ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Removal of Some Heavy Metals from Wastewater by Using Diatomaceous Earth.

Adly A Hanna, Marwa A Sherief*, and Reham MM Aboelenin.

National Research Centre, Dokki, P.O.Box: 12622, Postal code: 11787, Cairo, Egypt.

ABSTRACT

The aim of this work is stydying the removal of some divalent cations, Cd, Cu, and Co from their aqueous solutions by using the natural materials, diatomite. The diatomite material was characterized by the chemical analysis, IR, X-ray and TEM also the surface area was calculated. The results of characterization indicate that diatomite consist mainly from silica with some other oxide.The effect of pH values and the initial concentrations of the aquous solution on the efficiency of removing was studied. The results indicate that the efficienc of removing dependsgreatly on the pH values and the initial concentration of the cations with optimum value for each case. In general the effeciency of removing for these cations follows the following sequence Cd>Cu>Co. This behavior may due to the electronegativity and the ionic radius as well as the different species of these cations in their solutions

Keywords: Diatomaceous earth- adsorption – heavy metals- characterization- concentratrions

Corresponding author

INTRODUCTION

Waste streams encountered in mining operations, and various chemical processing industries, contain heavy metals which are non- biodegradable, toxic priority pollutants. Due to their tendency to accumulate in living organisms causing various diseases and disorders, the treatment methods for metal- bearing effluents are essential for environmental and human health protection. Among numerous commonly used techniques for water purification, adsorption technologies have gained the most attention because of their low cost and easy operation [1,2]. In recent years, an intensive research was can ducted on the technologies of adsorption. Focusing on the selection and /or production of low- cost adsorbents with good metal- binding capacities, which could be utilized as an alternative to the most widely used adsorbent in wastewater treatment- activated carbon. Natural materials of both organic and inorganic nature (such as chitosan, zeolites, clay and clay materials, etc) and certain waste products from industrial operation (such as fly ash, coal, oxides and silicates)are classified as low- cost adsorbents because they are economical and locally available [3,4]

Diatomite (DE) is fine grand, low density biogenic sediment, which consists essentially of diatoms. It is the fossilized remnants of diatoms, tiny plunktonic algae residing in all the earths water[5]. The death of large numbers of diatoms in an area leads to sedimentation of the minerals present in the cell walls leading to large depositsin their high purity, often greater than 85% silica [6]. As a result diatomite is both non-toxic and odourless, present naturally in large quantities and at high purities and it is available at low cost. Diatomite is of particular interest due to its unique properties such as high porosity, high permeability, small particle size, high surface area, low thermal conductivity, and chemical intertness [7].These properties of diatomite led to its early use for water purification, in which it was used to remove particulate matter from water for applications[6].

In previous work, the authers used some natural metals such as calcite and dolomite to remove some impurities[8]. On the other hand they used some prepared materials such as hydroxyapatite for purification of waste water[9].

$Cd^{+2}$is very toxic, which can couse serious damage to the kidneys and bones. It is known for its toxicity and for its association with Itai-Itai desease[10]

Copper is one of the biologically essential ions but is only required at low concentration, Concentrations4 higher than 1.0-1.5 mg/l in water lead to enviromental and health problem[11].

Although necessary for good health to the cobalt as a part of vitamin B12, the high or low levels of cobalt in the aqueous medium couse some health problems[12].

The aim of this study was to investigate the efficiency of low – cost adsorbents (diatomite) to remove some heavy metals from wastewater. Such as (Cd^{+2} ,1Cu^{+2}, Co^{+2},) and study the effect of some parameter such as (pH, initial concentrations) on the efficiency of uptaking for each cation.

MATERIALS AND METHODS

Natural (DE) was used without purification except washing with distilled water. It was charactezied by various techniques. Infrared absorption spectra (IR) were performed by the KBr disc technique using a fourier transformer infrared between 400 to 4000 cm-1. X-ray diffraction, XRD, was carried out by using Brukur D8 advance diffractomer (Germany) using CuKα radiation. The surface area of the natural DE was performed by using Quanachrome Inst. Quantachrome Nova Automated gas sorption system version 1.12. Transmition electron microscope (TEM) was performed to study the morphology of DE.

The dried DE was used as adsorbent to remove some divalent cations, Cd, Cu,Co from their aquous solutions.

In this work, 0.1 gm of the DE powder was dispersed in 20 mm^3aqueous solutions containing different concentrations of the divalent cations nitrates. The pH values of the solution were adjusted by adding 1N HNO_3 solution at 30 ºC, the solutions were left for 24h to attain the equilibrium state. After this period the solid parts were separated by filtration, the filtrate was analyzed by using atomic absorption route to determine the remainder amounts of Cd, Cu, andCo. The effect of the concentration of the divalent cations between 5-30 ppm and PH of solutions between 2-11 were investigated. The efficiency of removing was calculated by using the following formula, %= $(C_0 - C)/ C_{0,}$ where C_0 and C are the initial and the concentration of the divalent cations in the solution after removing respectively.

RESULT AND DISCUSSION

I-Characterion of DE sample

The chemical analysis of the DE sample shows that it consists mainly of silica (SiO2= 83.6) with relatively small percentage of other oxides such as Al_2O_3, Fe_2O_3, CaO, and other oxides, Table 1[13]. In comparison with other diatomite's it is clear that the silica content is nearly similar to silica content in china(14), Turkey(15), diatomite. From the results of the chemical analysis, it may conclude that the diatomite behaves in a similar way to amorphous silica due to the large quantity of silica present in its structure

Table 1: chemical analysis of diatomite earth

Oxide	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	K_2O	CaO	MgO	Loss/others
Percentage	83.6	4.24	1.07	——	——	——	6.17	——	4.86

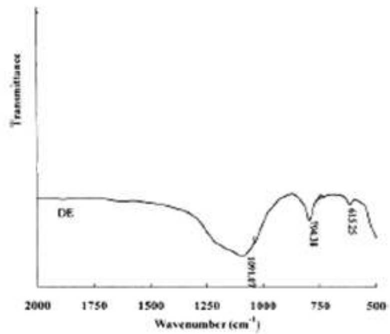
IR –spectra

The IR charts of the natural sample was illustrated in (Fig 1).From the chart, a series of absorbance bands were appeared at (790, 1000-1200 Cm^{-1}) corresponding to the silicates structure as pointed out [16]. Also, at 1080 cm^{-1}, a wide absorption band was appeared due to the vibration of the Si-O-Si. Also, a weak absorption band appeared at ~ 600 cm^{-1} which corresponding to Si-O deformation and Al-O stretching.

X-ray diffraction pattern:

The X-ray charts of the samples (Fig 2) indicate that the specified peaks of the silicon were illustrated, as reported [17].

Figure 1: IR spectra of natural diatomaceous earth, DE



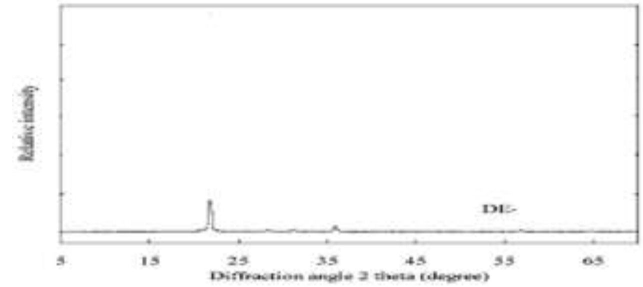


Figure 2: XRD of natural diatomaceous earth, DE

Transmission Electron Microscope (TEM):

Examining DEs samples with **(TEM)** (Fig 3), showed that the natural DE has very small number of crystals with the sharp edges and its surface area as calculated from the TEM equals to 7.3 m2/g . The shapes of crystals and the high surface area favored the using of the DE for removing the heavy metals.

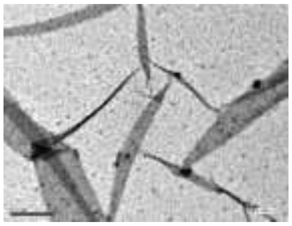


Figure 3: TEM of natural diatomaceous earth

Removing of di valent cations by DE:

In order to provide a quantitative description of Cd, Cu, Co onto diatomite surface, two types of adsorption experiments were carried,

(i) Adsorption of constant initial metal concentration as a function of pH.
(ii) Adsorption at constant pH as a function of metal concentration in its solutions.

In this study, the batch process was performed, where a certain weight of DE(0.1gm) was immersed in nitrate solutions of the divalent cations (Cd, Cu, Co) at the same concentration of these cations with continuous stirring to attain the equilibrium state (t= 24h) and pH = 2,4,6,8and 10 were adjusted by using the puffer solutions.

A study on the effect of the pH values of removing the considered cation from their aqueous solution was performed and the results were represented in Fig 4.Generally, it is observed that the effeciency of removing for the three cations increases as the pH value increases until reached to steady state.

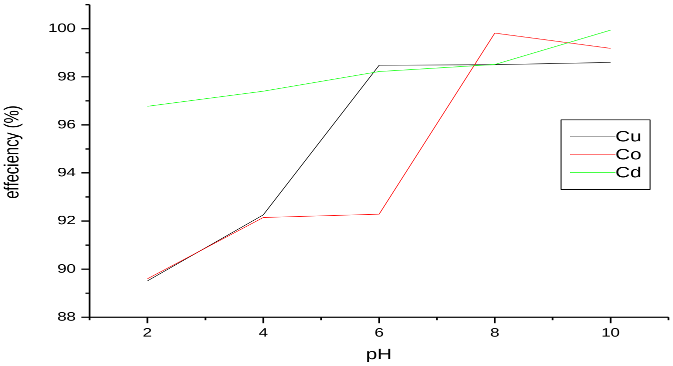


Figure 4: effect of Ph on the effeciency of removing cations

This state depend on the nature of the cations, where it recorded between 8-10 pH values for Cd^{+2} , 4-5.5 values for Cu^{+2}[18] ,and 6-7 values for Co^{+2}[19,20]. From these values it may conclude that the removing of Cd^{+2} is favoured at in the basic medium, while for Cu^{+2} at the acidic medium and for Co^{+2} in nearly neutral medium, this variation may due to the electronagitvities of there cations where it equals 1.69 for Cd^{+2}, 1.9 for Cu and 1.9 for Co. On other hand it depend on the ionic radius which equal 0.97for Cd, 0.73 for Cu, and o.74 for Co. Due to the difference in both the electronegativity and ionic radius of the considered cations, the removing of the three cations behave the following sequence Cd < Co <or=Cu where:-

(i) The more electronegative ions will be more strongly attracted to the surface of the diatomite
(ii) The smaller ionic radius will be easily enter into the smaller pores and have greater access.

Also, it is observed that the efficiency of removing Cd^{+2} increases smoothly from pH =2 to pH =8, and the effeciency increases strongly for the other two cations. This behaviour can be explained by the forming of different species of aqueous solution for Cd ions have little tendency to hydrolyze at pH values below 8, but above this values it tend to exist in hydroxo-complex compound. Cd ions in fresh water at pH =6-8, it predominant in $CdOH^-$, $Cd(OH)_2^-$, $Cd(OH)_3^-$and $Cd(OH)_4^-$ where these species capable to bind with the surface of the diatomite by forming an electrostatic forces [21].

For Cu ions in the acidic medium, the predominant species are Cu^{2+}, $Cu(OH)^{o}_2$, $CuHCO^{3+}$, $CuCO_3$ºand $CuOH^-$, which can formed some complex with the functions groups (carboxyl group) on the surface of the diatomes. At the basic medium pH >10 the major species are $Cu(OH)_4^{2-}$ and $Cu(OH)_3^-$ which less active to form bonds [22].

For Co cations the optimum extraction by diatomite from its aqueous solution is nearly in the natural medium (pH =6-8). This may explained by the presence of $Co(OH)^+$ and $Co(OH)_2$ species which allowing to the Co^+ to be easily extracted onto the negatively charged diatomite surface as pointed out by Shenget et al (23), who used the china diatomite in removing of Co cations from the aqueous solutions

To study the effect of the initial concentration of the three cations on the efficiency of removing by using diatomite, for different concentrations were prepared from each cations. These concentrations are 5,10,15,20,25,ppm and 30 ppm, and the same weight of diatomite was used. The filtrate after equilibrium attends was analyzed to calculate the effeciency. Fig 5, represents the dependence of the removing efficiency on the initial concentrations of the cations.

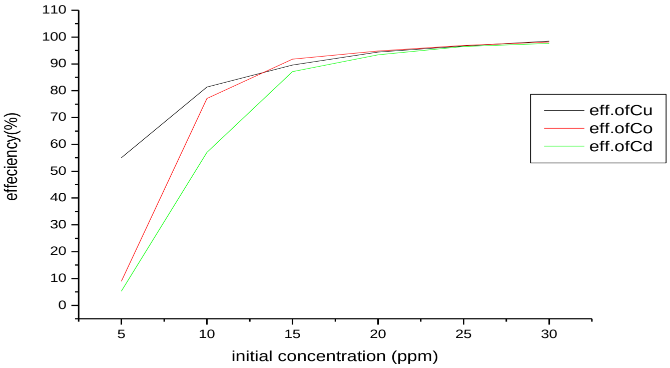


Figure 5: effect of the initial concentration on the effeciency of removing cations

The obtained results indicate that the efficiency increases rapidly at low concentration recording the maximum value for Cd=83, for Cu= 92 and Co= 85. After these values, the effeciency of removing are nearly independent on the concentration, thus may due to the saturation of the surface of diatomite [24]. It noteworthy that the dependence of the efficiency on the concentrations of the cations behaves the same trend as observed by studing the pH effect and following the same trend Cu>Cd=Co. Table 2 shows the data which illustrated the trends of extraction.

Table 2: shows the data which illustrated the trends of extraction

cation	electro negativity	Ionic radius	Max efficiency	PH value
Cd	1.69	0.97	83%	8-10
Cu	1.9	0.73	92%	4-5.5
Co	1.9	0.74	85%	6-7

CONCLUSION

From the study of removing Cd, Cu, and Co from their aqueous solution by using diatomite it may conclude that:-

(i) The main constituent of diatomite is amorphous silica with some other oxides with specific surface area = 7.3 m2/g

(ii) The effeciency of removing depent markedly on the pH value and the initial concentrations as well as the ionic species of each cation in their solution

(iii) The effeciency removing of the three cations behaves the following sequence Cd> Cu> Co

REFERENCES

[1] Rousseau RW. Handbook of separation process technology. Wiley-Interscience, new York, 1987

[2] Mckay G. Use of adsorbents for the removal of pollutants from wastewater. CRC. Press, Tokyo, 1996.

[3] Babel S, Kurniawan TA. J Hazard Mater 2003; B97(1-3): 219-243.

[4] Wang YH, Lin SH, Juang RS. J Hazard Mater 2003; B 102(2-3): 291-302.

[5] Wolf A. Diatomaceous earth, in: AWolff(Ed), Britannica Concise Encyclopedia, Encyclopedia Britannica Inc., Peru, 2006.

[6] GP Fulton. Diatomaceous Earth Filtration for safe drinking water, American society of civil engineers, USA, 2000.

[7] SE Bailey, TJ Olin, RM Bricka, DD Adrian. Water Res 1999; 33: 2469-2479.

[8] AA Hanna, MA Sherief and RMM Aboelenin. Phos Res Bull 2008; 22: 7-12.

[9] AA Hanna, MA Sherief, RMM Aboelenin, SMA. Canadian J Pure Applied Sci 2010; 4(1): 1087-1093.

[10] U NRC, Copper in Drinking Water, National Academy Press, Washington, DC, 2000.

[11] F Elmekyapar, A Aslan, YK Bayhan, A Cakici. J Hazard Mater 2006; 137: 293-298.

[12] http://www.lme.com/minormetals/6783.asp.Review

[13] SS Ibrahim, AQ Selim. Probl Miner Process 2012; 48:413-424.

[14] P Yuan, DQ Wu, HP He, ZY Lin. Appl Surf Sci 2004; 227: 30-39.

[15] RA Goyer, MO Amdur, J Doull, CD Klaasen(Eds.), Casarett and Doulls Toxicology, fourth ed., Pergamon, New York, 1991, pp.653-655.

[16] MA Vicente Rodriguez, M Suarez Barriers, and JD Lopez Gonzalez, MA Banares Munoz. Clay Miner 1994; 42: 724-730.

[17] WT Tsai, CW Lsi, and KJ Hsien. J Colloid Interface Sci 2006; 297: 749-754.

[18] SM Lee, AP Davis. Water Res 2001; 35: 534-539.

[19] A Netzer, DE Hughes. Water Res 1984; 18: 927-928.

[20] A Gelabert, OS Pokrovsky, C Reguant, J Schott, A Boudou. J Geochem Exploration 2006; 88: 110-113.

[21] D Mohan, KP Singh. Water Res 2002; 36: 2304-2309.

[22] I Bodek, WJ Lyman, WF Reehl, DH Rosenblatt. Environmental In organic Chemistry: Properties, Process and Estimation Methods , Pergamon, New York,1998.

[23] M Koyuncu. Physicochem Probl Miner Process 2012; 48: 485-494.

[24] M Federoff, J Jeanjean, JC Rouchaud, L Mazerolles, P Trocellier, TP Maireles, and DJ Jones. Solid State Sci 1991; 1: 71-76.