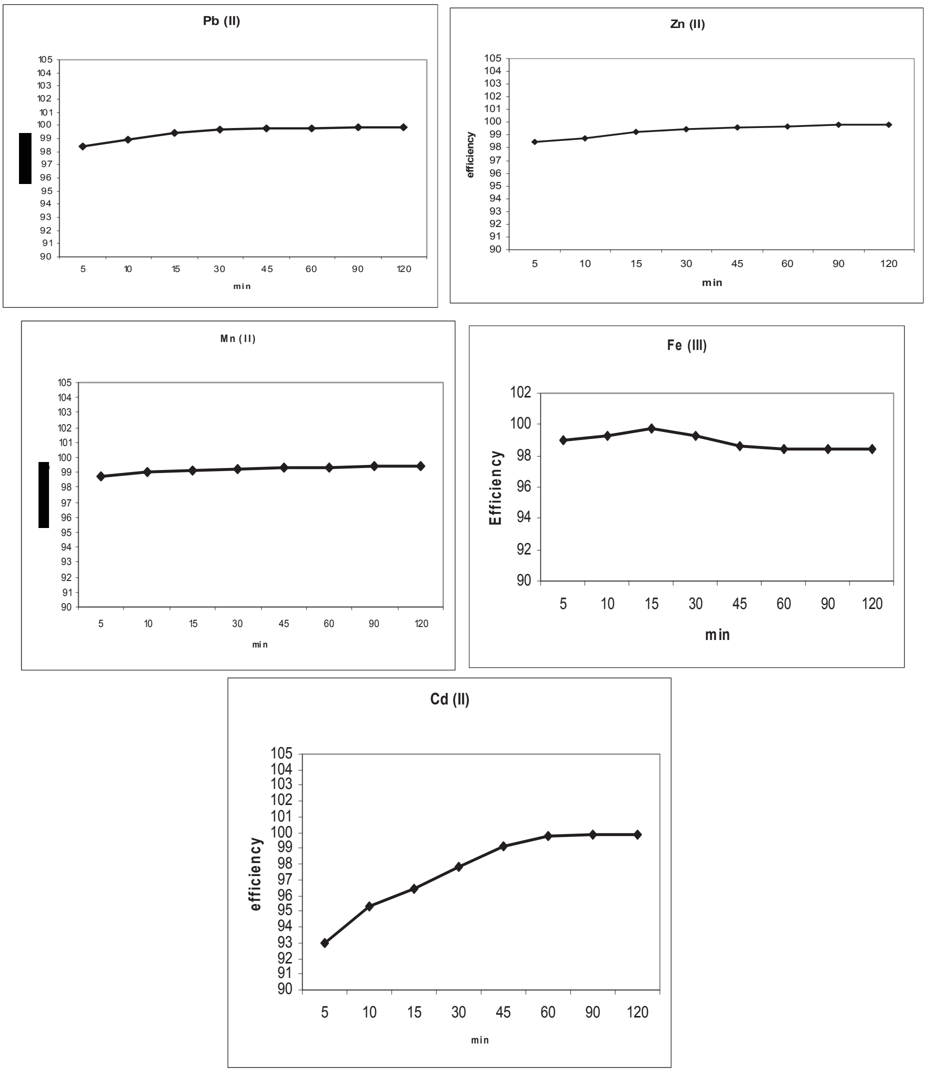
3. Results And Discussion

3.1 Effect Of Contact Time On The Removal Of The Heavy Metal Ions

The effect of contact time on the removal of heavy metal ion is shown in Fig. 1.The results show that: The removal efficiency of heavy metal ions is increasing by increasing contact time expect for Fe^{3+}. The removal efficiency increased rapidly at the beginning of the experiments and then decreased slowly until equilibrium was reached. The maximum equilibrium time was 60 min in case of Zn and Cd ions, then 30 min in case of Mn and the minimum equilibrium time was 15 min in case of Pb and Fe.

Equilibrium times of each metal ion were taken in all coming experiments.

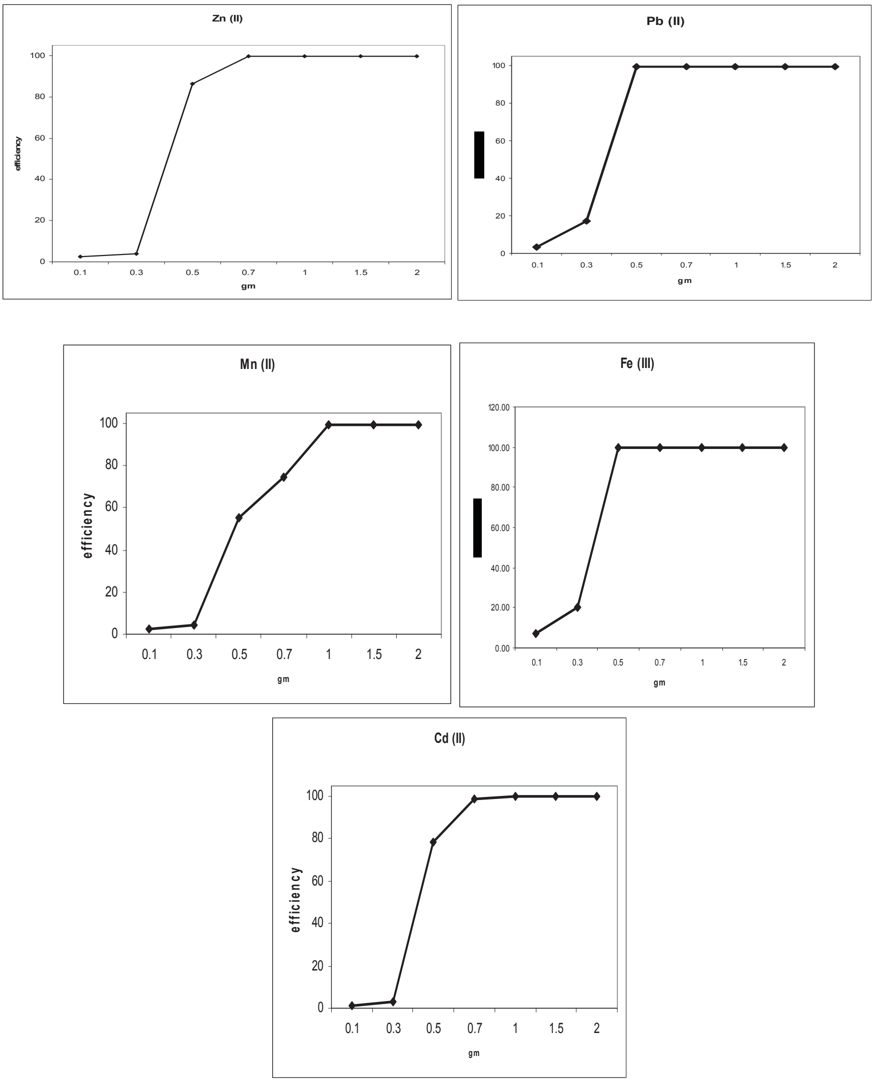
Fig. 1 The effect of contact time on the removal efficiency.



3.2 Effect Of Weight Of (CRS) On The Removal Of The Heavy Metal Ions

The effect of weight of CRS on the removal of heavy metal ion is shown in Fig. 2. The results show that: The removal efficiency of heavy metal ions is increasing by increasing weight of CRS expect for Fe^{3+}. The removal efficiency increased quit at the beginning of the experiments, then sharp increase and then further increased did not change the removal percentage significantly. The maximum weight was 1 gm in case of Mn and Cd ions, then 0.7 gm in case of Zn and the minimum weight was 0.5 gm in case of Pb and Fe. This is due to the fact that increasing the adsorbent dose provides a grater surface area or more adsorption sites for the metal ions. The weights of CRS of each metal ion were taken in all experiments.

Fig. 2 The effect of weight of CRS on the removal efficiency.

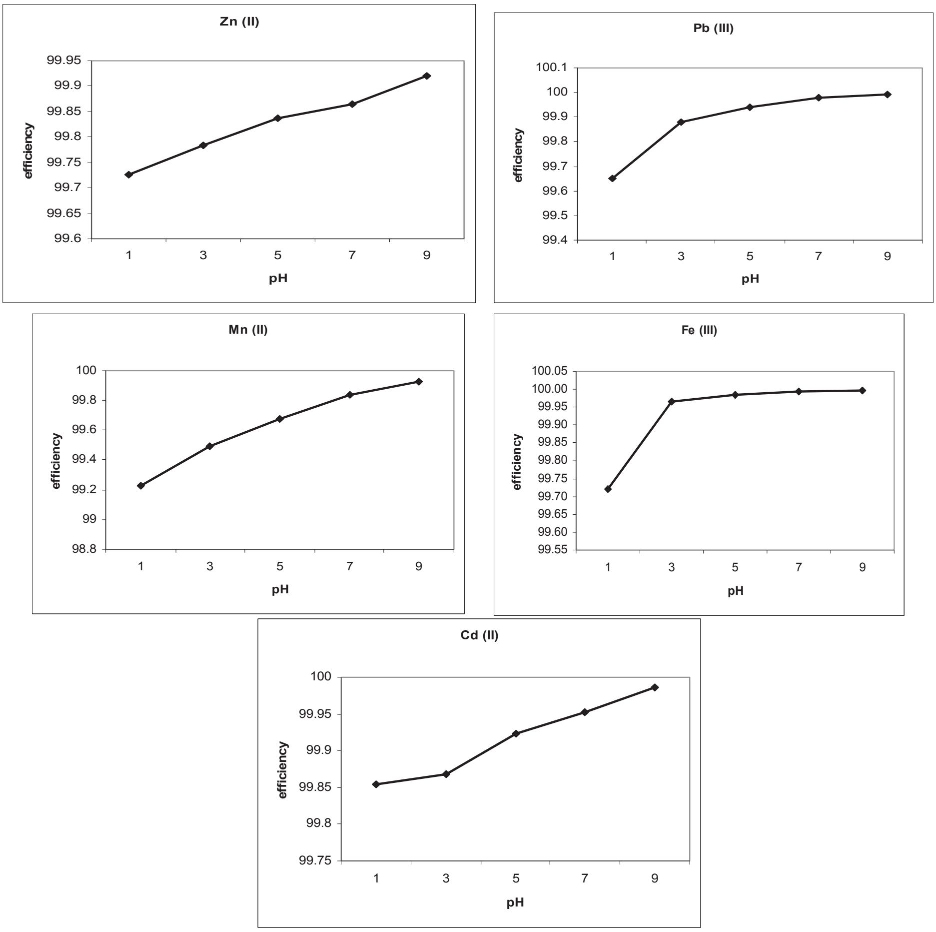


3.3 Effect of PH On The Removal Of The Heavy Metal Ions

The pH of the solution has a significant impact on the uptake of heavy metals since it determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. The effect of pH on the removal of heavy metal ion is shown in Fig. 3. The results show that: The removal efficiency of heavy metal ions is increasing by increasing pH for all ions. Raising pH from 1 to 9 was not effective, since the efficiency was above 99% at pH=1.

For all experiments the pH of metal ion solutions was =1, because if the pH was high, many ions would precipitate out deflecting the purpose of sorption process.

Fig. 3 The effect of ph on the removal efficiency.



3.4 Effect Of Initial Concentration Of Metal Ions On The Removal Percentage

The results show that: In case of Mn^{2+} and Cd^{2+} the removal efficiency of heavy metal ions was decreased by increasing initial concentration. In case of Pb^{2+} the removal efficiency was constant until 40 mg/L then decreased by increasing initial concentration. The removal efficiency of Fe^{3+} was decreased until 60 mg/ L then increased. The removal efficiency of Zn^{2+} was increased by increasing initial concentration then decreased for concentration over 40 mg/L.

3.5 Adsorption Isotherms

The Langmuir equation:

By plotting (1/qe) against (1/C) Langmuir constants Q0 and b can be obtained

The Langmuir linear relation of some metal ions is shown in Fig. 4.

The Freundlich equation:

By plotting (log qe) against (log C) Freundlich constants Kf and n can be obtained.

The Freundlich linear relation of some metal ions is shown in Fig. 5.
Freundlich and Langmuir constants are shown in table (1).

Table 1: Freundlich and Langmuir constants.

Adsorption constants for the adsorption of metal ions on CRS						
Metal ions	**Freundlich constants**			**Langmuir constants**		
	n	Kf	R^2	Q0	b	R^2
Fe^{3+}	1.00	7.79	0.86	58.82	0.137	0.96
Mn^{2+}	1.40	2.31	0.99	3.43	1.46	0.99
Zn^{2+}	1.05	7.17	0.99	55.55	0.14	0.99
Pb^{2+}	3.03	6.06	0.89	4.13	60.53	0.97
Cd^{2+}	2.23	4.18	0.93	2.30	39.52	0.98

Langmuir isotherm fits well with the experimental data. This may be due to homogenous distribution of active sites on CRS, since the Langmuir equation assumes that the surface is homogenous (Wang, Boyjoo and Choueib, 2005).

Fig.4 The Langmuir linear relation of some metal ions.

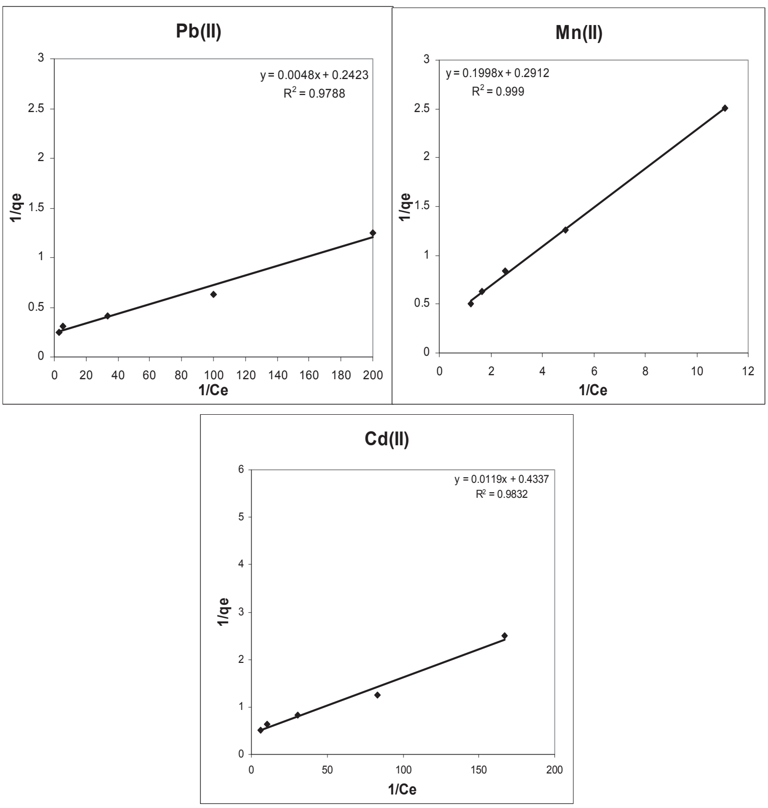
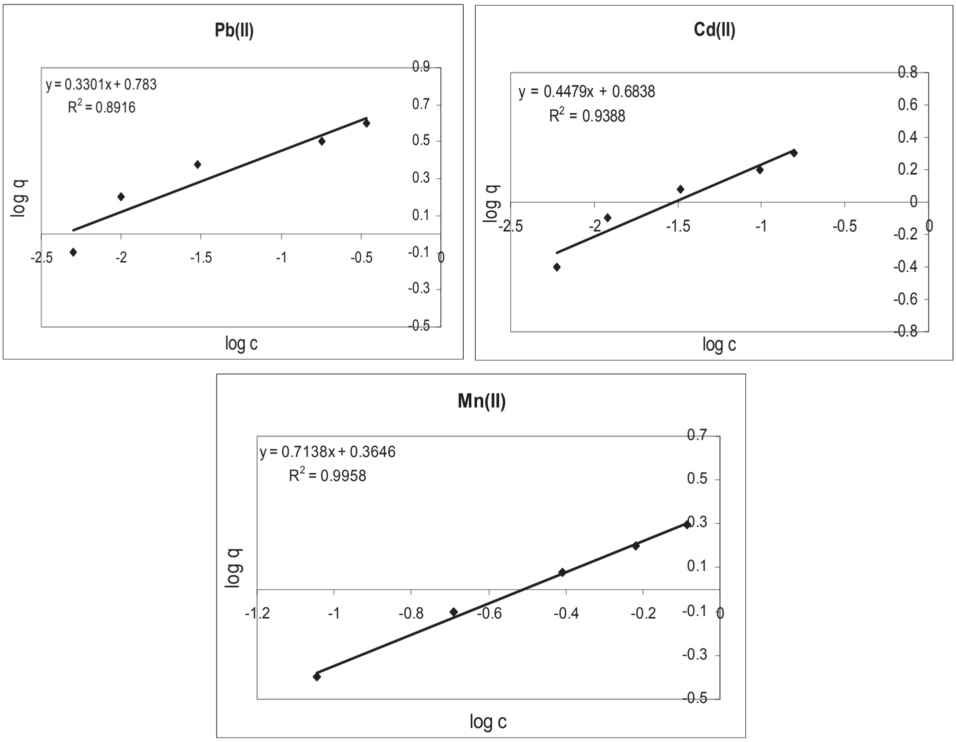


Fig. 5 The Freundlich linear relation of some metal ions.



3.6 Competition Among Metal Ions

In wastewaters, the metals of interest are usually found with a number of other metals, so we should test the binding of each metal ion in the presence of other metals. Table 2 shows the percentage of adsorption each ion in the presence of others. The general binding affinity for the metals studied, in order decreasing affinity is Pb(II)> Cd(II)> Mn(II)> Zn(II)> Fe(III).While it is clear that some of the metal ions compete with one another for bark binding sites, it is of interest to note that the binding of Pb (II) is relatively unaffected by other metals (Bulut and Tez, 2007; Gloaguen and Morvan, 1997).

Table 2: The percentage of adsorption of each ion.

Removal efficiency with complex metals %		
Weight of CRS	**1 g**	**1 g**
Contact time	**30 min**	**60 min**
Fe^{3+}	99.52	99.45
Mn^{2+}	99.83	91.86
Cd^{2+}	99.88	99.94
Zn^{2+}	99.80	94.83
Pb^{2+}	99.90	99.98

3.7 Cost Of Adsorbents

The production of rice straw in Egypt is about 4.7 million ton annually. The adsorbent material used in this study is generally available at a relatively cheap rate, 100 L.E. /ton for rice straw. The treatment of $1m^3$ of wastewater with CRS would cost approximately 31.25 L.E.

4. Conclusion

The effect of weight of CRS, contact time, pH and initial concentration were studied by batch method and the equilibrium concentration of metal ions was measured by atomic absorption spectrophotometer. It was found that the percentage of removal was increased by increasing weight of adsorbent and contact time expect for Fe^{3+}. Raising pH from 1 to 9 did not increased the percentage too much as it was over 99% at pH = 1. Adsorption of metal ions was fitted with Langmuir isotherm more than Freundlich isotherm. Thus, it could be concluded that CRS is a good low-cost adsorbent for many heavy metal ions from wastewater at low and high pH values with high efficiency.

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