RETENTION OF ZN, PB, CU AND CD METAL IONS ONTO SEWAGE IRRIGATED SOIL

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ABSTRACT

The sorption isotherm and kinetic of Cu^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+} 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 Cu^{2+}, Pb^{2}, Zn^{2+}, and Cd^{2+} 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 Cu^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+} 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 aretransported 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. Sourcesandtoxicologicaleffectsofsomeheavymetals **(Ahalya et al 2003)**

Heavy Metal	Sources	Effects
Zinc	• 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. Photocopier paper, wallpaper printing inks etc.,	• Littel 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 hand proportionally Large concentrations of zinc, too much zinc can still cause -eminent health problems ,such as stomach cramps, skin irritations vo1miting, nausea and anemia. Very high levels of zinc can damage the pancreas and disturb the protein metabolism, and cause arteriosclerosis.
Cadmium	• 80% of cadmium currently produced is used in rechargeable nickel-cadmium batteries. • Cadmium was often used to e-lec.troplate stee-l 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 rube 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.	• 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
Copper	• 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	• Mental disorders., Anaemia; Arthritis/ • Rheumatoid arthritis; Hypertension, Nausea/vomiting, Hyperac.tivity, Schizophrenia, Inson'U1ia, Autism, inflammation and enlargement of liver, heart problem, Cystic fibrosis.
Lead	• Industries such as mining, steel, automobile, and batteries and paints Pollutants arising from increasing kidney industrialization	• 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.

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 Zn^{2+}, Pb^{2+}, Cu^{2+} 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 iso-
therms were analyzed to obtain the Langmuir and
Freundlich and D–R isotherm constants. Kinetics
of the adsorption process on the soil is well char-
acterized by the pseudo-second order reaction
rate. The obtained results gave a better under-
standing 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 Cop-
per, cadmium, zinc and lead were prepared using
analytical grade $CuSO_4$, $PbNO_3$, $ZnSO_4$ 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 Per-
kin-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 to-
gether carefully and then a representative soil
sample was selected. The soil sample wasdried 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_2O_3) and
aluminum oxide (Al_2O_3) were extracted twice with
an acid ammonium oxalate solution, shacked 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 dis-
tilled 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 ex-

periments 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 spec-
trometer (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 be-
tween the equilibrium concentration and the initial
concentration. The amount of ion retained in the
solid phase q_e(mg/g) was calculated using the rela-
tion:

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

Where C_o and C_e are the initial and equilibrium
concentrations (mg/L) of ions solution, respective-
ly, 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:

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

The Langmuir equation model used is

$$\frac{C_e}{q_e} = \left[\frac{1}{Q^o b}\right] + \left[\frac{1}{Q^o}\right] C_e$$

Where: C_e and q_e are the equilibrium ion concen-
tration (mg/ L) and the amount of ion sorbed
(mg/ kg), respectively. The empirical con-
stants b and k are related to the adsorption
maximum and bonding strength of the ad-
sorbent, 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_e=
logK_f+ 1/n logC_e

Where: q_e= the amount of ion sorbed, C_e= concen-
tration of the considered ion in the equilibri-
um 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 ofCu, 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)**:
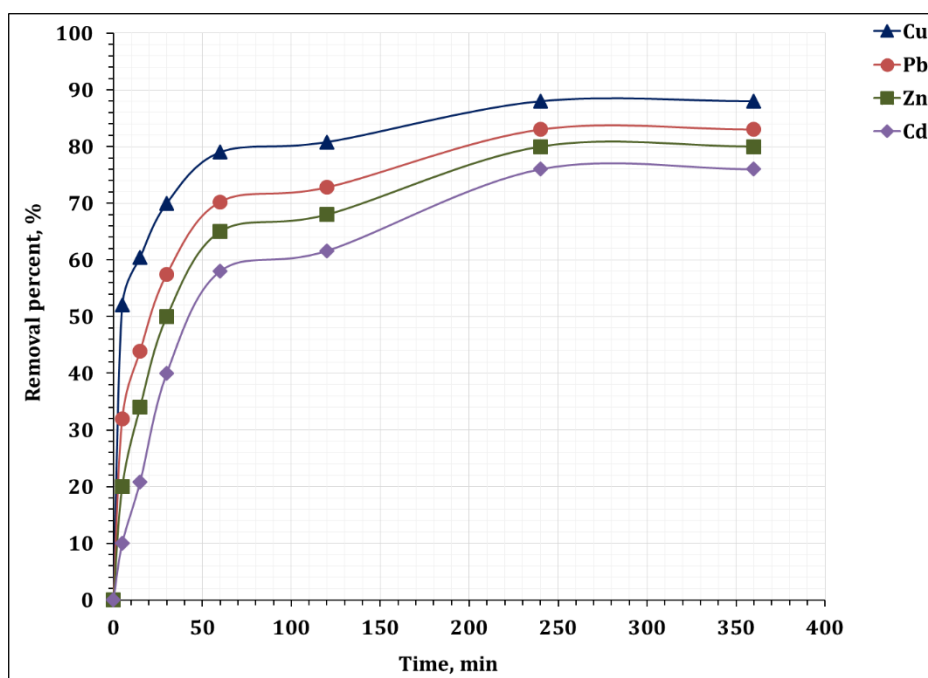
$$\log q_e = \log K_f + \frac{1}{n}\log C_e$$

Figure 1.   Effect of time on theremoval ofCu, Pb, Zn and Cd onto sewage irrigation soil.
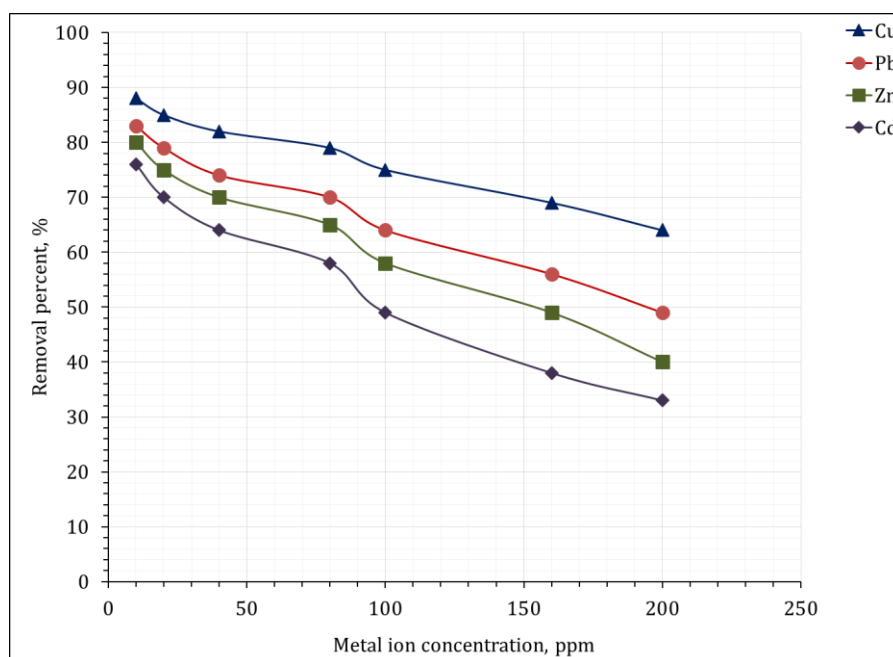
Figure 2.   **Effect of metal ion concentration on the removal of Cu, Pb, Zn and Cd onto sewage irrigation soil.**

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 iden-

tical. 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_e 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.
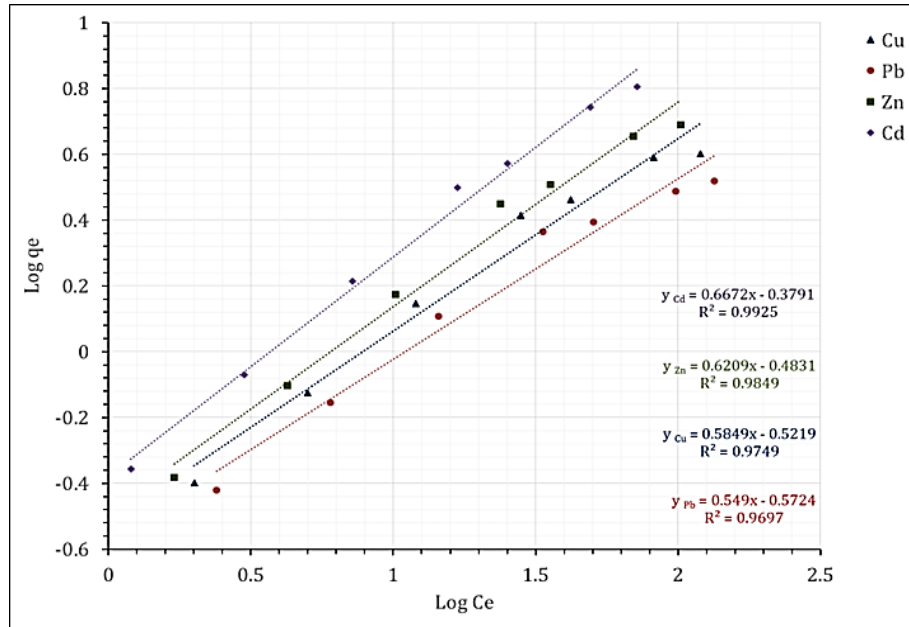
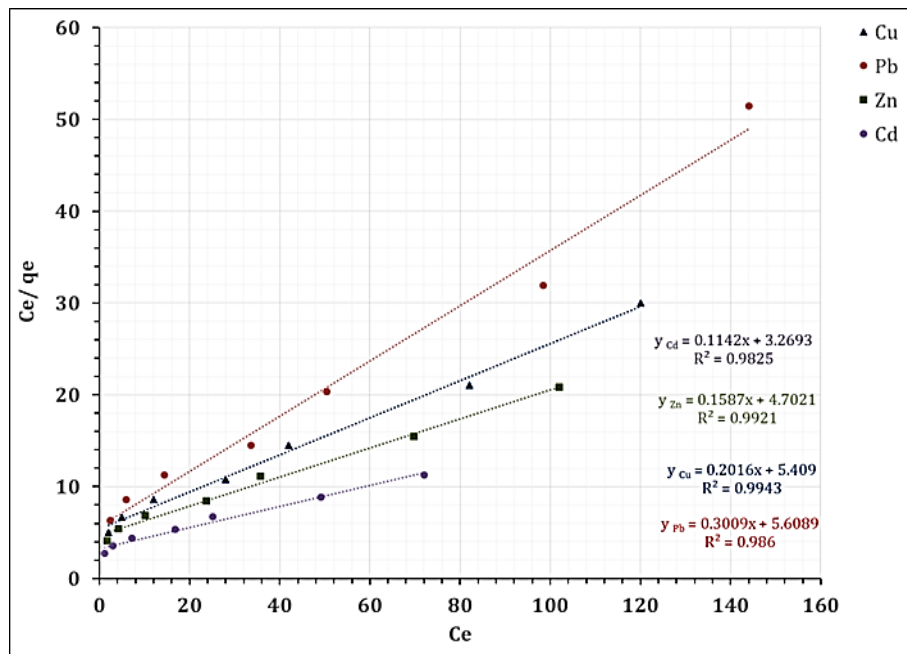**Figure 3.** Freundlich isotherm plots for removal of Cu, Pb, Zn and Cd onto sewage irrigation soil.

Figure 4. Langmuirisotherm 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.

Metals	Freundlich model parameters			Langmuir model parameters			D-R model parameters		
	1/n	K_1 (mg/kg)	R^2	Qo (mg/kg)	B(L/mg)	R^2	β (mol2 kJ^2)	Q_m (mmol/g)	R^2
Cu	0.56	0.30	0.97	4.96	0.037	0.99	-0.23	223	0.34
Pb	0.55	0.26	0.97	3.32	0.053	0.98	-0.72	272	0.31
Zn	0.62	0.32	0.98	6.30	0.033	0.99	-0.38	110	0.36
Cd	0.66	0.41	0.99	8.75	0.035	0.98	-0.08	26	0.39

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**):

$$\ln q_e = \ln q_m - \beta\varepsilon^2$$

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), β the constant related to the sorption energy (mol^2/kJ^2); and ε is the polanyi potential = RT $\ln(1+1/C_e)$, where R is the gas constant (kJ/mol K), and T is the solute temperature (K).

The D–R plots of in q_e versus ε^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 in q_e and ε^2 resulted in the derivation of q_m, β, and the correlation factor (R^2). 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.

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

$$\text{Log}(q_e-q_t) = \text{Log } q_e - \frac{K1}{2.303}\, t$$

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 Lagergreen 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 qe with the linear correlation coefficients (R^2) 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)**:
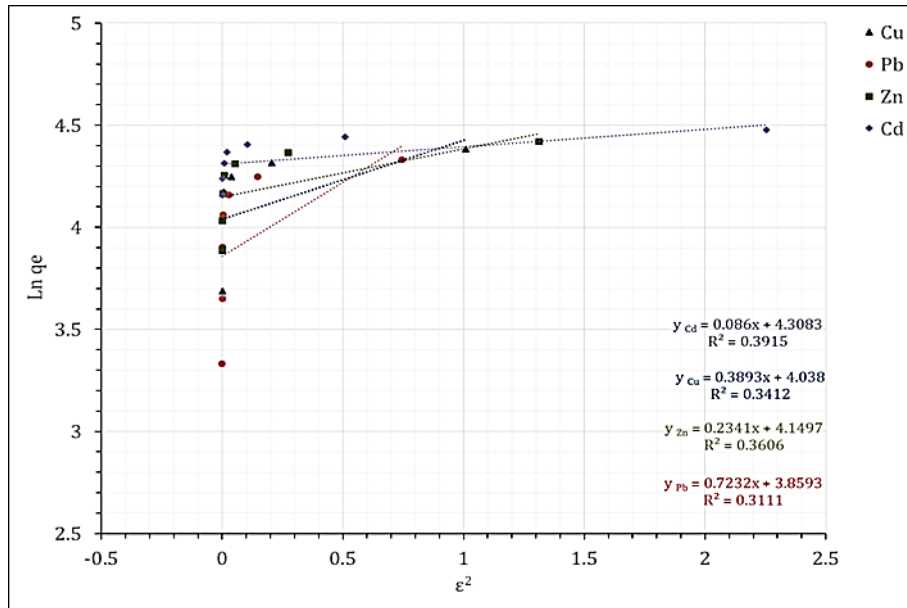
$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}\, t$$

Figure 5. D–R isotherm plots for removal of Cu, Pb, Zn and Cd onto sewage irrigation soil.
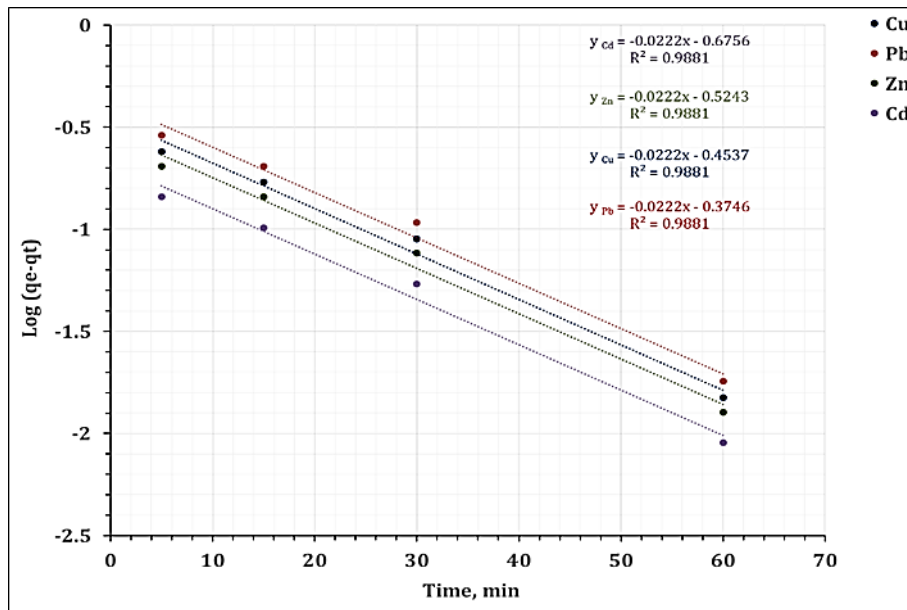

Figure 6. Lagergreen plots for removal ofCu, Pb, Zn and Cd onto sewage irrigation soil.

Where K_2 is the rate constant of pseudo second-order equation (kg/mg. min)). The kinetic plots of t/q_t 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_2qe^2 is the initial sorption rate represented as $h = K_2qe^2$.

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 (qe) 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)**.
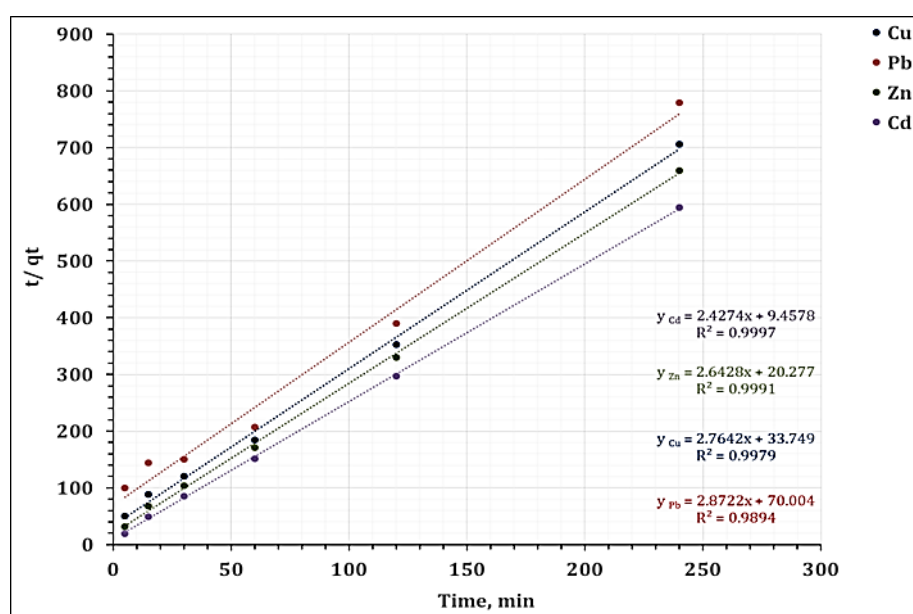

Figure 7. Pseudo second-order plots for removal of Cu, Pb, Zn and Cd onto sewage irrigation soil.

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.

Metals	First order kinetic parameters				Second order kinetic parameters			
	K1	qe$_{cal}$ (mg/kg)	qe$_{exp}$ (mg/kg)	R^2	K2	qe$_{cal}$ (mg/kg)	qe$_{exp}$ (mg/kg)	R^2
Cu	0.05	0.35	0.40	0.98	4.41	0.36	0.40	0.99
Pb	0.05	0.42	0.38	0.98	8.48	0.34	0.38	0.98
Zn	0.05	0.29	0.42	0.98	2.90	0.37	0.42	0.99
Cd	0.05	0.21	0.44	0.98	1.60	0.41	0.44	0.99

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

Ahalya, N., Ramachandra, T.V., Kanamadi, R.D. 2003. Biosorption ofheavy metals. **Res. J. Chem. Environ., 7, 71-78.**

Asdeo, A. and Loonker, S. 2011. A comparative analysis of trace metals in vegetables. **Research Journal of Environmental Toxicology, 5, 125–132.**

Fu, F., and Wang, Q. 2011. Removal of heavy metal ions from wastewaters: a review, **Journal of Environmental Management, 92(3), 407–418.**

Ho, Y.S. and McKay G. 1999. A kinetic study of dye sorption by biosorbent waste product pith. **Resour. Conserv. Recycl. 25, 171–193.**

McKay, G., and Ho, Y.S.1999. Pseudo second-order model for sorption processes, **Process Biochem. 34, 451–460.**

Mckeague, J.A. and Day, J.H.1966. Dithionite and oxalate-extractable Fe and Al as aids in differentiating various classes [J]. **Canadian Journal of Soil Science, 46(1), 13−22.**

Peric, J., Trgo, M. and Medvidovic, N.V. 2004. Removal of zinc, copper and lead by natural zeolite-a comparison of adsorption isotherms, **Water Res. 38, 1839–1899.**

Takahashi, Y., Minai, Y., Ambe, S., Makide, Y., and Ambe, F. 1999. Comparison of adsorption behavior of multiple inorganic ions on kaolinite and silica in the presence of humic acid using the multitracer technique. **J. Geochimcaet Cosmochimica Acta, 1999, 63(6), 815−836**.

Xu, D., Tan, X.L., Chen, C.L. and Wang, X.K. 2008. Adsorption of Pb(II) from aqueous solution to MX-80 bentonite: Effect of pH, ionic strength, foreign ions and temperature. **J. Applied Clay Science, 41(1/2), 37−46.**