Desalination and Water Treatment
www.deswater.com

51 (2013) 2343–2350
February

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doi: 10.1080/19443994.2013.734581

Applicability of Egyptian diatomite for uptake of heavy metals

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Received 15 February 2012; Accepted 5 August 2012

ABSTRACT

Three types of natural, classified, and refined diatomite were examined for their abilities to remove metal ions from aqueous solutions at different operating conditions including pH, contact time, amount of adsorbent, and metal concentrations. Batch adsorption experiments revealed that equilibrium was practically attained after 15 min for Cd and Zn, and after 30 min for Cu. On the other hand, Ni and Pb attained equilibrium after 60 min. The optimum dose for the removal of all understudied metals was recorded to be 9.0 g/L at an optimum pH of 4.7. According to the optimum condition study, refined (acid-washed) diatomite is the most efficient one with the selectivity sequence given as $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}$ due to the correlation between the ionic radii of heavy metals with external and internal pore diameters of diatomite.

Keywords: Diatomite; Low-cost sorbent; Heavy metals; Optimum conditions

1. Introduction

Industrial wastewater is one of the major sources of aquatic pollution. Among the aquatic pollutants, heavy metals have gained relatively more significance in view of their persistence, biomagnification, and toxicity [1–3].

There are many treatment processes which have been proposed for the removal of heavy metals. Chemical precipitation, membrane filtration, ion exchange, and alum coagulation are some of the most commonly used methods for the treatment and disposal of pollutant containing wastes [4–6].

Remediating wastewater containing heavy metals by adsorption is one of the most promising cost-effective techniques. The adsorption systems have many advantages including process simplicity, fastness, and suitability for wastewater containing moderate and low concentrations of metals [7–10].

Basically, any solid material with a microporous structure can be used as an adsorbent, e.g. bone and coal char, clays, iron oxides, synthetic and natural zeolites, and activated carbon. Moreover, adsorbents must have a large surface area; the chemical nature and polarity of the adsorbent surface influence the attractive forces between the adsorbent and adsorbate [11–16].

Diatomaceous earth, or diatomite ($SiO_2 \cdot nH_2O$), is a naturally occurring structure containing up to 80–90% voids. It is a white-colored, sedimentary silica mineral composed of hydrated silica microfossils shells of the single-cell algae, diatoms. It typically consists of 86–94% silicon dioxide (SiO_2), with significant quantities of calcite, clay, or gypsum and small amount of iron oxide and feldspars [17]. Its porous structure, low density, and fine particle size (typically 10–200 μm)

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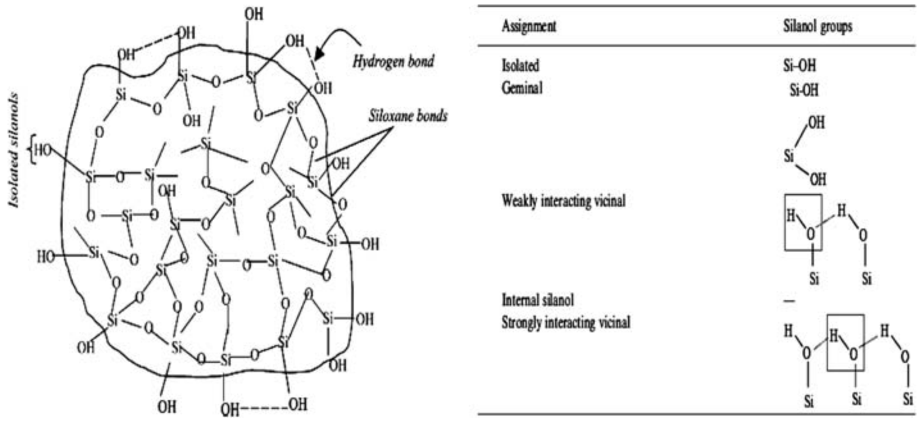

Fig. 1. The hydroxyl structure and charge density profile of diatomite sample.

result in industrial applications such as filter aid, fillers, catalyst carriers, biofilm/biomass supports, packed materials for chromatography separation, anticaking agents, natural insecticides, fertilizer conditioners, thermal insulators as well as absorbents for pet litter and oil spills [18–21]. Diatomite has been used as adsorbent by many authors. It was used for the removal of dyes from wastewater [7,8,11,12], heavy metal adsorption [4–21], municipal wastewater treatment, and herbicides' removal [10].

Similar to synthetic amorphous silicas, the reactivity of diatomite intrinsically links to the presence of reactive sites on its surface, (Fig. 1). Reactive sites not only condition the charge, acidity, solubility, and hydrophilicity of the surface, but they are also the sites of grafting and ligand-exchange reactions, so that they govern the properties of related diatomite products to a great extent [18].

The objective of this work is to utilize diatomite ore from Gebel Elow El Masakheet locality, southwest El-Fayoum Governorate, Egypt as well as classified and refined diatomite as a low-cost adsorbent to remove heavy metals, specifically Pb, Cd, Zn, Cu, and Ni from synthetic wastewater.

2. Experimental

2.1. Materials and characterization

The raw diatomite used in this study was thoroughly disintegrated to $-45\,\mu m$ via attrition scrubbing and 3-hydroxy-cyclone classifier. The classified product was further refined from the accompanied inorganic carbonates by leaching with hot hydrochloric acid.

Sample characterization was conducted using X-ray diffractometer model "PW 1010" and "Perkin-Elmer Analyst 200" atomic absorption unit. Size analysis was applied using "Fritsch" shaker with a series of ASTM standard sieves and "Warman" cyclosizer for sub-sieve sizing below $45\,\mu m$. The diatomite skeletal has been microscopically viewed using scanning electron microscope (SEM) of the type JEM-1230, JEOL and transmission electron microscope JSM T-20, JEOL. Surface area and pore characteristics were measured by nitrogen isotherm at 77 k using "Quantachrome NOVA" automated gas sorption system.

Surface charges of the diatomite sample were measured using Zetasizer (Malvern Zetasizer 2000), Malvern Instruments Ltd, Malvern, UKL, equipped with a video recorder. HCl and NaOH were used as pH modifiers. Prior to the measurements, the sample was conditioned in 1 mM NaCl at the desired pH. An average of two readings for two individual runs was presented in this work.

2.2. Analytical methods

2.2.1. Determination of metals concentration

The concentrations of metals in all samples were determined according to APHA (2005) [22] using Atomic Absorption Spectrometer (Varian SpectrAA (220)) with graphite furnace accessory and equipped with deuterium arc background corrector. Precision of the metal measurement was determined by analyzing (in triplicate) the metal concentration of all the samples.

2.3. Quality control

For each series of measurements, absorption calibration curve was constructed which composed of a blank and three or more standards from Merck (Germany). Accuracy and precision of the metals' measurement were confirmed using external standard reference material for trace elements in water from National Institute Standards and Technology.

2.4. Batch adsorption studies

Each of the batch adsorption studies was carried out by contacting the adsorbent with the metal ions at room temperature (25 ± 0.1 °C) in a glass tube. Studies were conducted to determine the effects of pH, contact time, sorbent dosage, and initial ion concentration on the adsorption of Cd (II), Cu (II), Ni (II), Pb (II), and Zn (II).

Each experiment was conducted in a mechanical shaker at 120 rpm. All the samples were filtered through Whatman filter paper (No. 42) and the metal ion concentration was determined in the filtrate. To distinguish between possible metal precipitation and actual metal sorption, controls were used without adsorbent materials.

All the experiments were carried out in triplicate and the mean of the quantitative results were used for further calculations, the percent relative standard deviation for results was calculated and if the value of standard deviation for any sample was greater than 5%, the data were not used.

3. Results and discussion

3.1. Characterization of diatomite

Electron microscopic study of Gebel Elow El Masakheet diatomite showed the diatomaceous skeletons (frustules) of diatomite imbedded in a calcareous matrix and belonged mainly to centric and pinnate types, as shown in Fig. 2. The chemical analysis of the ore sample was illustrated in Table 1, which reveals that the main content of diatomite ore is 37% SiO_2, 32% CaO, and minor amount of alumina reaching 2% Al_2O_3. While, the silicon content increased to 61.65 and 96.66% in classified and refined diatomite, respectively, as shown in (Table 1).

Table 1
Chemical analysis of −45 μm classified and refined diatomite and El Masakheet diatomite ore

Constituent	Classified wt.%	Refined wt.%	El Masakheet diatomite ore wt.%
Wt.	58.52	40.06	–
SiO_2	61.65	96.66	37.09
CaO	21.27	–	32.09
Al_20_3	2.09	3.06	2.01
Fe_2O_3	1.65	–	0.85
LOI	16.54	0.27	27.96

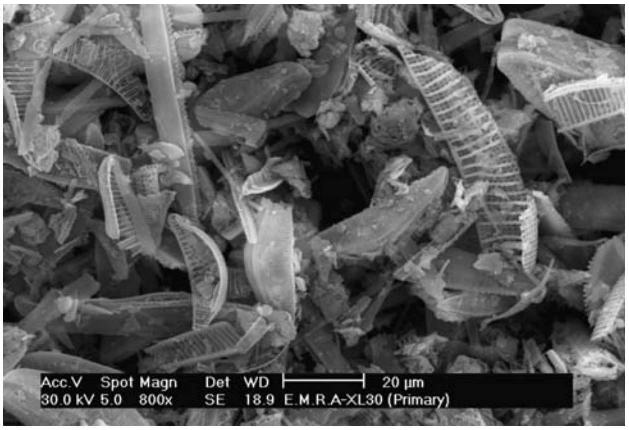

Fig. 2. SEM of diatomite frustules.

The surface area analysis of diatomite sample showed an external surface area of 25.77 m^2/g and mean pore diameter of 20.19 Å with a wide distribution of pore size indicating the presence of pore diameter ranging from macropores to mesopores, as shown in (Table 2).

The Zeta potentials of diatomite sample at various pH values are illustrated in Fig. 3. It is clear that the Zeta potential of diatomite sample varies with the changing pH. As is evidenced by the negative value of Zeta potential, the surfaces of diatomite are negatively charged in the wide pH range of 2–12, and the negative Zeta potential increases with increasing pH in this range, indicating that the quantity of negatively charged functional groups on the diatomite surface increases with the rise in pH, Fig. 3. The isoelectric point for the sample was observed at pH 3.

The studies demonstrated the importance of the various functional groups, available on the surface of diatomite, on the mechanism of adsorption [23]. Diatomite surface is terminated by OH groups and oxygen bridges, Fig. 1, which act as adsorption sites. –OH groups act as centers for adsorption through forming hydrogen bonds with the adsorbate [23] and could be divided into: (i) isolated free silanol (–SiOH), (ii) geminal free silanol ($–Si(OH)_2$), and (iii) vicinal or bridged or –OH groups bound through the hydrogen bond [24]. In addition, diatomite consists of siloxane groups or –Si–O–Si– bridges with oxygen atoms on the surface.

A comparison of metal uptake percentage on different types of diatomites (ore, classified, and refined diatomite) was performed. Fig. 4 shows that refined diatomite has the highest metal uptake percentage for all studied metals, especially for lead it reached to 75.8%. This was attributed to the increase in the diatomite phase contents in the order of 1:1.66:2.61 for ore,

Table 2
Surface characteristics for diatomite

Micropore volume, micropore area, mesopore volume, mesopore area, total pore volume, average pore radius, and percentage of micropores and mesopores of ore and calcined diatomite

Adsorbent	Microp-volume (cm^3/g)	Microp-area (m^2/g)	Mesop-volume (cm^3/g)	Mesop-area (external surface area) (m^2/g)	Total pore volume (cm^3/g)	Average pore radius (nm)	Content of microp- and Mesop-	
							Microp- (%)	Mesop-(%)
Diatomite (hydrocyclone over flow)	0.0233	12.6	0.1863	110.4	0.2096	2.418	11.10	88.9

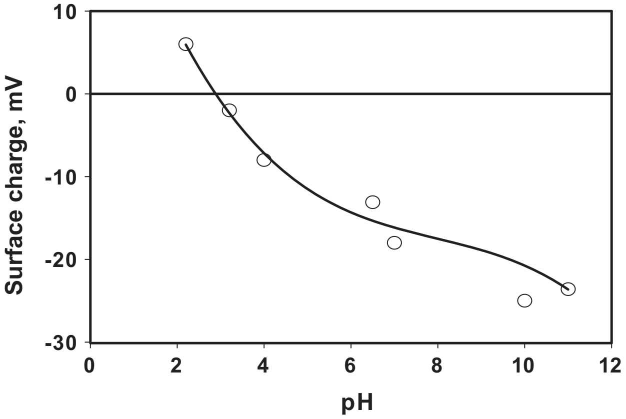

Fig. 3. Electrokinetic measurement for diatomite sample.

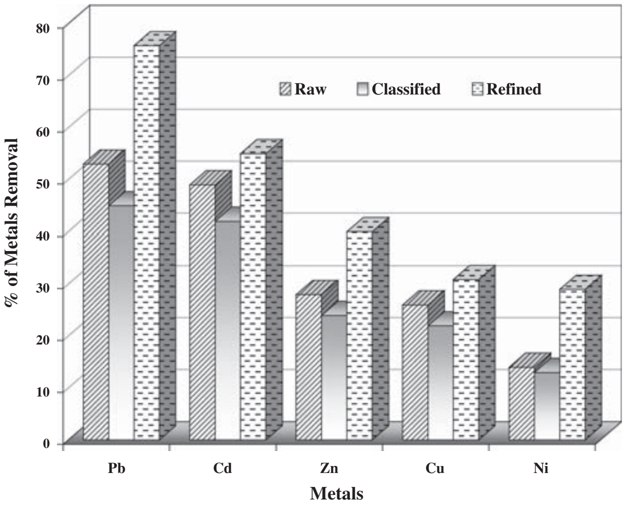

Fig. 4. Percentage of metal removal by different type of diatomites.

classified, and refined diatomites, respectively, as shown in Tables 1. Also, Fig. 5 illustrates the porous structure of diatomite before and after refining which shows that the pores are blocked by impurities in case of ore diatomite while they are clean for the processed diatomite. Therefore, metals were adsorbed on inner pore surface in mono-layer and then were condensed inside the inner pores which improve its adsorption behavior [13]. Therefore, further experiments were carried out using refined diatomite.

In order to verify the activity of various functional groups available on the surface of diatomite, the effect of pH on adsorption of Cd (II), Cu (II), Pb (II), Ni (II), and Zn (II) was investigated in the pH range 1.5–5.5 with constant refined diatomite amount of 10 g/L, a shaking time of 120 min, and metal concentration of 50 mg/L. Fig. 6 reveals that the efficiency of metal ion removal increased significantly as pH increased from 1.5 to 4.7 and remains constant from 4.7 to 5.5 for all the studied metals. At low pH, less metal ion adsorption occurs that may be explained on the basis of the binding sites being protonated, resulting in a competition between H^+ and metal ions for occupancy of the binding sites [25]. However, by increasing the pH, the competition between positive charges decreases as these surface active sites become more negatively charged, which enhances the adsorption of the positively charged metal ions through electrostatic force of attraction [4,26]. Thus, conducting the experiments at optimum pH 4.7 ensures the presence of the divalent form of the ions and preserves the chemical stability of the diatomite, the removal efficiency values for Pb(II), Cd(II), Zn(II), Cu(II), and Ni(II) were 75.8, 55, 40, 30.9, and 29%, respectively.

3.2. Adsorption procedure

3.2.1. Adsorption kinetics

The equilibrium time required for the adsorption of the studied metals on refined diatomite at different time intervals from 5 to 120 min was studied at con-

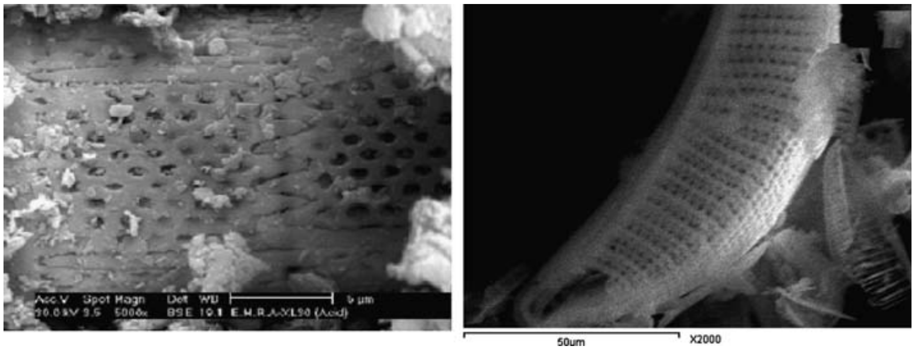

Fig. 5. Blocked and clean pores in case of ore and processed diatomite.

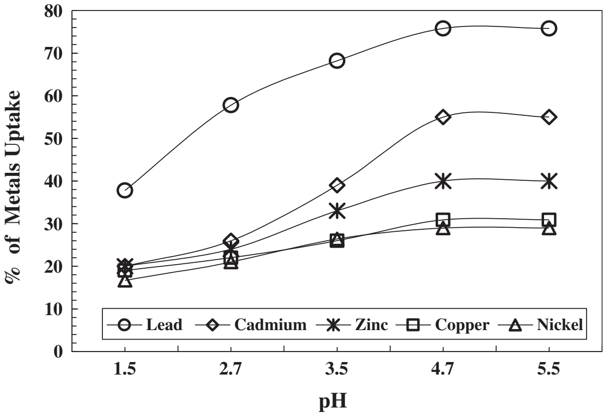

Fig. 6. Effect of pH on metal removal by refined diatomite.

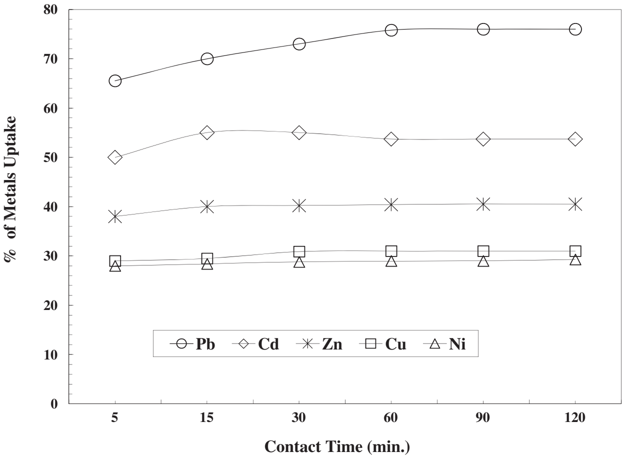

Fig. 7. Effect of contact time on metal removal by adsorption on diatomite.

stant refined diatomite amount of 10 g/L and metal concentration of 50 mg/L. The relation between the contact time and uptake percentage of metal ions by refined diatomite is shown in Fig. 7. The results showed that the equilibrium contact time was found to be 15 min in case of Cd (II) and Zn (II) and 30 min for Cu (II) while the equilibrium in case of Ni and Pb (II) was 60 min; and the removal percentages followed the order:

Pb (74%)>Cd (55%)>Zn (40%) Cu (30%)>Ni (29%)

The results indicated that the removal percentage of studied metals increases with the increase in the adsorption time. However, it remains constant after an equilibrium time, which indicated that the adsorption tends toward saturation, where, the rate of adsorption is higher in the beginning due to large available surface area of the adsorbent. This means that, at equilibrium, the rate of uptake is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [27].

3.2.2. *Effect of adsorbent loading*

Various amounts of adsorbent refined diatomite, ranging from 1 to 10 g/L, were used with a constant shaking time of 120 min and metal concentration of 50 mg/L. Fig. 8 shows that the percentage of metal removal increased with the increase in the amount of adsorbent and attained equilibrium after 9 g/L of adsorbent dosage and the removal efficiency reached to 75.6% for Pb(II), 54.8% for Cd(II), 30.4% for Cu (II), 29.4% for Ni(II), and 39.7% for Zn(II). This is due to the availability of more adsorbent as well as greater availability of surface area [28]. At adsorbent dosage > 9 g, there is no further increase in the removal percentage, as the surface metal ions concentration and the solution metal ions concentration come to equilibrium with each other [29]. Thus, increased adsorbent dosage did not enhance the removal percentage of the studied metal ions.

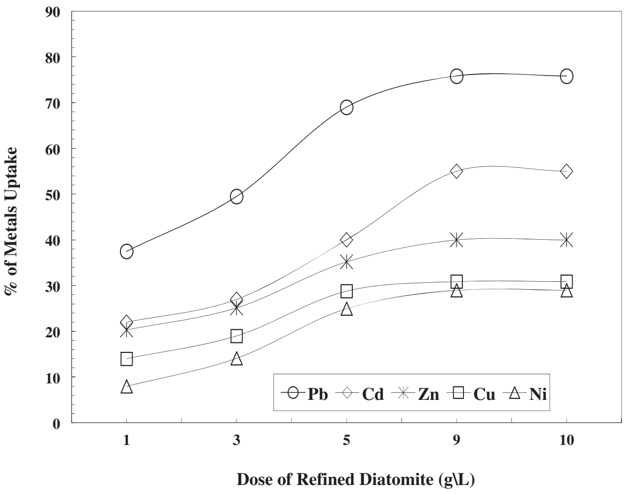

Fig. 8. Effect of sorbent dose on metal removal by refined diatomite.

3.2.3. *Effect of metal concentration on the distribution ratio (K_d)*

The distribution ratios (K_d) of Cd (II), Cu (II), Ni (II), Pb (II), and Zn (II) onto refined diatomite as a function of their concentrations in the solutions were studied at constant temperature (25 ± 0.1˚C). This was calculated as follows [29]:

$$K_d = [\text{amount of metal on adsorbent} / \text{amount of metal in solution}] \times V/m \qquad (1)$$

where, V = volume of the solution (ml) and m = adsorbent loading (g).

The metal adsorption percentage and K_d (ml/g) can be correlated by the following equation:

$$\text{Adsorption } \% = 100K_d/[K_d + V/m] \qquad (2)$$

Fig. 9 illustrates the distribution ratio K_d as a function of metal ion concentrations. Results showed that the K_d values decreased with increasing concentration of metal ions. This can be attributed to the involvement of the energetically less favorable sites with increasing metal concentration in solution, which accompanied with an increase in the amount of metal adsorbed on refined diatomite with a nonsignificant value compared to the amount of metal in concentrated solution. Accordingly, a decrease in K_d values also occurred [30]. On the other hand, in diluted solution, i.e. lower metal concentration, more chances were created to occupy the high energetically favorable sites, that increased the amount of adsorbed metal on diatomite, leading to increment of K_d values [8].

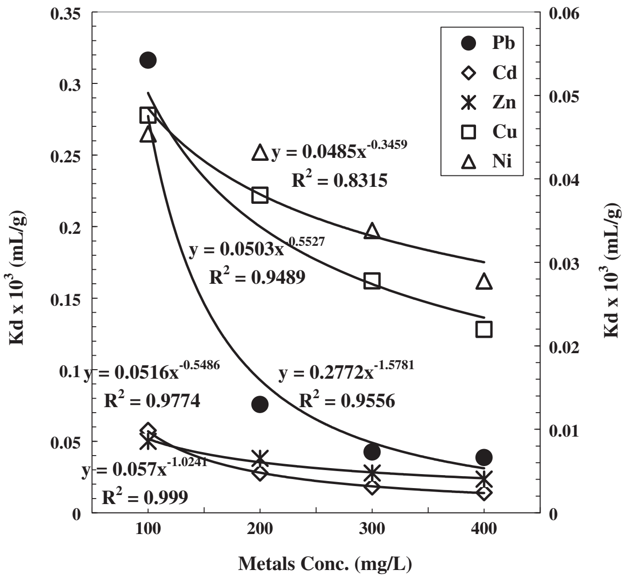

Fig. 9. The effect of metal ion concentration on their distribution ratios (K_d) on diatomite surface at the optimum operation conditions for each metal.

The relation between adsorption percentage of different heavy metals on diatomite with their ionic radii and diatomite pore size and volume was tried to be followed up in this study. The adsorption affinity of heavy metal on diatomite was noticed to be in agreement with the order of their ionic radii ($Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+}$), Table 3. Diatomite sample had an average pore diameter of 24.18 Å and average pore volume of 0.0301 cc/g. The ionic radii of the metals ranged between 0.69 and 1.2 Å, which were very small to retain in the mesopores. Consequently, the more increase in metal crystal radius, the more retention in the mesopores and more adsorption could be expected as a result. The higher ionic radii (1.2 Å) and higher electronegativity of lead (2.33) could

Table 3
Correlation between metal characteristic parameters and percentage removal of heavy metals at the optimum operation condition for each metal and constant metal concentration of 50 mg/L

Metal	Ionic radius (Å)	Hydrated ionic radius (Å)	Electro negativity	% removal
Lead	1.2	4.01	1.8	74
Cadmium	0.97	4.29	1.7	34.1
Zinc	0.74	4.30	1.6	31
Copper	0.72	4.19	1.9	30
Nickel	0.69	4.04	1.6	29

explain that lead is more favorable for adsorption than other metals [31]. On the contrary, Abd-Elfattah and Wada [32] reported that the selectivity sequence and estimation of the competitive adsorption of several heavy metals show that most of the observed sequences are correlated neither with the sequence of ionic radii nor with the sequence of electronegativity (Table 3). Furthermore, several authors [31,33,34] pointed out that, there is a parallel relation between the adsorption sequence and the hydrolysis properties of the heavy metal cations.

4. Conclusion

The aim of this paper was to explore and present diatomite's capability, from jointed fissile of Gebel Elow El Masakheet, to uptake certain heavy metal contaminants. Therefore, natural, classified, and refined diatomite was used for the removal of metals from aqueous solutions. Refined diatomite with unblocked porous structure adsorbed metals on inner pore surface in mono-layer and then condensed it inside the inner pores, which improves its adsorption behavior. The optimum operating conditions for the removal of heavy metals using easy and simple pretreatment of diatomite were determined. Pb (II) ions show the highest removal efficiency that reached 75.6% at a pH of 4.7 and 9.0 g/L optimum dose due to the correlation between the ionic radii of lead with external and internal pore diameters of diatomite. Therefore, based on the results of this study, diatomite can serve as a potential sorbent for the real applications for the removal of heavy metals from industrial wastewater; and further investigations on diatomite surface modification will be carried out in order to increase its efficiency for metal removal.

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