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Utilization of surface modified phyllosilicate mineral for heavy metals removal from aqueous solutions

Khaled A. Selim [a], Rasha Smair El-Tawil [b], Merit Rostom [c,*]

[a] Central Metallurgical Research & Development Institute, Minerals Technology Department, CMRDI, Cairo, Egypt
[b] National Research Center, Inorganic Chemistry Department, NRC, Cairo, Egypt
[c] Academy of Scientific Research and Technology, ASRT, Cairo, Box 11562, Egypt

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ABSTRACT

The objective of this work is to enhance the adsorbing performance of the natural Egyptian phyllosilicate mineral, glauconite (greensand), through surface modification to obtain a particular combination of physical and chemical properties. It was found that Zn removal increased from 84% to 94%, while Pb removal varied from 96.67% to 99% by using 10–25 g/l modified glauconite in a solution having 50 mg/l Zn^{2+} and 30 mg/l pb^{2+} ions. Adsorption data were investigated using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms. Linear regression methods are used to determine adsorption capacities and optimum adsorption isotherms. R^2 value of Langmuir isotherm model for pb^{2+} is higher than other models. The maximum monolayer coverage (Q_o) from Langmuir isotherm model was calculated to be 15.363 and 21.654 mg/g and the separation factor indicating a favorable sorption experiment is 0.0324 and 0.13207 for Zn^{2+} and Pb^{2+} respectively. Also from Freundlich isotherm model, the intensities of adsorption (n) that indicated favorable sorption are 1.3036 and 1.364 for Zn^{2+} and Pb^{2+} respectively. The heat of sorption process was calculated from Temkin isotherm model to be 6.44101 and 4.1353 J/mol for Zn^{2+} and Pb^{2+} respectively, that indicated to the physisorption process which B < 20 kJ/mol so, Temkin isotherm is not fitted with experimental adsorption but the mean free energy was calculated from DRK isotherm which are 24.693 and 47.093 kJ/mol, where E_D < 8 proved that the adsorption experiment followed a chemisorption process. So the relative adsorption capacity for metals was in the order Pb < Zn.

1. Introduction

Water contamination due to increased population and industrial activities is one of the most challenging issues to the researchers, because it is continuously increasing threats to both human health and the environment. This pollution mainly caused by waste water drain from different industries e.g. metal plating, mining processes, fertilizer industries, tanneries, batteries, paper industries and pesticides, etc. [1,2]. This wastewater contains mainly heavy metals which their concentrations increase especially in developing countries. Heavy metals are well known as non-biodegradable unlike some organic contaminants. The toxicity of some heavy metals can accumulate in living organisms cause severe illness such as hyper tension, anemia, cancer, renal kidney disease, nervous system damage and mental disorder [3,4]. Zinc and lead are the most hazardous heavy metals which take intensive attention as popular containments of industrial wastewaters. In more details contaminated water with zinc in a level of 3–5 mg/l may appear clear forming a plating film on boiling. Owing to the standard limits of water, it generates a strong demand to improve the efficiency of existing methods for removing Pb and Zn from the water. Many techniques are used for the effective removal of toxic heavy metals from aqueous solutions such as adsorption, flocculation, coagulation, membrane filtration, electrochemical process, solvent extraction, bio-sorption, chemical precipitation, ion-exchange, as well as various other processes [5,6]. However, most of these techniques have several disadvantages such as production of secondary pollution, high cost, high levels of energy and chemicals needed, and weak treatment operation at low metal concentrations. [7,8]. Adsorption method is an effective and economic way for heavy metal wastewater treatment. The adsorption process show design and operation flexibility and usually produce high-quality treated effluent. In addition, adsorbents can be regenerated by desorption process due to reversibility of adsorption in some cases. Many natural and artificial materials are used for adsorption process. Therefore,

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* Corresponding author.
E-mail address: m.rostom75@yahoo.com (M. Rostom).

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researchers are now interested on using new natural adsorbents with low cost and local availability such as olive stone waste, phosphate rock, clay minerals, oil shale ash, chitosan, zeolite, fly ash, and biosorbents. Glauconite is a group of dioctahedral, potassium, iron rich, compositionally heterogeneous, phyllosilicate minerals and it has been recognized as useful in water treatment [9]. Manganese oxides could be used for the adsorption and removal of different heavy metals from aquatic environment as reported in researches. For example, removal of copper (II) and lead (II) from aqueous solutions by manganese oxide-coated Zeolite [10], removal of lead (II) from aqueous solution by manganese oxide-coated carbon nanotubes [11,12], for the removal of the toxic hexavalent chromium by manganese oxide nanofibers [13] and removal of Cadmium by MnO_2 loaded D301 resin [14]. The aim of this paper is to enhance the adsorbing performance of Egyptian glauconite (greensand) through surface modification by coating with MnO_2 forming manganese greensand for removal of Zn and Pb from industrial waste water through filter model that could be used easily in the removal process. The adsorption equilibrium was fitted using Langmuir, Freundlich, Temkin and Dubinin-Raduskevich isotherm models

2. Materials and methods

2.1. Materials

Glauconitic sandstone samples were collected from the Abu Tartur mine which is located 650 km southwest of Cairo, Egypt, in the Western Desert. Manganese sulfate and potassium permanganate from Aldrich were used in glauconite coating forming manganese greensand. Heavy metals solutions of Pb and Zn were prepared from analytical grade chemicals.

2.2. Methods

2.2.1. Surface modification of glauconite

Glauconite sample was screened to the proper effective size (−850 +250 μm), followed by water washing for clay removal from the surface. Due to the friability of glauconite mineral as most of the pellets appeared soft and can be crushed with the fingernail, the research team decided to use the chemical treatment for glauconite mineral instead of mechanical treatment which causes a lot of turbidity, 130,000 NTU which affects the color of water after treatment. Manganese dioxide coating was applied to the media by soaking the washed glauconite grains in a plastic or a glass jar, (1: 3) solid /liquid ratio, in a solution of $MnSO_4$ and shacked gently from time to time. The coating was applied by going through a series of exhaustion and regeneration cycles. Each cycle deposited manganese dioxide that was held on the filter grain by ion exchange. After definite time and several cycles, enough manganese dioxide coated the filter grain to act as oxidizing catalyst to speed up the oxidation reduction reaction and make sure it is carried to completion in the filter, not after it. Perkin-Elmer Atomic Absorption "A Analyst 200" was used in measuring the initial and equilibrium concentrations of heavy metals [15].

2.2.2. Characterization

A Philips PW 1730 powder X-ray diffractometer with Fe-filtered Co (K-alpha) run at 30 kV and 20 mA was used to determine the qualitative and the semi-quantitative mineralogical composition of glauconite. Infrared vibrational spectra were recorded on a Nicolet Magna 750 Fourier-transform spectrometer. For glauconite sample, 28 scans were accumulated over the 4000–400 cm^{-1} spectral range employing the transmittance mode and a resolution of 4 cm^{-1}. The pressed KBr disc employed for this purpose was prepared using 0.4 mg of sample and 200 mg of KBr. Samples were observed on fresh surface under a JSM-6400 scanning electron microscope (SEM) to examine the morphology of glauconite before and after treatment. A laser Zeta Meter 'Malvern Instruments Model Zeta Sizer2000' was used for zeta potential measurements. Surface area of the glauconite samples was measured using the Quantachrome NOVA Automated Gas Sorption [15].

2.2.3. Separation experiments

The separation experiment was carried out in greensand filter. First of all, a good filter medium should have some characteristics including low resistance to filter flow, resists chemical attack and have sufficient strength to withstand the filtration pressure and mechanical wear. According to the above recommendations, as seen in Fig. 1, greensand filter consists of 3-Liter polyacrylate filter column with dual media sand (0.1 mm) for removal of precipitated iron and any other suspended materials in water and manganese greensand (0.03–0.1 mm) of about 17 cm thickness and a diameter of about 5 cm. This filter was designed by the Research team and was manufactured in Egyptian National Research Center Workshop, NRC by local materials to be available and more economic. A flow direction from the top to the bottom of the filtration column, Fig. 2, is the favorable direction due to the gravity power but in the presence of clay-sized particles, it is preferred to water to be flowed from bottom to the top of filter unit to prevent these particles from transportation by fluid flow. The operating conditions are depending on the physical characteristics of the coated

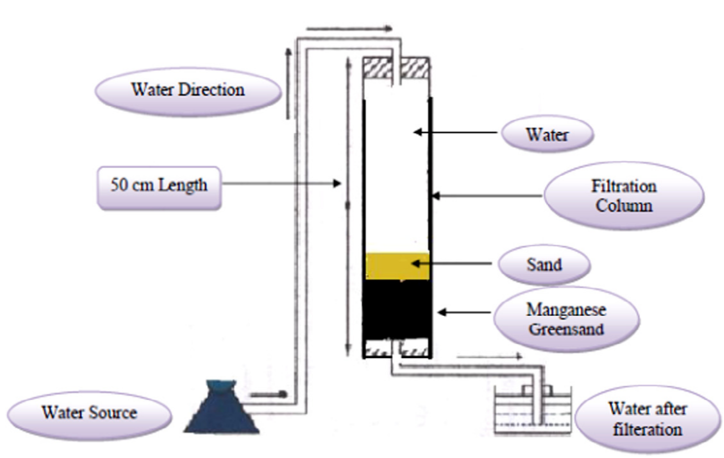

Fig. 1. Sketch of Green Sand Filter Unit.