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ORIGINAL RESEARCH ARTICLE

Copper and lead ions removal from aqueous solution using MgO, nanostractured MgO

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ABSTRACT

This study investigated elimination of Cu^{+2} and Pb_2^{+2} from prepared stock solutions using MgO, nanostractured MgO sorbents. The maximum cumulative values for copper and lead were 410, 200, 494.9, and 214.6 $mg \cdot g^{-1}$, for Nanostractured MgO, MgO, respectively. Freundlich and Langmuir models describe the sorption equilibrium isotherms. Freundlich model gives the best interpretation for experiment data for these ions.

The most adequate model describing the kinetic with the experimental data using MgO, Nanostractured MgO was a first-order kinetic model. Nanostractured MgO probably has an efficient way to remove metal ions due to its high capability to adsorb these ions.

Keywords: Heavy Metals; Nanoparticles; Peanut Peels

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1. Introduction

Uncontrolled release of metal particles turns into a noteworthy issue. These metal ions tend to accumulate either by bioconcentration, bioaccumulation, or biomagnifications through soil, and water, constant exposure of human to these metals leads to a significant risk[1–3]. Heavy metals in wastewater can have detrimental effects on all forms of life when discharged directly into the environment[4].

As a result, the way to correctly and effectively remove unwanted metals from eco structures is still essential but nonetheless challenging assignment for environmental safety engineers. In recent times, several strategies had been suggested for elimination of heavy metal from wastewaters, inclusive of however no longer limited to membrane filtration, precipitation, and other known techniques[5–8].

Amongst heavy metals, Pb^{+2}, Cu^{+2}, are most of the fundamental pollutants for environment, which might be leaked to soil and eco systems via fertilizers, insecticides, biosolids, metallic mining and milling procedures, consumed commercial wastes, and airborne resources[9].

The high surface area provided by nanoparticles in addition to the amount of pores present, and diversity of surface active groups, making nanoparticles have large capacity with selective metal in elimination of these ions[10,11].

(NMOs) show high ability to selective adsorb with high potential, as a result of that, adequate elimination of poisonous ions might be expected to fulfill more and more strict policies[12]. Size of NMOs in the range of nano scale causing negative stability.

Eventually, NMOs are liable to aggregation and tendency to take different interactions under the effect of some forces such as Van der Waals[13], causing decreasing in potential of NMOs and selectivity or even vanished. In addition, aggregation of NMOs in any type of flow causes pressure drop consequently unstablity. To enhance efficiency had been then spread through supports of high porosity to get composite absorbing materials[14]. Activated carbon, natural materials, artificial polymeric hosts are widely used for porous supports.

Those sorbents were tested in batch manner for elimination of Pb^{+2}, and Cu^{+2} existing in prepared solutions. Experimental facts received during batch equilibrium runs were analysed using Langmuir and Freundlich isotherm models. Kinetic investigations were done by two kinetic models, pseudo-first-order, and pseudo-second order. Alternatively, the outcomes of numerous parameters along with solution pH, contact time, and adsorption isotherm, at the sorbents have been studied.

2. Material and methods

2.1 Chemicals

Solutions of metal ions were prepared from their (Merck, Germany). Stracture, nanostructured MgO were purchased (purity, 99.5%) from Nabond (China). Varian Spectra AA 220 atomic absorption spectrophotometer was used to conduct analysis.

2.2 Peanut peels preparation

Peanut Peels was rinsed in distilled deionized water then heated at 100 °C for one day in order to get low moisture content. They have been then grinding by home mill and sieved. To leach out active functional groups from Peanut Peels with diameters less than 100 mesh (passed through 100 standard sieves) rinsed in 0.1 N HNO_3 in the ratio of 1 tog to 10 mL for 20 h at 80 °C then, centrifuged with adjusting its pH to 5. After that use a 0.45 µm filter membrane (Sartorius Company) to filtered solution, cooled and stored at 4 °C prior to use.

2.3 Adsorption analysis

Adsorption capacity and Kinetic experiments were carried out in conical flasks 100 mL with 0.05 g (2 g/L) of MgO, and nanostructured MgO with 50 mL of 50 mg/L metal ion solutions without changing pH value. The mixtures were shaken (1000 rpm) at 25 °C. Separation of solid from liquid were done using centrifugal working at (2000 rpm) After that the used samples have been filtered by 0.42 µm filter membrane (Sartorius, Germany). Atomic absorption spectroscopy was used to analyze concentration of metal ions. It was documented that the ratio of removal metal ions has been calculated as:

$$\%\,removal = \left(\frac{C_0 - C_e}{C_0}\right) * 100 \tag{1}$$

where C_o and C_e denotes to primary and final concentrations of metals in the liquid phase. Each experiment was repeated twice and the mean value was taken as a final result used.

2.4 pH effect

By adding 0.1 N NaOH or 0.1 N HNO_3 to the solution, pH was adjusted in a range from 2 to 7, and all other variables are fixed.

2.5 Contact time

Batch mode experiments were done for flasks with different times of 10, 20, 40, 60, 90, 120, 180, and 1440 min, with no change of other variables.

In order to investigate the .... kinetic model has been used here in this study.

2.6 Kinetics study

In order to investigate the mechanism and rate of the metal adsorption process, kinetic models has been in this study, linearization of first order equations[15], pseudo-first order[11–18] and pseudo-second order[16,19].

The first-order model is:

$$\ln\left(q_0 - q_t\right) = a - b \tag{2}$$

where q_t is the cumulative amount of the metal ions adsorbed at time t, q0 is the maximum of the metal ions adsorbed, and a ($mg \cdot g^{-1}\ min^{-1}$) and b $(mg \cdot g^{-1})^{-1}$ are constants. An important term in these equations is the constant b, which indicates the metal adsorption rate.

The model of pseudo-first-order kinetic is given as:

$$\log\left(q_e - q_t\right) = \log q_e - b\left(\frac{k_1}{2.303}\right)t \tag{3}$$

where q_e denotes to the amounts of the ions adsorbed on the adsorbent in $mg \cdot g^{-1}$ at equilibrium and q_t denote the same manner at any time, t, while K_1 is first-order equation constant .

The pseudo-second-order kinetic model of is given as:

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where K_2 is the rate constant in $g \cdot mg^{-1} \cdot min^{-1}$.

2.7 Adsorbent dosage

Experiments were conducted in a batch mode by mixing different adsorbents weight of 0.05, 0.1, 1, 2, 3, and 4 $g \cdot L^{-1}$, with no change of other variables.

2.8 Adsorption isotherms

To conduct adsorption isotherm, experiments were carried out with 0.05 g nano structured materials with different initial concentrations of Cu^{+2}, and Pb^{+2} in solutions at (0, 10, 20, 30, 60, 100, and 200, $mg \cdot L^{-1}$) at 25 °C.

Freundlich equation is used to describe the heterogeneity of the surface of the absorbent material and it is represented by:

$$\log q_e = \log K_F + \frac{1}{n} - \log C_e \tag{5}$$

The adsorption capacity ($mg \cdot g^{-1}$) represent by k_F which is also known as Freundlich constant, while adsorption intensity represent by a constant n (dimensionless). If n within the domain $n \le 1$, that's indicates unfavorably adsorption , and if $1 < n < 10$ that will gives favorable adsorption. If we assumed that the adsorbent medium is a structurally homogeneous, the Langmuir equation is based, as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_0} + \frac{1}{q_0 b} \tag{6}$$

Weight of adsorbed over weight of adsorbent equilibrium is q_e ($mg \cdot g^{-1}$), while Ce is solution concentration at equilibrium ($mg \cdot L^{-1}$), q_0 (q_{max}) is the maximum adsorption when monolayer coverage ($mg \cdot g^{-1}$) is assumed, and b (K_L) is a constant correlates adsorption energy that quantitatively reflects affinity bonding sites ($L \cdot mg^{-1}$).

3. Results and discussion

3.1 Initial pH effect

Figure 1 shows the effect of the acidic scale pH on the adsorption process. Acidic conditions are associated with the lowering of adsorption of metal. The reason for that is attributed to the protonation of functional groups. In general, chemical adsorption occurs easily on the surface of oxides. Were hydroxyl groups is finally covered the surface layer, but, in the case of MgO, the chemical adsorption of OH extends to the inside of the solid. These hydroxyls (functional groups) can receive and release protons to the water, accordingly, surface charge will be positive or negative, as shown in the following equations[20]:

$$M - OH + H^{+} + OH^{-1} \rightarrow M - H_2^{+} + OH^{-} \tag{8}$$

$$M - OH + H^{+} + OH^{-1} \rightarrow M - O^{-} + H_2O + H^{+} \tag{9}$$

Acidity of particle surface is strong while solvent is basic. Therefore the surface will carry a negative charge by giving its proton to solvent. On the contrary, basicity of the particle surface is strong, acidic solvent, due to particles received proton from solvent[20].

MgO has high pH of zero point charge (pH_{zpc}), high basic nature, and acidic stock solution (pH between 4.5–6.0 before equilibrium), therefore, Equation (8) is the dominant mechanism.

Thus, OH^- can precipitate some heavy metals in hydroxide forms while increasing pH up to 10–10.4 (equilibrium pH after 1440 min) can increase negative pH-dependent charge in MgO and increase electrostatic sorption.

At low pH, nanostractured MgO binding sites

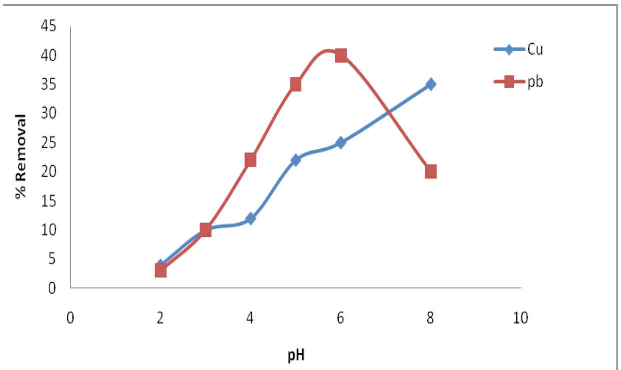

Figure 1. Effect of pH on sorption of metal ions, reaction volume = 50 mL, adsorbent weight = 0.1 g, C0 = 10 mg/L.

were dominated by H ions leading to protonate functional groups. Active sites decreased with increasing the protonated metal-binding adsorbent groups. Competing effect of H ions decreased as pH increased, giving an increasing of heavy metal ion adsorption onto the adsorbent[21] .

However, in both of these adsorbents the adsorption suddenly increased at pH > 6 in some cases. This rapid increase may be attributed to metal complexes formation or precipitation[22].

The amount of removal was always high (removal of tow metals >90%). Therefore, the native pH of all solutions (pH = 5) was considered to be the optimum value for all adsorbents and metals.

3.2 Effects of dosage of adsorbent

Figure 2 shows the effect of nanoparticle dose. Adsorption of heavy metals was studied after a 24 h contact time with an initial heavy metal concentration of 100 mg L^{-1}. Dosage increase starting at 0.5 to 3 gL^{-1} resulting an increase in the removal capacity of Cu^{2+} and Pb^{2+}.

However, this was not always the case, overlapping active sites at higher dosages could decreases heavy metal adsorption. Decreased effective surface area results from conglomeration of exchange particles[19]. Maximum removal efficiency of Cu^{+2} and Pb^{+2}, is 90 %, and 95%, respectively.

3.3 Contact time effect

Removal of heavy metal increased with time at native pH, **Figure 3** indicates that adsorption reached a maximum value after 40 to 80 min. After that period there is no change in the efficiency of the removal process. **Table 1** shows rate equations and related constants.

3.4 Kinetic and isotherme

Table 2 and **Table 3** give the Langmuir and Freundlich parameters which indicates that Langmuir give best fitting with experimental data. **Figures 4**, **5** show the Lagergren first order and Hoes second order models, it can be seen that Lagergren model give best fitting .

4. Conclusion

Here, in the current study the results showed

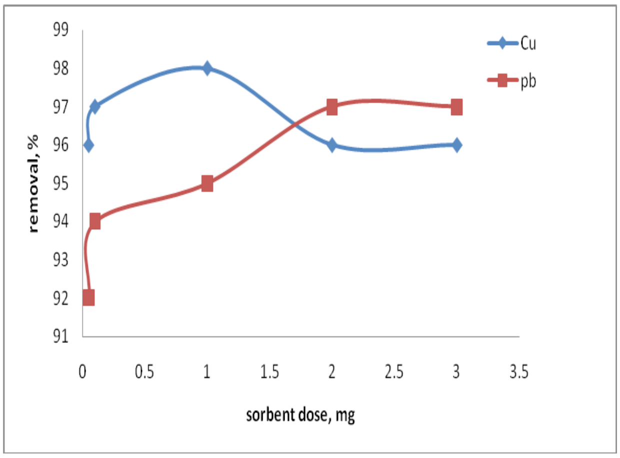

Figure 2. Effect of sorbent dose on biosorption of metal ions, reaction volume = 50 mL, pH = 5.5, C_0 = 50 mg/L.

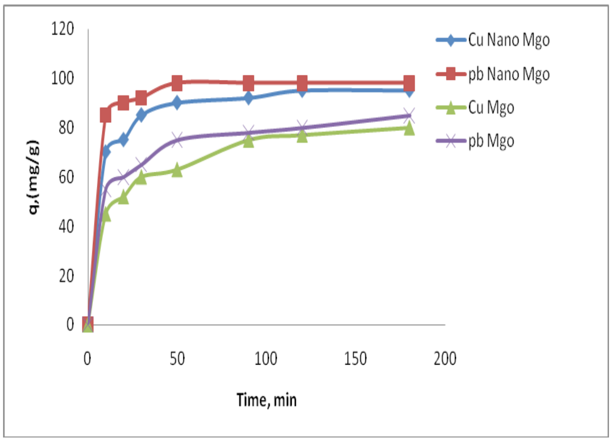

Figure 3. Effect of contact time on sorption of metal ions, reaction volume = 100 mL, adsorbent weight = 0.1 g.

Table 1. First-order kinetics model constants (at concentration of 50 mg/L)

C0 = 100 mg/L	MgO			Nanostractured MgO		
Ions	**a ($mg\cdot g^{-1}\cdot min^{-1}$)**	**b ($mg\cdot g^{-1})^{-1}$**	**R^2**	**a**	**b**	**R^2**
Cu^2	-.0.0041	1.492	0.979	-0.27	3.53	0.981
Pb^2	-0.0048	1.282	0.978	-0.28	6.25	0.995

that the process of adsorption affected by several factors, such as pH, contact time, and concentration, the most important results suggest that the process of adsorption depends heavily on the scale of acidity and showed the study of kinetics that adsorption follows the interaction of the second order equation and the best model simulates the results is Langmuir model. Nanoparticles can be used after being restricted with a certain medium to conduct adsorption of heavy metals from water.

Conflict of interest

The authors declare that they have no conflict of interest.

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Table 2. Langmuir and Freundlich parameters of lead ions at different initial concentrations

Lead Ions conce. (mg/L)	Langmuir parameters		R^2	Freundlich parameters		R^2
	q_m (mg/g)	b (l/mg)		K (l/mg)	n	
98	105.69	8.2	0.8605	51.11	32.05	0.8455
57.67	62.24	17.44	0.8862	41.81	53.47	0.8522
20.34	21.32	6.54	0.9591	8.92	26.738	0.9263

Table 3. Langmuir and Freundlich parameters of copper ions at different initial concentrations

Copper Ions conce. (mg/L)	Langmuir parameters		R^2	Freundlich parameters		R^2
	q_m (mg/g)	b (l/mg)		K (l/mg)	n	
93.59	42.32	7.72	0.7833	16.46	28.7	0.778
59.37	23.1	11.17	0.8833	20.00	24.71	0.7915
19.62	9.88	22.90	0.967	7.41	65.22	0.9069

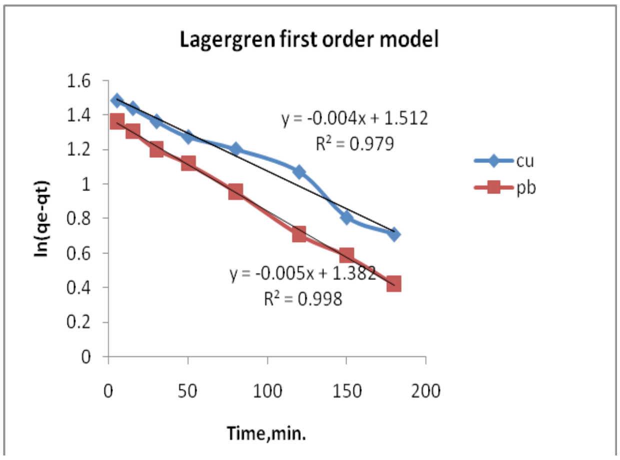

Figure 4. Lagergren first order model for copper and lead.

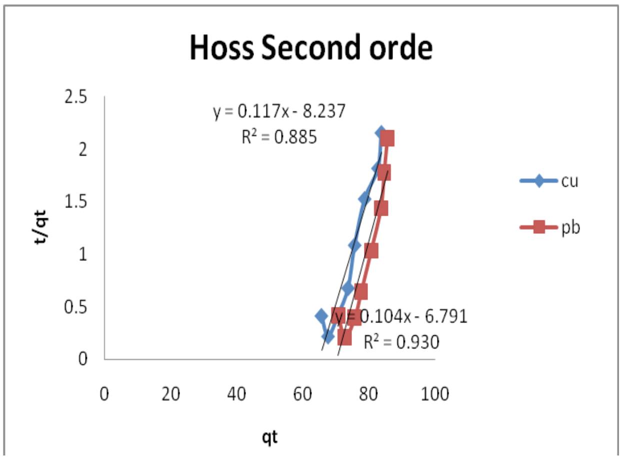

Figure 5. Hoss second order model for copper and lead.

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