

Removal of Mercury (II) from Aqueous Solutions by Activated Bentonite

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Abstract

In this work, natural clay(Bentonite)from (Al Safra-AL Anbar-Iraq) was acid activated and chemically treated using sulfur compounds(sodiumsulfide).It was characterized by using X-ray diffraction, Atomic force microscope and scan electron microscope. The Bentonite used for adsorption of mercury from aqueous solution sample. Variations in the quantity of adsorbed mercury (II) ions as a function of pH, effect of contact time and initial concentration and the adsorption kinetic were studied.

Key Words: Clay, Bentonite, Acid Activation and Mercury.

أزالة أيونات الزئبق الثنائي من المحاليل باستخدام البنتونايت المنشط

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بغداد - العراق

الخلاصة

درس بهذا البحث تنشيط الطين الطبيعي (البنتونايت) المأخوذ من منطقة الصفرة في محافظة الأنبار، ومعالجته كيميائياً باستخدام احد مركبات الكبريت (كبريتيد الصوديوم) . وصف البنتونايت المستخدم بهذه الدراسة باستخدام الأشعة السينية ومجهر القوة الذرية إضافة الى المجهر الإلكتروني الماسح واستخدمت مادة البنتونايت لأمتزاز أيونات الزئبق الثنائي من المحاليل المائية . وتمت دراسة درجة الحمضية وتأثير زمن تلامس البنتونايت مع المحلول بتراكيز اولية مختلفة وميكانيكية الأمتزاز ..

الكلمات المفتاحية : الأيطان ، البنتونايت ، التنشيط الحامضي والزئبق

Introduction

The presence of toxic heavy metals in industrial effluents has become a matter of environmental concern. Mercury (Hg) is one of the heavy metals of concern to environments and has been found in the wastewaters coming from manufacturing, oil refining and materials processing. It also appears naturally in some water. Mercury is considered one of the most harmful metals found in the environment. Hence, it is necessary to remove Hg(II) from wastewaters before it is discharged. It poses serious health hazards such as neurological and renal disturbances and impairment of pulmonary functions (Krishnamoorthi and Vishwanathan, 1991). The tolerance limit for discharging Hg(II) into inland surface waters is 10 µg/l and for drinking water it is 1 µg/l (EPA agency). Various types of technology are available for removing Hg from water including chemical precipitation (Patterson and Passion, 1990) reverse osmosis (Larson, 1992), ion-exchange (Chiale *et al.*, 2000) and adsorption (Namasivayam and Senthikumar, 1997). However, these technologies do not seem to be economically feasible because of their relatively high costs, and developing countries may not be able to afford such technologies.

Since adsorption is one of the most effective methods for removing heavy metals from wastewater, a naturally occurring adsorbent would make the removal of these metals from wastewater by this method an economically viable alternative. Many materials found in nature present adsorption and ion-exchange properties. The majority of these natural ion-exchange materials are made up of crystalline aluminosilicates with cation exchange properties, although certain aluminosilicates may also act as anion exchangers such as zeolites, apatite.

Adsorption is a complex process involving physical, chemical and electrical interactions at the sorbent surfaces. Surfaces of solid materials can be modified with organic groups in order to enhance the adsorption efficiency of the material towards metal ions from aqueous solutions. (Malakul *et al.*, 1998)

The aim of this paper is to assess the capacity of granular bentonite to adsorb (Hg⁺²) from aqueous solutions. The effect of pH, contact time and initial concentration of the metal solution were investigated.

Materials and Methods

The bentonite used in this study was obtained from Iraqi Geological Survey Institute. The bentonite powder

was granulated and only particles smaller than 71 μm (200 mesh) were used for the sorption experiments. Powder X-ray diffractogram was obtained.

Cation exchange capacity (CEC) was determined by methylene blue method. All reagents were of analytical grade and used without further purification (Hang and Brindley, 1970). The concentration of Hg (II) in the filtrate were measured by Buck Scientific cold vapor, Flow Injection Mercury System Atomic Absorption Spectrometer, model VGP210 which has a detection limit of (2ppm).

Bentonite Sample Preparations

Bentonite was activated by heating at 150°C for 5 h, and then treated with 0.5 M solution of potassium permanganate and sulphuric acid solution (6M). The mixture was stirred at 80°C for 4 h, and then filtered, washed with deionized water and dried at 80°C.

Impregnation Procedure

About 10 g of activated bentonite was immersed in 0.1 M acetone solution of sodium sulfide, stirred for 4 h and the solvent evaporated. Due to ion exchange, the original calcium bentonite is converted to sodium bentonite by activation with sodium sulfide, the results showed that the cation exchange capacity (CEC) was affected by sodium

sulfide activation. The material was washed with deionized water to remove any non-adsorbed reagent and dried at 80°C.

Mercury (II) Solution

A 500 ml of a stock solution of 1000 mg/l Hg (II) was obtained from SCP SIENCE. This solution was diluted to obtain a standard solution containing 100 $\mu\text{g/l}$ Hg (II).

Adsorption Measurement Procedure

About 0.05g of bentonite was mixed with 25ml of 100 ppm Hg(II) solution. The pH of the solution was adjusted to the desired value using 0.1 M NaOH and HCl. The mixture was stirred at 400 rpm at 34°C. The amount of Hg(II) ions in the supernatant was measured. The amount of Hg (II) adsorbed was calculated.

Atomic Force Microscope and Scan Electron Microscope

A suspension of bentonite powder in alcohol solution was prepared and the crystal size distribution was determined by Advanced Inc, Atomic Force Microscope (AFM), model AA3000 and Tescan Scan Electron Microscope (SEM) model Vega III.

Effect of pH

The adsorption of Hg (II) was studied by varying pH between 3 and 8

using treated bentonite. Contact time was 80 min. A plot of q_e the amount of Hg (II) adsorbed at equilibrium (mg/g) versus at various pH

Kinetics and Equilibria of Adsorption

Two important physic-chemical aspects for evaluation of the adsorption process are the kinetics and the equilibria of adsorption. Kinetics and equilibria of adsorption of treated clays were investigated using aqueous solutions of Hg(II) with concentrations from 100-300 ppm .

.A fixed adsorbent weight of 1 g was added to 50 ml of Hg(II) solution. The uptakes of Hg (II) over time (0-80 min) at pH 6 for different initial concentration of Hg (II) ion were measured.

Results and Discussion

Chemical composition of bentonite

The chemical, mineralogical and physic-chemical characteristics of the natural sample are summarized in Table (1)

Table (1) Physico-chemical, Chemical and Mineralogical Characteristics of Bentonite

SiO ₂ %	FeO ₃ %	Al ₂ O ₃ %	CaO%	MgO%	Na ₂ O%	K ₂ O%	TiO ₂ %	SO ₃ %	L.O.I%
55.7	5.29	13.76	5.27	3.48	1.43	0.49	0.81	1.06	11.35

It is evident that bentonite contains silica and aluminas as major constituents while other oxides of metals are present in lesser amounts.

Atomic Force Microscope and Scan Electron Microscope

A suspension of bentonite powder in alcohol solution was prepared and the crystal size distribution was

determined by Advanced Inc, Atomic Force Microscope (AFM), model AA3000 & Tescan Scan Electron Microscope (SEM) model Vega III.

Tables (2 and 3) and Figures (1 and 2) shows the particle size and the distribution of the bentonite particles in the sample. In Figure (1) aggregated particles are seen on mica surface. Particles diameters range from 50 nm to 500 nm. Most of the

partials have blocky shapes typical for their monoclinic crystal symmetry. Figure (2) shows 3D-image of the bentonite surface. Figures (3 - 6) show the high-resolution scanning electron microscopic images of bentonite, indicate its microstructures. The observed bentonite show hexagonal or

slightly rounded plates, micro pits, micro islands, individual crystallites and broken edges.

Table (3) AFM for Bentonite Suspension Sample

Granularity Cumulation Distribution Report								
Sample: CdTeSi_01_003			Code: CdTeSi_01_003			AFM ذقلاج المجهز الضوئي		
Line No.: line no			Grain No.: 83			الماسح		
Instrument: CSPM			Date: 2013-03-26			مجهز القوة الأرية		
Avg. Diameter: 544.06 nm			=<10% Diameter: 200.00 nm					
<=50% Diameter: 450.00 nm			=<90% Diameter: 800.00 nm					
Diameter (nm)-	Volume (%)	Cumulation (%)	Diameter(n m)-	Volume(%)	Cumulation (%)	Diameter(n m)-	Volume(%)	Cumulation (%)
100.00	3.61	3.61	500.00	9.64	50.60	1000.00	1.20	91.57
150.00	2.41	6.02	550.00	8.43	59.04	1050.00	3.61	95.18
200.00	1.20	7.23	600.00	8.43	67.47	1150.00	1.20	96.39
250.00	4.82	12.05	650.00	4.82	72.29	1200.00	1.20	97.59
300.00	2.41	14.46	700.00	7.23	79.52	1250.00	1.20	98.80
350.00	7.23	21.69	750.00	3.61	83.13	1750.00	1.20	100.00
400.00	8.43	30.12	800.00	3.61	86.75			
450.00	10.84	40.96	850.00	3.61	90.36			

Table (2)AFM for Bentonit Suspension Sample

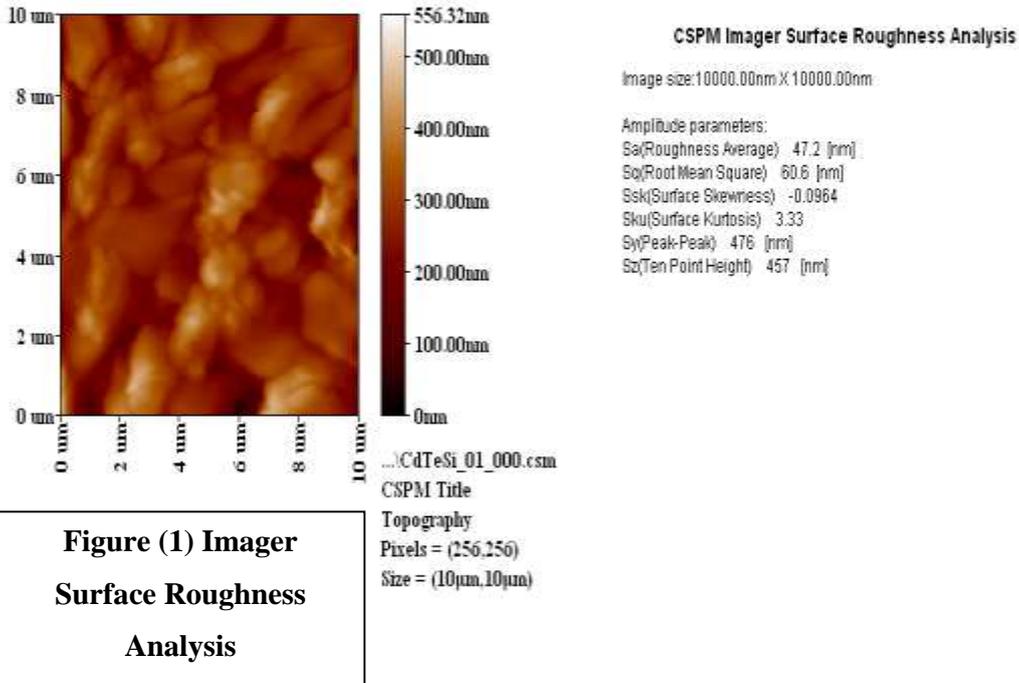


Figure (1) Imager Surface Roughness Analysis

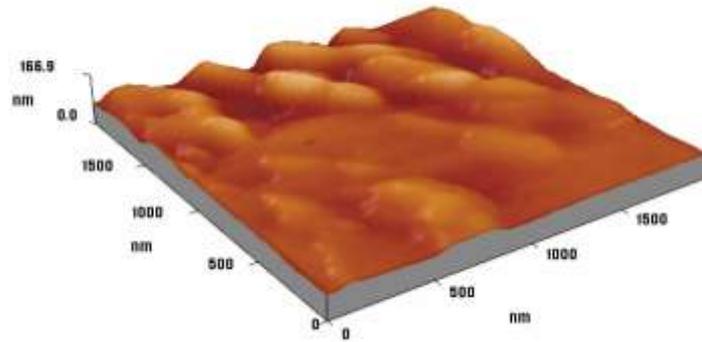


Figure (2) (3D)-Image of the Bentonite Surface

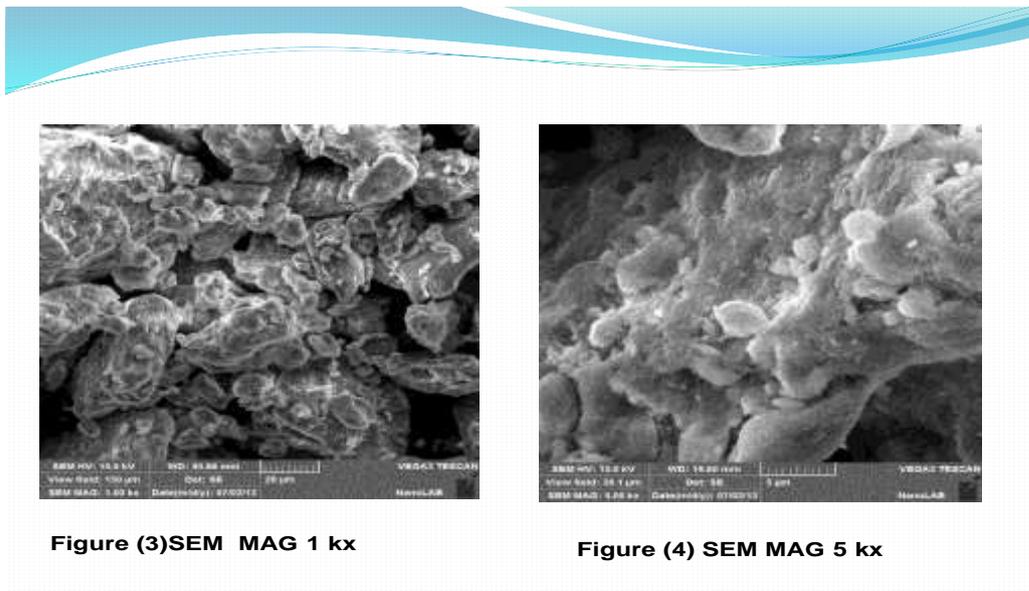


Figure (3) SEM MAG 1 kx

Figure (4) SEM MAG 5 kx

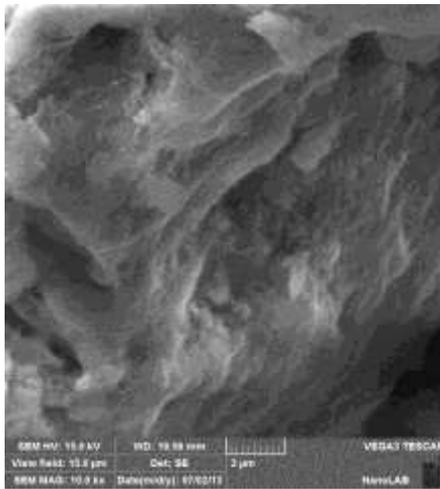


Figure (5) SEM MAG 10kx

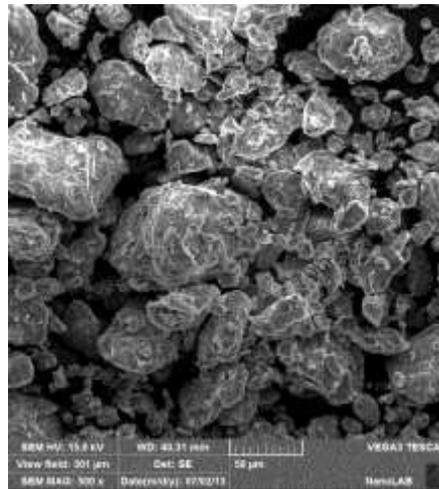


Figure (6) SEM MAG 500 kx

Effect of pH

The adsorption of Hg (II) was studied by varying pH between 3 and 8 using treated bentonite. Contact time was 80 min. A plot of q_e the amount of Hg (II) adsorbed at equilibrium (mg/g) versus at various pH is shown in Figure (7). In acidic condition, both the adsorbent and the adsorbate are positively charged Hg^{+}

and H^{+}) and therefore the net interaction is that of electrostatic repulsion. Also, the higher concentration of H^{+} ions present in the reaction mixture competes with the positively charged Hg (II) ions for the surface adsorbing sites resulting in a decrease in the removal of Hg (II) . It was observed that there was very little effect of pH on the adsorption of Hg (II) in pH range of 6-8 which is consistent with other work on kaolinite.

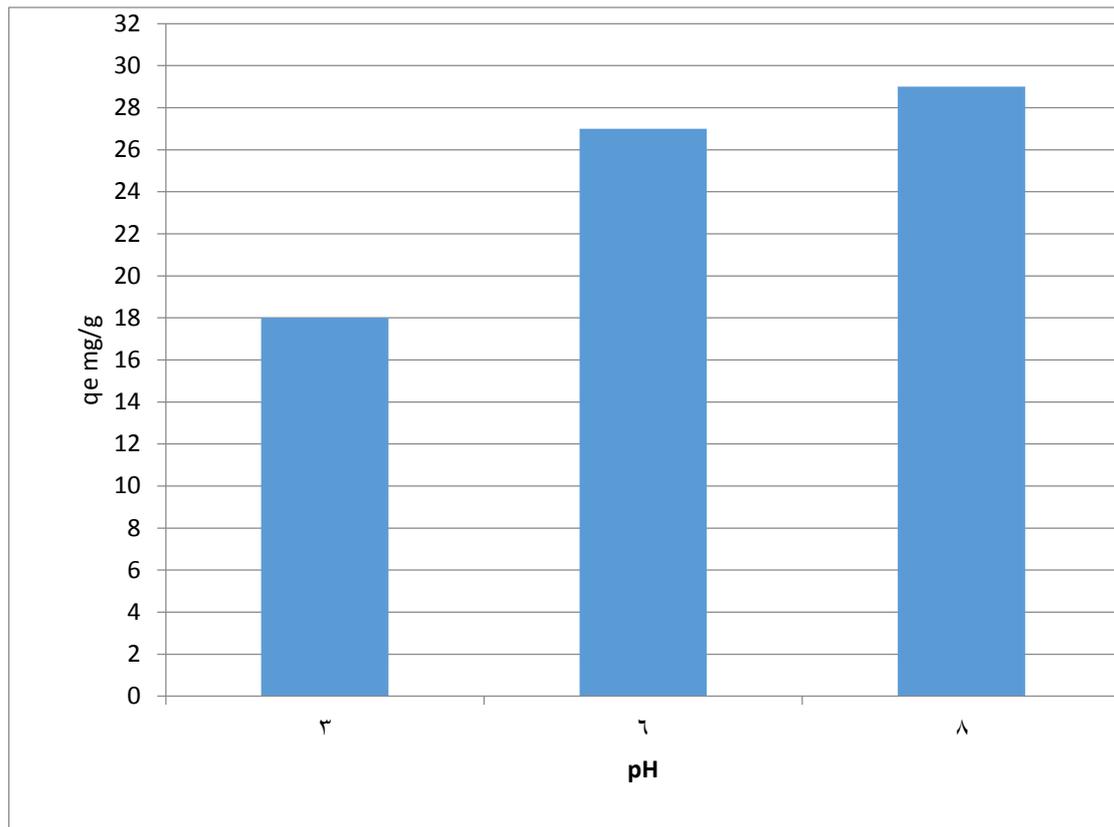


Figure (7) The Amount of Hg (II) Adsorbed at Equilibrium Various at Various pH

At low pH ,in the acidic condition ,both the adsorbent and the adsorbate are positively charged (Hg^{2+} and H^+) and therefore the net interaction is that of electrostatic repulsion.Also ,the higher concentration of H^+ ions present in the reaction mixture competes with the positively charged $\text{Hg}(\text{II})$ ions for the surface adsorbing sites resulting in a decrease in the removal of $\text{Hg}(\text{II})$.It was observed that there was very little effect of pH on the adsorption of mercury in the pH range 7-8 which is consistent with other work on kaolinite (Sarkar, *et al.*, (2000).

On acid activation, the alumina content of the raw clay was decreased and the surface area was increased .It was observed that acid treatment increased surface area and the material becomes more porous (Filho, *et al.*, 1995).

Effect of Time and Initial Concentration

The adsorption of $\text{Hg}(\text{II})$ on the treated bentonite over time and at pH of 6 for different initial concentrations of $\text{Hg}(\text{II})$ ion are shown in figure (8).

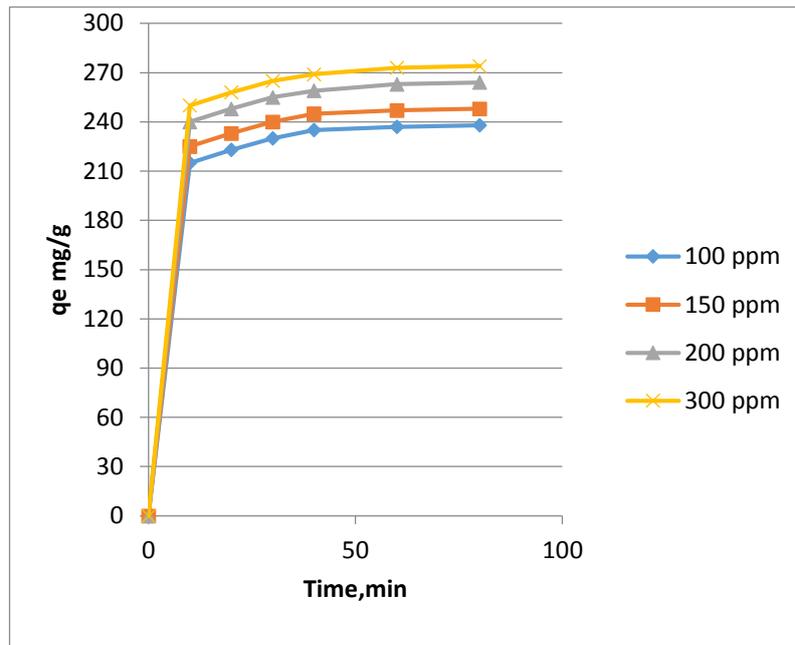


Figure (8) Kinetics Curves of Treated Bentonite

It was observed that for all concentrations, the adsorption was rapid and reached saturation. The amount of Hg (II) adsorbed increased with contact time until attaining equilibrium at 20 minutes. This result is interesting because equilibrium time is one of the important parameters for economical

wastewater treatment applications. The adsorption of Hg(II) from liquid phase to solid phase is normally assumed to be controlled by physic-chemical processes. The mechanism of metal removal is thought to be complexation and ion exchange (Manohar, *et al.*, 2000).

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