RETENTION OF ZN, Pb, Cu AND Cd METAL IONS ONTO SEWAGE IRRIGATED SOIL

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ABSTRACT

The sorption isotherm and kinetic of Cu²⁺, Pb²⁺, Zn²⁺, and Cd²⁺ ions onto sewage irrigated soil (El-Gebal El Aasfar-Qalubia) was examined as a function of the retention time and initial ion concentration using batch equilibrium sorption experiments. Results show that the Cu, Pb, Zn and Cd metal ions onto the soil is relatively rapid and sorption reaches equilibrium at about 240 minutes. Kinetics of the sorption process on the soil is well characterized by the pseudo-second order reaction rate. Langmuir, Freundlich and D–R isotherm models are fitted for the sorption of Cu²⁺, Pb²⁺, Zn²⁺, and Cd²⁺ ions onto the soil. The constants of all models were calculated for each metal ion and compared. It indicated clear differences between the sorption characteristics of Cu²⁺, Pb²⁺, Zn²⁺, and Cd²⁺ ions on the sewage irrigated soil.

INTRODUCTION

Recently, deterioration of environment is occurring rapidly particularly in the largest cities. Industrial effluents, sewage and farm wastes are the major pollutants contaminating the environment. Most of the industries discharge wastewater and their effluents containing toxic materials into rivers without adequate treatment. Environmental pollution particularly from heavy metals and minerals in the wastewater is one of the most serious problems in Egypt. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewater. Most of the point sources of heavy metal pollutants are industrial wastewater from mining, metal processing, tanneries, pharmaceuticals, pesticides, organic chemicals, rubber and plastics, lumber and wood products. The heavy metals are transported by runoff water and contaminate water sources downstream. The untreated sewage water was the main cause of soil pollution in this region that leads to the increase of toxic metal concentration in leafy vegetables grown in the fields of this area (Asdeo et al 2011).

Heavy metals are elements having atomic weights between 63.5 and 200.6, and a specific gravity greater than 5.0. Most of the heavy metals are dangerous to health or to the environment. Heavy metals in industrial wastewater include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel (Ahalya et al 2003). The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the World Health Organization (WHO). Acute heavy metal intoxications may damage central nervous function, the cardiovascular and gastrointestinal (GI) systems, lungs, kidneys, liver, endocrine glands, and bones. Chronic heavy metal exposure has been implicated in several degenerative diseases of these same systems and may increase the risk of some cancers as shown in Table 1. Non-biodegradable contaminants pose a serious health and environmental hazard and removal of these wastes cannot be achieved using secondary methods. Hence, tertiary/advanced wastewater treatment methods such as ion exchange, precipitation, membrane separation, electrolysis and adsorption can be used to remove these recalcitrant wastes.
Table 1. Sources and toxicological effects of some heavy metals (Ahalya et al 2003)

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>Sources</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>• It is used principally for galvanizing iron. More than 50% of metallic zinc goes into galvanizing steel, but is also important in the preparation of certain alloys. It is used for the negative plates in some electric batteries and for roofing and gutters in building construction. • Zinc is the primary metal used in making automobile industry. Zinc oxide is used as a white pigment in water colors or paints, and as an activator in the rubber industry. As a pigment zinc is used in plastics, cosmetics. Photocopyer paper, wallpaper printing inks etc.</td>
<td>• Little zinc they can experience a loss of appetite, decreased sense of taste and smell, slow wound healing and skin sores. Zinc shortages can even cause birth defects. • Although humans can handle proportionally Large concentrations of zinc, too much zinc can still cause -eminent health problems, such as stomach cramps, skin irritations vomiting, nausea and anemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis.</td>
</tr>
<tr>
<td>Cadmium</td>
<td>• 80% of cadmium currently produced is used in rechargeable nickel-cadmium batteries. • Cadmium was often used to electroplate steel and protect it from corrosion. It is still used today to protect critical components of aero planes and oil platforms. • Other past uses of cadmium included phosphors in cathode ray tube colour TV sets, and yellow, orange and red pigment. • Cadmium absorbs neutrons and so is used in rods in nuclear reactors to control atomic fission.</td>
<td>• Diarrhoea, stomach pains and severe • Vomiting-Bone fracture • Reproductive failure and possibly even Infertility • Damage to the central nervous system • Damage to the immune system Psychological disorders • Possibly DNA damage or cancer development</td>
</tr>
<tr>
<td>Copper</td>
<td>• Water pipes; Copper water heaters frozen greens and canned -greens using copper to produce an ultra green color. Alcoholic beverages from copper brewery equipment. Pesticides, insecticides; fungicides; Copper; jewelry Cooper, cooking pots</td>
<td>• Mental disorders. • Anaemia; Arthritis/ • Rheumatoid arthritis; Hypertension. Nausea/vomiting, Hyperacitivity, Schizophrenia, Inson’U1ia, Autism, inflammation and enlargement of liver, heart problem, Cystic fibrosis.</td>
</tr>
<tr>
<td>Lead</td>
<td>• Industries such as mining, steel, automobile, and batteries and paints Pollutants arising from increasing kidney industrialization</td>
<td>• Nausea Encephalopathy. Headache vomiting. Learning difficulties. Mental retardation. Hyperactivity, Vertigo, damage, Birth defect. Muscle weakness, Anorexia, Cirrhosis of the liver, Thyroid dysfunction, Insomnia, Fatigue, Degeneration of motor neurons, Schizophrenic- like behavior.</td>
</tr>
</tbody>
</table>

So far, a number of efficient methods have been developed for heavy metal removal. (Fu and Wang, 2011) reviewed various methods for the removal of heavy metals such as chemical precipitation, ion exchange, reverse osmosis, electro dialysis, ultrafiltration, Nano filtration, coagulation, flocculation, floatation, etc. Generally, these processes are efficient in removing the bulk of metals from solution at high or moderate concentrations. However, chemical processes produce a large amount of metallic sludge, making metal recovery difficult. The sludge also needs further disposal. The objective of the present work is to explore the retention of \( \text{Zn}^{2+}, \text{Pb}^{2+}, \text{Cu}^{2+} \text{and Cd}^{2+} \) by sewage irrigated soil and to characterize the efficiency of ion sorption by the soil. The metals adsorption efficiencies were taken as a function of the following parameters of contact time and initial
metals concentration. Equilibrium adsorption isotherms were analyzed to obtain the Langmuir and Freundlich and D–R isotherm constants. Kinetics of the adsorption process on the soil is well characterized by the pseudo-second order reaction rate. The obtained results gave a better understanding of the ENS of Zn$^{2+}$, Cd$^{2+}$, Cu$^{2+}$ and Pb$^{2+}$ adsorption phenomenon.

MATERIALS AND METHODS

Chemical and Reagents

All chemicals and reagents used were of Copper, cadmium, zinc and lead were prepared using analytical grade CuSO$_4$, Pb(NO$_3$)$_2$, ZnSO$_4$ and CdSO$_4$ obtained from Winlab, England. Analytical grade phosphoric acid solution (Adwic) was used.

The concentrations of the heavy ions studied were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES) in a Perkin-Elmer 2100DV apparatus.

Preparation of the Soil Sample

About five surface (0-10 cm) soil samples were collected from different sites at ElGebal El asfar area Qaliubiya governorate, dried and mixed together carefully and then a representative soil sample was selected. The soil sample was dried in an electric oven at about 105°C and then sieved using 150 µm ASTM standard sieves. The Soil particles less than 150 µm were selected and used for adsorption studies. Soil pH was measured with a glass electrode using a suspension with soil-to-water mass ratio of 1:5. Ferric oxide (Fe$_2$O$_3$) and aluminum oxide (Al$_2$O$_3$) were extracted twice with an acid ammonium oxalate solution, washed in dark for 1 h at a soil-to-water mass ratio of 1:25 (McKeague and Day, 1966).

Procedure

Cu, Pb, Zn and Cd solutions were prepared by dissolution of certain weights of their salts in distilled water to obtain solutions containing 10.0 mg/L for each ion. The ionic strength was adjusted to 0.1 mol/L with NaNO$_3$, and the ionic strength adjustment was to limit the effect of a change in ion concentrations on the adsorption properties. The initial pH of solutions was adjusted using KOH and HNO$_3$ to 7.6 and it was not further modified during these experiments in order to simulate the real environmental conditions. Batch sorption experiments were performed by shaking 1.0 g of the soil sample with 50 mL of the ions solution in a shaker bath at (25 ± 1°C). After the corresponding time interval, the solutions were centrifuged at 4000 rpm /min for 20 min and the supernatants solutions were filtered through a 0.45 µm pore size membrane. The Cu, Pb, Zn and Cd concentrations in the filtered solutions were determined using an inductively coupled plasma optical emission spectrometer (Optima 2100DV, Perkin-Elmer). All the experiments were carried out in triplicate and the mean values were presented. The amount of the ion uptake was calculated by the difference between the equilibrium concentration and the initial concentration. The amount of ion retained in the solid phase $q_d (mg/g)$ was calculated using the relation:

$$q_d = (C_o - C_e) \times \frac{V}{m}$$

Where $C_o$ and $C_e$ are the initial and equilibrium concentrations (mg/L) of ions solution, respectively, $V$ is the volume of solution (L) and $m$ is the weight (g) of the adsorbent. The removal percent of ions from the aqueous phase is calculated from the relation:

$$R \% = \frac{C_o - C_e}{C_o} \times 100$$

The distribution coefficient ($K_d$) of ions between the aqueous bulk phase and the solid phase was calculated from the following relation:

$$K_d = \frac{C_e - C_o}{C_o} \frac{V}{m}$$

The Langmuir equation model used is

$$\frac{C_e}{q_d} = \frac{1}{Q_oK_d} + \frac{1}{Q_o} C_e$$

Where: $C_o$ and $q_d$ are the equilibrium ion concentration (mg/ L) and the amount of ion sorbed (mg/ kg), respectively. The empirical constants b and k are related to the adsorption maximum and bonding strength of the adsorbent, respectively. This equation will be used to compare the adsorption maximum (b) of the four studied elements since the experimental conditions are identical. The linear form of Freundlich equation is log $q_d = \log K_f + 1/n \log C_o$

Where: $q_d$ = the amount of ion sorbed, $C_o$ = concentration of the considered ion in the equilibrium solution (mg/L), $K_f$ and $n$ are Freundlich isotherm constants.
RESULTS and DISCUSSION

Removal Kinetics

The removal kinetics of Cu, Pb, Zn and Cd ions at a concentration of 10.0 mg/L for each by sewage irrigation soil are studied as a function of shaking time at different time intervals ranged from 5 to 360 min at fixed initial pH of 6 (Xu et al 2008). The result of adsorption kinetic of Cu, Pb, Zn and Cd ions are shown in Figure 1. From the Figure, it was found that the removal of Cu, Pb, Zn and Cd ions are increased with increasing shaking time until a steady state is attained after about 240 min and there is no significant change in the removal percent after that time. This means that the equilibrium of the four elements is reached after 240 min.

Data also show that the removal percentages of the studied elements are in the following descending order Cu < Pb < Zn < Cd.

Figure (2) indicated that as the metal ion concentration increased the removal percentage calculated on the basis of added concentration is decreased. Also, increasing the added ion concentrations reflected lower percentage of sorbed ions and this behavior was clear for the four ions. Data also showed similar descending order as shown in removal kinetics.

Sorption isotherms

Several common sorption isotherm models such as Freundlich, Langmuir, Temkin and Dubinin–Radushkviech (D–R) isotherm models were considered to fit the obtained isotherm data.

Freundlich isotherm model

Freundlich equation is derived to model the multilayer sorption and for the sorption on heterogeneous surfaces. The logarithmic form of Freundlich equation is written as follow Takahashi et al (1999):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$
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Where: $K_f$ is the constant indicative of the relative adsorption capacity of the adsorbent (mg/kg) and $(1/n)$ is the constant indication of the intensity of the adsorption process. The illustration of log $q_e$ versus log $C_e$ is shown in Figure 3 which suggests that the sorption of the four studied ions obeys Freundlich isotherm over the entire range of sorption concentration studied. The numerical values of the constants $(1/n)$ and $K_f$ are computed from the slope and intercepts by means of a linear least square fitting method and are given in Table 2. The Freundlich intensity constant $(1/n)$ for all cases is less than unity, indicating a concentration dependent sorption for all ions onto the sewage irrigation soil.

**Langmuir isotherm model**

Langmuir sorption isotherm models the monolayer coverage of the sorption surfaces and assumes that sorption occurs on a structurally homogeneous adsorbent and all the sorption sites are energetically identical. The linearized form of the Langmuir equation is given by

$$\frac{C_e}{q_e} = \left( \frac{1}{Q_o b} \right) + \left( \frac{1}{Q_o} \right) C_e$$

Where: $q_i$ is the amount of solute sorbed per unit weight of adsorbent (mg/kg), $C_o$ is the equilibrium concentration of the solute in the bulk solution (mg/L), $Q_o$ is the monolayer adsorption capacity (mg/kg) and $b$ is the constant related to the free energy of adsorption ($b = a e^{-\Delta G/RT}$).

The graphic representation of $(C_e/q_e)$ versus $C_e$ gives straight lines for all ions sorbed onto sewage irrigation soil as represented in Figure 4 confirming that this expression is indeed a reasonable representation of chemisorptions isotherm. The numerical value of constants $Q_o$ and $b$ evaluated from the slope and intercept of each plot are given in Table 2. The value of saturation capacity $Q_o$ corresponds to the monolayer coverage and defines the total capacity of the adsorbent for a specific metal ion.

Figure 2. Effect of metal ion concentration on the removal of Cu, Pb, Zn and Cd onto sewage irrigation soil.
Figure 3. Freundlich isotherm plots for removal of Cu, Pb, Zn and Cd onto sewage irrigation soil.

Figure 4. Langmuir isotherm plots for removal of Cu, Pb, Zn and Cd onto sewage irrigation soil.
Table 2. Freundlich, Langmuir D–R isotherm parameters for the sorption of Cu, Pb, Zn and Cd onto sewage irrigation soil.

<table>
<thead>
<tr>
<th>Metals</th>
<th>Freundlich model parameters</th>
<th>Langmuir model parameters</th>
<th>D-R model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1/n</td>
<td>K_1 (mg/kg)</td>
<td>R²</td>
</tr>
<tr>
<td>Cu</td>
<td>0.56</td>
<td>0.30</td>
<td>0.97</td>
</tr>
<tr>
<td>Pb</td>
<td>0.55</td>
<td>0.26</td>
<td>0.97</td>
</tr>
<tr>
<td>Zn</td>
<td>0.62</td>
<td>0.32</td>
<td>0.98</td>
</tr>
<tr>
<td>Cd</td>
<td>0.66</td>
<td>0.41</td>
<td>0.99</td>
</tr>
</tbody>
</table>

Dubinin–Radushkviech isotherm (D–R isotherm)

To study the nature of the sorption processes, the D–R isotherm was also verified in the form (Peric et al. 2004):

\[
\ln q_e = \ln q_m - \beta \epsilon^2
\]

Where: \( q_m \) is the maximum amount of ion that can be sorbed onto unit weight sewage irrigation soil, i.e. sorption capacity (mg/kg), \( \beta \) the constant related to the sorption energy (mol² /kJ²); and \( \epsilon \) is the polanyi potential = RT ln(1+1/Ce), where R is the gas constant (kJ/mol K), and T is the solution temperature (K).

The D–R plots of \( q_e \) versus \( \epsilon^2 \) for the sorption of Zn, Cd, Cu and Pb ions onto sewage irrigation soil are given in Figure 5. These linear plots indicate that the D–R isotherm expression is followed for each metal ion. Linear regression analysis using paired of \( q_e \) and \( \epsilon^2 \) resulted in the derivation of \( q_m, \beta, \) and the correlation factor (R²). These parameters are listed in Table 2.

Sorption kinetic modeling

It is well recognized that the characteristic of the sorbent surface is a critical factor that affect the sorption rate parameters and that diffusion resistance plays an important role in the overall transport of the ions. Pseudo-first order and pseudo-second order rate equations were applied to experimental data for evaluating the adsorption of Cu, Pb, Zn and Cd ions on sewage irrigation soil at 25 °C.

Laguerre pseudo first-order expression is written as: (Ho and McKay (1999))

\[
\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303} t
\]

Where \( q_e \) is the concentration of the ion sorbed at equilibrium (mg/kg), \( q_t \) is the concentration of the ion sorbed at time t (mg/kg) and \( K_1 \) is the overall rate constant.

It was observed that the sorption of all ions followed the Laguerre equation. From the slopes of the plots, as shown in Figure 6 the values of the first-order rate constants (K_1) and the theoretical sorption capacities (\( q_e \)) were evaluated. The calculated values of K_1 and \( q_e \) with the linear correlation coefficients (R²) of each plot are listed in Table 3.

Straight lines obtained from the pseudo first-order kinetic plots suggest the applicability of this model to fit the experimental data over the initial stage of the sorption process (5–45 min). But it is also required that the theoretically calculated equilibrium sorption capacities, \( q_e \) should be in accordance with the experimental sorption capacity values. As can be shown from Table 3, although the linear correlation coefficients of the plots are so good, the \( q_e \) (calculated) values are not in agreement with \( q_e \) (experimental) for all studied sorption process. So, it could suggest that the sorption of the four studied ions onto impregnated charcoal is not a first-order rate reaction.

The pseudo second-order rate model is expressed as (McKay and Ho (1999)):

\[
\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}
\]
Figure 5. D–R isotherm plots for removal of Cu, Pb, Zn and Cd onto sewage irrigation soil.

Figure 6. Lagergreen plots for removal of Cu, Pb, Zn and Cd onto sewage irrigation soil.
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Where $K_2$ is the rate constant of pseudo second-order equation (kg/mg. min)). The kinetic plots of $t/q$ versus $t$ for zinc, cadmium, copper, and lead ions sorption onto sewage irrigation soil are represented in Figure 7. The relations are linear and the values of the correlation coefficients ($R^2$) suggest strong relationships between the parameters and also explain that the process of sorption of ions follows the pseudo second-order kinetic model. The products $K_2q_e^2$ is the initial sorption rate represented as $h = K_2q_e^2$.

The kinetic parameters of this model are calculated from the slope and intercept of the linear plots and are given in Table 3. The correlation coefficients ($R^2$) have an extremely high values and its calculated equilibrium sorption capacity ($q_e$) is consistent with the experimental data. So, it is possible to suggest that the sorption of all ions onto sewage irrigation soil followed the pseudo second-order kinetic model and that the overall rate constant of each sorption process appears to be controlled by the chemical sorption process (McKay and Ho (1999)).

![Figure 7](image-url)  
Figure 7. Pseudo second-order plots for removal of Cu, Pb, Zn and Cd onto sewage irrigation soil.

<table>
<thead>
<tr>
<th>Metals</th>
<th>First order kinetic parameters</th>
<th>Second order kinetic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_1$</td>
<td>$q_{cal}$ (mg/kg)</td>
</tr>
<tr>
<td>Cu</td>
<td>0.05</td>
<td>0.35</td>
</tr>
<tr>
<td>Pb</td>
<td>0.05</td>
<td>0.42</td>
</tr>
<tr>
<td>Zn</td>
<td>0.05</td>
<td>0.29</td>
</tr>
<tr>
<td>Cd</td>
<td>0.05</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Table 3. The calculated parameters of the pseudo first-order and pseudo second-order kinetic models for Cu, Pb, Zn and Cd ions sorbet onto sewage irrigation soil.
CONCLUSION

The results of Zn$^{2+}$, Pb$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ ions sorption onto sewage irrigation soil reported, showed that the sorption process is relatively rapid and reaches equilibrium at about 4 h and the pseudo second order equation is fit for the sorption of Cu, Pb, Zn and Cd ions onto sewage irrigation soil. The sorption process of these four ions onto sewage irrigation soil takes place via a particle diffusion mechanism, Langmuir, Freundlich and D–R isotherm models are the best choice to describe the observed equilibrium data.

REFERENCES