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Characterization and Adsorption of Heavy Metals on Natural Diatomite

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Abstracts: Natural diatomite was characterized by X-ray fluorescence spectroscopy (XRF), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and specific surface area (BET) analysis. The percentage of chemical compositions of silicon dioxide (SiO_2), aluminium oxide (Al_2O_3), iron oxide (Fe_2O_3) and the other oxides were found to be 71.88, 10.13, 6.83 and 3.65, respectively. The morphology of diatomite was generally cylindrical in shape with the average particle diameter size of 7.72x20.5 µm. The element composition was indicated by energy dispersive values. The characteristic X-ray radiation showed silicon (Si) = 1.739 keV, oxygen (O) = 0.525 keV, aluminium (Al) = 1.486 keV and iron (Fe) = 6.398 keV. The surface area and average pore size were 54.26 m^2.g^{-1} and 54.30 Å. The adsorption of heavy metal ions were determined by atomic absorption spectroscopy (AAS). The percentage adsorptions of Cd(II), Pb(II), Cu(II) and Zn(II) ions were 88.71 %, 90.54%, 88.23 % and 94.56%, respectively.

Keywords: Adsorption, Heavy metals, Natural diatomite

1. INTRODUCTION

Environmental pollution arises from industrial waste streams as a consequence of the industrialization process is one of the major problems that have to be solved or controlled. Many industrial facilities such as metal plating, mining operations, fertilizer industry, tanneries, textile industry discharge heavy metals via their waste effluents. The disposal of these effluents into natural water resources causes damage to the aquatic environment and in humans. Some of these metals, even in small amounts can cause severe physiological and health effects. Therefore, heavy metals are permitted to be discharged only at very low concentrations in wastewaters to prevent public streams and water resources from becoming contaminated [1].

Water is considered an important and scarce commodity in many countries around the world. In particular, the contamination of surface and ground water with heavy metal is a concern. Industries such as plating, ceramics, glass, mining and battery manufacturing are considered the main source of heavy metal, e.g. lead, cadmium, chromium and mercury, in the local water streams is a major concern to public health [2]. The presence of heavy metals in aqueous wastewater has become a problem due to its harmful effects on human health. It is known that legal standards on environment control are becoming strict and, as a result, the discharge of heavy metals into aquatic bodies and sources of potable water is being rigorously controlled [3].

A variety of technologies have been developed and applied for the treatment of wastewater. The commonly used techniques include membrane filtration with the aid of coagulants, ion exchange, chemical oxidation, precipitation, activated carbon adsorption and constructed wetland. Activated carbon adsorption is one of the most commonly used methods for the treatment and disposal of metal containing wastes. Activated carbon adsorption is considered to be a particularly competitive and effective process for the removal of heavy metals at trace quantities. However, the use of activated carbon is not suitable in developing countries due to the less economics and high costs associated with production and regeneration of spent carbon and disposal of regenerate wastes. As a result, over recent years there has been growing interest in using low-cost natural minerals for treating wastewater. The use of alternative low cost materials as potential adsorbents for the removal of heavy metals has been highlighted. These cost-effective materials range from industrial by-products or waste, such as waste rubber tyres, to agricultural products such as wool, rice straw, coconut husks and peat moss. Other known natural materials like clay, zeolite and diatomite have been investigated for their potential use as adsorbents for heavy metals [4,5].

Diatomite ($SiO_2.nH_2O$) is a pale-colored and lightweight sedimentary rock composed principally of silica microfossils of aquatic unicellular algae. Diatomite consists of a wide variety of shape and sized diatoms in a structure containing up to 80–90% void. Diatomite's high porous structure, low density and high surface area results in a number of industrial applications such as filtration media for various inorganic and organic chemicals, absorbents, catalyst carrier, filler and so on. In aqueous solution diatomite particles are negatively charged, and possesses strong attractability for positively charged species [6]. Diatomite exists in large deposits around the world so it can be applied to various industrial processes. Diatomite usually contains other sediments such as clay and fine sand but its deposits sometimes consists of diatom shells only. In Thailand, the Thai Department of Mineral Resources has found 500,000,000 tons of natural raw diatomite mainly in Lampang Province. Thus, diatomite is naturally available in large quantities at an extremely low cost [7].

2. EXPERIMENTAL

Diatomite was obtained through the natural resources in China. The chemical composition on natural diatomite was characterized using X-ray fluorescence spectrometer (Bruker, Germany). Moreover, the surface area was determined by specific surface area analyzer (Quantachrome, England). The morphology, particle size distribution and element composition of natural diatomite was measured by scanning electron microscope (Jeol-JSM5410LV, Japan), laser particle size analyzer (Malvern, England) and energy dispersive X-ray spectrometer (Oxford-ISIS300, England). The sample was washed with deionized water to remove fines and other adhered impurities, (adjusted to pH 7 with dionized water), dried at 100 °C, desiccated and stored in tightly stoppered glass bottles [6]. Standard Cd(II), Pb(II), Cu(II) and Zn(II) (1000 mg.dm^{-3}) solutions were prepared by dissolving $3CdSO_4.8H_2O$, $Pb(NO_3)_2$, $Cu(NO_3)_2$ and $Zn(NO_3)_2$ powders, respectively, in deionized water. Diluted solutions were prepared from the stock solutions (1000 mg.dm^{-3}). All chemicals used in this research were of analytical reagent grades. The adsorption percentage for natural diatomite was

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determined by adding 1.000 g of natural diatomite to 20 dm^3 of the standard solutions with concentration of 150 mg.dm^{-3} for Cd(II), 20 mg.dm^{-3} for Pb(II), 200 mg.dm^{-3} for Cu(II) and 300 mg.dm^{-3} for Zn(II) then shaking and standing for 1h at room temperature. The decanted solutions were filtered, diluted with deionized water. Metal ions were determined using atomic absorption spectrometer (PerkinElmer, U.S.A.).

3. RESULTS AND DISCUSSION

Chemical composition of natural diatomite was obtained by the X-ray fluorescence spectrometer. The analysis shows that silicone dioxide (SiO_2) is the main component (71.88%) and the metal oxides; aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3) are the main minor constituents, respectively as shown in Table 1.

Table 1 Chemical composition of natural diatomite

Oxide	Composition (%)
SiO_2	71.88
Al_2O_3	10.13
Fe_2O_3	6.83
Other oxide	3.65
LOI	7.51

LOI = lost on ignition

Figure 1 shows the morphology of natural diatomite. It was generally cylindrical in shape with the average particle size of 7.72x20.5 μm and corresponding with the data from the particle size distribution as shown in Figure 2.

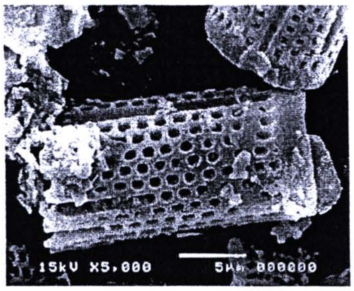

Fig. 1 SEM micrograph of natural diatomite

Table 2 Element composition of natural diatomite

Element	Energy dispersive values (keV)
Si	1.739
O	0.525
Al	1.486
Fe	6.398

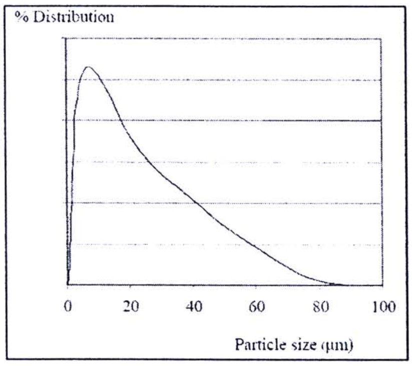

Fig. 2 Particle size distribution of natural diatomite

Fig. 3 shows the energy dispersive spectra of natural diatomite. The characteristic X-ray radiation showed silicon (Si) = 1.739 keV, oxygen (O) = 0.525 keV, aluminium (Al) = 1.486 keV and iron (Fe) = 6.398 keV and according to the energy dispersive values detailed in Table 2.

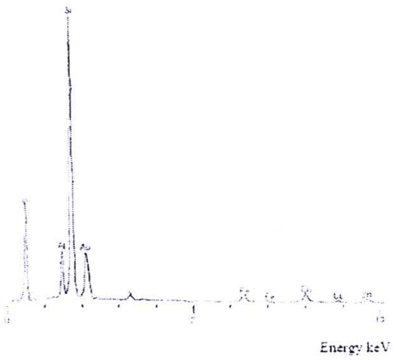

Fig. 3 EDS spectra of natural diatomite

The adsorption percentage of Cd(II), Pb(II), Cu(II) and Zn(II) solutions onto natural diatomite were 88.71 %, 90.54%, 88.23 % and 94.56%, respectively as shown in Table 3 and Figure 4.

Table 3 The adsorption percentage of standard solutions onto natural diatomite

Metal ions	Adsorption (%)
Cd(II)	88.71
Pb(II)	90.54
Cu(II)	88.23
Zn(II)	94.56

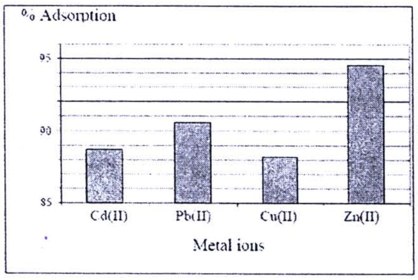

Fig. 4 The adsorption percentage of standard solutions onto natural diatomite

The surface area and average pore size of natural diatomite were 54.26 $m^2.g^{-1}$ and 54.30 Å, respectively, corresponding with the SEM micrograph as shown in Figure 1. The high surface area of natural diatomite was the main reasons for choosing it as a potential adsorbent for heavy metal ions because of negatively charged of hydroxyl groups (–OH) present on the surface structure [8]. The batch isotherm studies were conducted under slightly natural conditions (pH 7) for two main reasons. Firstly, heavy metals normally start to precipitate (by forming metal oxides and hydroxides) under alkaline conditions. In the concentration study, heavy metals are expected to precipitate at $pH \geq 8$, therefore, a slightly acidic solution ensures that adsorption on diatomite is restricted to divalent ions rather than to highly adsorbable metal hydroxide species. In addition, heavy metals are usually found in a cationic form in wastewater. Secondly, diatomite powder is slightly unstable in higher pH conditions. It is known that silica containing materials precipitate (dissolve) when exposed to alkaline solution [2].

4. CONCLUSIONS

The main component of natural diatomite is silicon dioxide (SiO_2). The particle is the generally cylindrical in shape with the average particle size of 7.72x20.5 μm. The surface area and average pore size of natural diatomite were 54.26 $m^2.g^{-1}$ and 54.30 Å. The adsorption percentage of Zn(II) standard solution onto natural diatomite is highest.

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ADSORPTION OF HEAVY METALS ONTO NATURAL AND MODIFIED DIATOMITE

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ABSTRACT

In this research, the adsorption of heavy metal standard solutions onto natural and modified diatomite was studied. Natural diatomite was modified with hydrochloric acid by the hydrothermal method. Chemical composition of diatomite was characterized by X-ray fluorescence spectroscopy (XRF). The morphology of diatomite was investigated by scanning electron microscopy (SEM). The particle size of diatomite was studied by the particle size distribution analysis. The surface area was determined by specific surface area analysis (BET). The adsorption of heavy metal standard solutions was determined by atomic absorption spectroscopy (AAS).

KEYWORDS: Modified diatomite, heavy metals, XRF, SEM, BET and AAS

1. INTRODUCTION

Diatomite ($SiO_2 \cdot nH_2O$), or diatomaceous earth, is a soft lightweight rock available in large deposits around the world. This pale coloured sedimentary rock consists principally of silica microfossils of aquatic, unicellular alga varying in shape and size of diatom. Diatomite is highly porous, with its structure containing up to 80–90% voids. It is used in a number of industrial applications, e.g. as a filtration media for various beverages, and inorganic and organic chemicals, and as an adsorbent for pet litter and oil spills. Although diatomite has a unique combination of physical and chemical properties, its use as an adsorbent in wastewater treatment [1-9]. Acid modification of diatomite is a common chemical modification to enhance its adsorption capacity and to give it certain properties for desirable applications. The previously reported results only the purification of diatomite in hydrochloric acid [10-11]. The aim of this research is to examine the effectiveness of local diatomite (63% SiO_2) and diatomite was modified by hydrochloric acid for the removal of heavy metal ions from standard solutions. Furthermore, the characteristic of surface loading with heavy metal ions on adsorbent structure and adsorption capacity were studies.

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2. MATERIALS AND METHODS

Natural diatomite was obtained through the natural resources in China. Natural diatomite was modified by the hydrothermal method, with 1M HCl at 100 °C for 1h and adjusted to pH 7 by 0.1M NaOH then filtered and dried at 105 °C with hot air oven (Honeywell-DC1040, Thailand) overnight, desiccated and stored. The chemical composition on natural and modified diatomite was characterized using X-ray fluorescence spectrometer (Bruker-SRS3400, Germany). Moreover, the morphology and particle size distribution of diatomite were measured by scanning electron microscope (Jeol-JSM5410LV, Japan) and laser particle size analyzer (Malvern-Mastersizer S, England). The surface area was determined by specific surface area analyzer (Quantachrome-Autosorp 1MP, England). Standard Cd(II), Pb(II), Cu(II) and Zn(II) (1000 $mg.L^{-1}$) solutions were prepared by dissolving $CdSO_4$, $Pb(NO_3)_2$, $Cu(NO_3)_2$ and $Zn(NO_3)_2$ powders, respectively, in deionized water. Diluted standard metal ion solutions were prepared from the stock solutions (1000 $mg.L^{-1}$). All chemicals used in this research were of analytical reagent grades. The adsorption capacity for natural and modified diatomite was determined by adding 1.0000 g of adsorbent to 20 mL of the standard solution in the range concentration of 40-160 $mg.L^{-1}$for Cd(II), 10-60 $mg.L^{-1}$ for Pb(II), 80-200 $mg.L^{-1}$ for Cu(II) and 100-600 $mg.L^{-1}$ for Zn(II), respectively, then shaking and standing for 1h at room temperature. The decanted solutions were filtered, diluted with deionized water. Heavy metal ions were determined using atomic absorption spectrometer (Perkin Elmer-AAnalyst 100, U.S.A.). The morphology of diatomite after adsorption of heavy metals was investigated by scanning electron microscope (Jeol-JSM5410LV, Japan).

3. RESULTS AND DISCUSSIONS

Chemical composition of natural and modified diatomite was obtained by the X-ray fluorescence spectrometer. The analysis shows that silicon dioxide (SiO_2) is the main component and the metal oxides; aluminium oxide (Al_2O_3) and iron oxide (Fe_2O_3) are the minor constituents, respectively, as shown in Table 1.

Natural diatomite was modified by treating with hydrochloric acid for purification of silica on diatomite's surface, however, only a small amount of silica is dissolved, while significantly reducing the contribution of undesirable aluminium, calcium, magnesium, iron and alkaline elements [10-11].

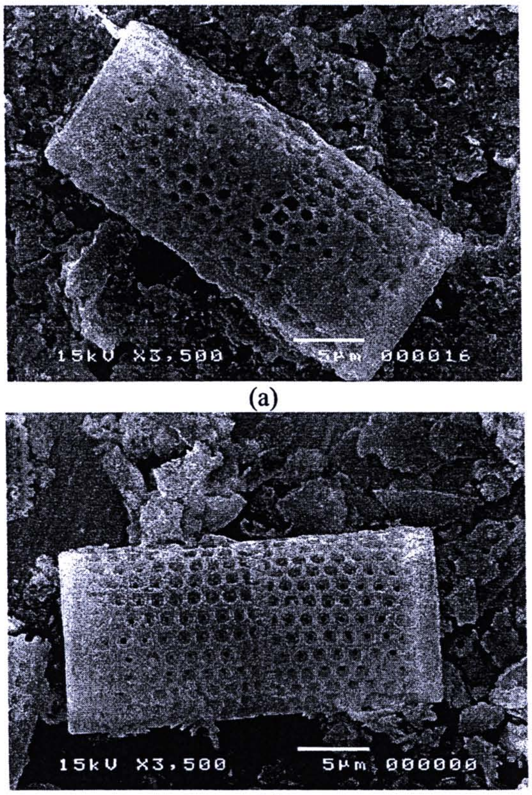
Table 1 Chemical composition of natural and modified diatomite

Compound	Chemical composition (%)	
	Natural diatomite	**Modified diatomite**
SiO_2	63.31	56.79
Al_2O_3	13.42	12.15
Fe_2O_3	12.58	10.11
Na_2O	0.74	2.37
CaO	0.49	0.08
Cl	<0.01	9.12
Loss On Ignition (LOI)	6.54	6.73

Figure 1 shows SEM micrograph of natural and modified diatomite. The morphology of diatomite was generally cylindrical in shape with the range of particle size of 10-15 μm in width and 20-30 μm in length. The average pore size was 0.35 μm and 0.30 μm of the natural diatomite, Fig. 1(a) and modified diatomite, Fig. 1(b), respectively. The average particle size, surface area, pore volume and average pore size of modified diatomite were higher than natural diatomite, and corresponding with the data from the particle size distribution as shown in Table 2 and Figure 3.

Table 2 Characterization of natural and modified diatomite

Properties	Natural diatomite	Modified diatomite
Average particle size (µm)	11.83	15.82
Surface area ($m^2.g^{-1}$)	54.26	55.67
Pore volume ($cm^3.g^{-1}$)	0.1461	0.1525
Average pore size (Å)	54.30	54.77



(a)

(b)

Figure 1 SEM micrograph of (a) natural and (b) modified diatomite

The active silica surface with large specific surface area is of great importance in adsorption and ion exchange applications. At the surface, the structure terminates in either siloxane group (Si–O–Si) or silanol groups (Si–OH) by the treatment of hydrochloric acid [12-16].

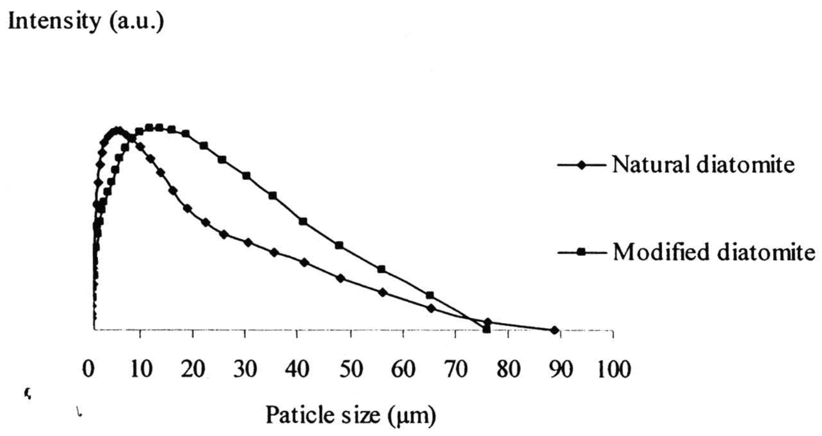


Figure 2 Particle size distribution of natural and modified diatomite

Adsorption isotherms of heavy metals onto natural and modified diatomite are shown in Figures 3-6. The adsorption isotherms take the form of monolayer adsorption (Langmuir Type), according to the classification of adsorption isotherms in solution. As shown, the quantity of metal adsorbed increases with increasing metal concentration until a maximum adsorption is established [17-19]. Furthermore, the isotherms show that adsorption capacity of diatomite is greatly improved by modification with hydrochloric acid.

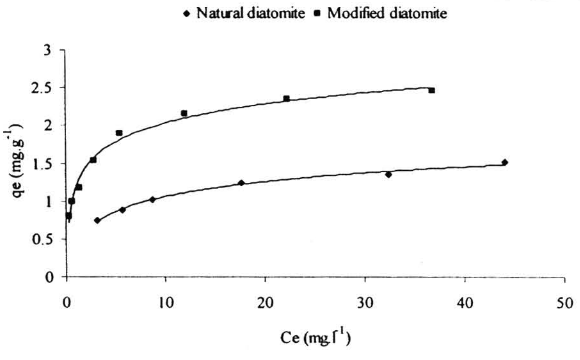


Figure 3 Adsorption isotherm of cadmium ion onto natural and modified diatomite

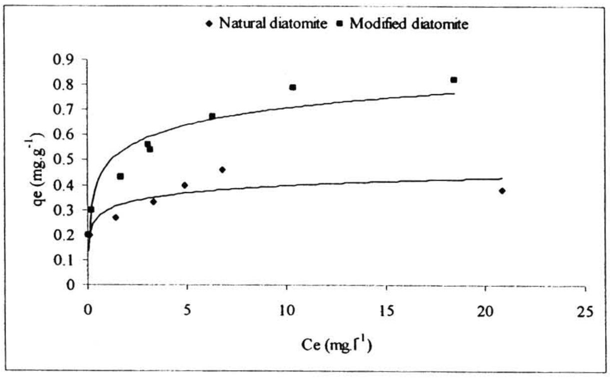


Figure 4 Adsorption isotherm of lead ion onto natural and modified diatomite

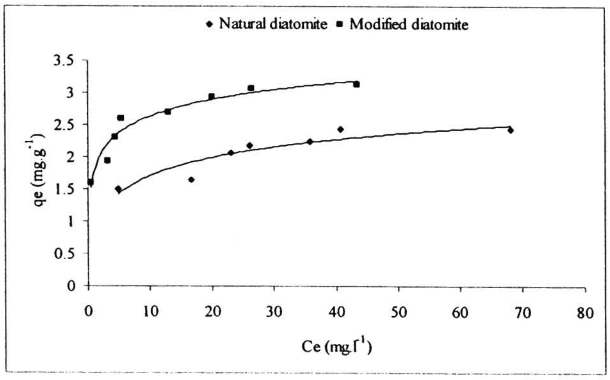


Figure 5 Adsorption isotherm of copper ion onto natural and modified diatomite

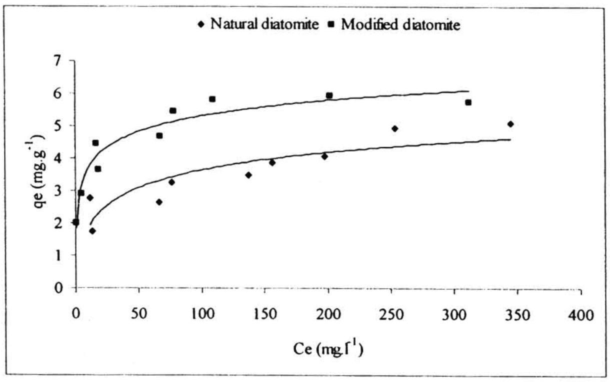


Figure 6 Adsorption isotherm of zinc ion onto natural and modified diatomite

The model is applicable in cases where only one molecular layer of adsorbate is formed at the adsorbent surface. Monolayer adsorption is distinguished by the fact that the amount adsorbed reaches a maximum value at a moderate concentration; this corresponds to complete coverage of the adsorbent surface by a monomolecular layer of adsorbate, which remains constant even at higher adsorbate concentrations [17-19].

The time required to attain equilibrium adsorption was 1h for diatomites. Batch isotherm studies were conducted at pH 7. The data were fitted to the linear form of the Langmuir equation

(equation (1)) [16-17] and the results are represented in Figures 7-10. The maximum adsorption capacities (Q) reported in Table 3.

$$Ce/qe = (1/Kl) + (1/Q)Ce \qquad (1)$$

where Ce is the equilibrium concentration for heavy metal ions (mg.L^{-1}), qe the surface concentration for heavy metal ions on the solid surface (mg.g^{-1}), Kl the Langmuir constant (mg.L^{-1}), and Q the saturation capacity for heavy metal ions on the solid surface (mg.g^{-1}).

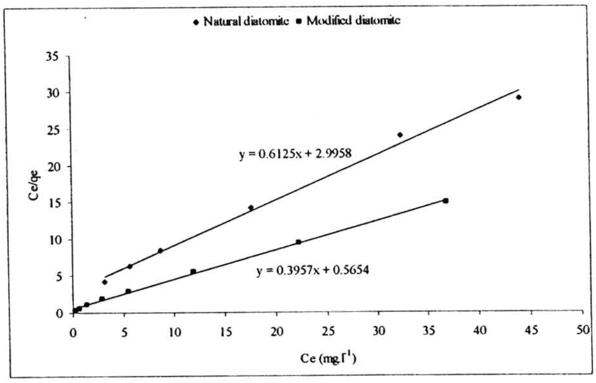


Figure 7 Langmuir isotherms for cadmium ion adsorption onto natural and modified diatomite

The saturation capacity, indicating relative sorption intensities in the equilibrium of heavy metals concentration in the range of 0-45 mg.L^{-1} for Cd(II), 0-20 mg.L^{-1} for Pb(II), 0-70 mg.L^{-1} for Cu(II) and 0-350 mg.L^{-1} for Zn(II) was 1.632, 0.387, 2.720 and 4.040 mg.g^{-1} for natural diatomite and 2.527, 0.856, 3.226 and 6.097 mg.g^{-1} for modified diatomite. It is evident that chemical modification enhanced the sorption of lead ions significantly. This may be attributed to the surface purification for the modified diatomite as well as the resultant surface charge offered by the formation of the silanol group on the diatomite surface. SEM micrograph of diatomite after adsorption heavy metal standard solutions was shown in Figures 11-12, respectively.

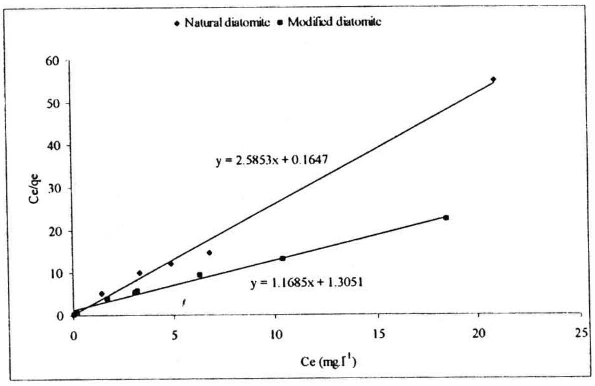


Figure 8 Langmuir isotherms for lead ion adsorption onto natural and modified diatomite

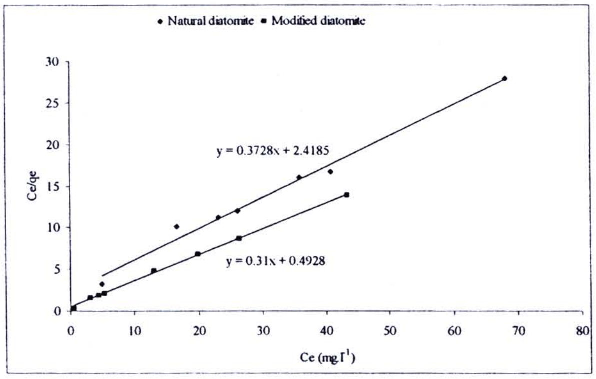


Figure 9 Langmuir isotherms for copper ion adsorption onto natural and modified diatomite

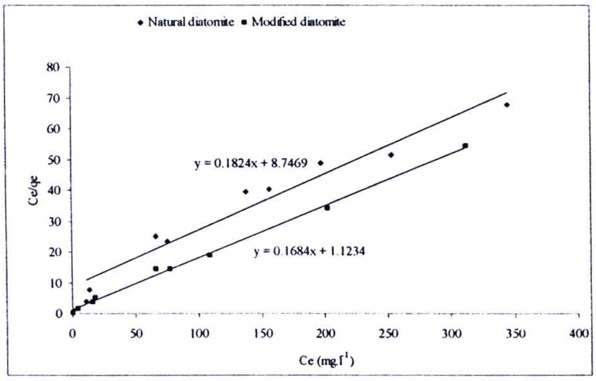


Figure 10 Langmuir isotherms for zinc ion adsorption onto natural and modified diatomite

Table 3 Adsorption capacity of natural and modified diatomite

Diatomite	Adsorption capacity of diatomites (mg.g^{-1})			
	Cd(II)	Pb(II)	Cu(II)	Zn(II)
Natural	1.632	0.387	2.720	4.040
Modified	2.527	0.856	3.226	6.097

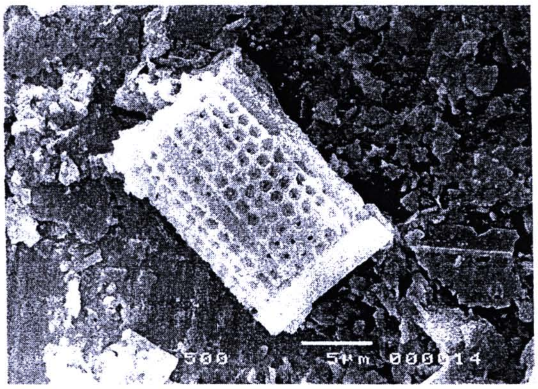


Figure 11 SEM micrograph of natural diatomite after adsorption of standard solutions

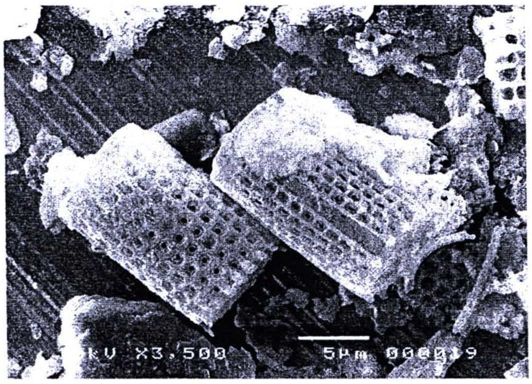


Figure 12 SEM micrograph of modified diatomite after adsorption of standard solutions

4. CONCLUSIONS

The main chemical composition of natural and modified diatomite was silicon dioxide (SiO_2) as 63.31 and 56.79 %, respectively. The morphology of diatomite was generally cylindrical in shape. The average particle size of diatomite was 11.83 and 15.82 μm, respectively, and corresponding with the data from the particle size distribution. The surface area was 54.26 and 55.67 $m^2.g^{-1}$, respectively. The adsorption capacities of cadmium (Cd(II)), lead (Pb(II)), copper (Cu(II))and zinc (Zn(II)) ions onto modified diatomite were the highest as 2.527, 0.856, 3.226 and 6.097 $mg.g^{-1}$, respectively.

5. ACKNOWLEDGEMENTS

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Adsorption of some Heavy Metals on Modified Diatomite

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ABSTRACT

Adsorption of some heavy metal ions from standard solutions by modified diatomite was investigated. Natural diatomite was modified by hydrothermal method with 1M hydrochloric acid at 100 °C for 1h then adjusted to pH 3 and 7. The morphology and pore size of both modified diatomite was investigated by scanning electron microscopy (SEM) and Brunauer–Emmett–Teller analysis (BET) surface area analysis. The particle was generally cylindrical in shape with the average particle size of 10 μm in width and 15 μm in length. The average pore size was 0.25 μm and 0.35 μm of the diatomite modified at pH 3 and 7, respectively. The concentration of cadmium, lead, copper and zinc ions from standard solutions were determined by atomic absorption spectroscopy (AAS). The percentage adsorption range of metal ions on modified diatomite at pH 7 was from 96.6 to 99.7 and higher than at pH 3 about 15 percent.

Keywords
Modified diatomite, SEM, BET, AAS

1. INTRODUCTION

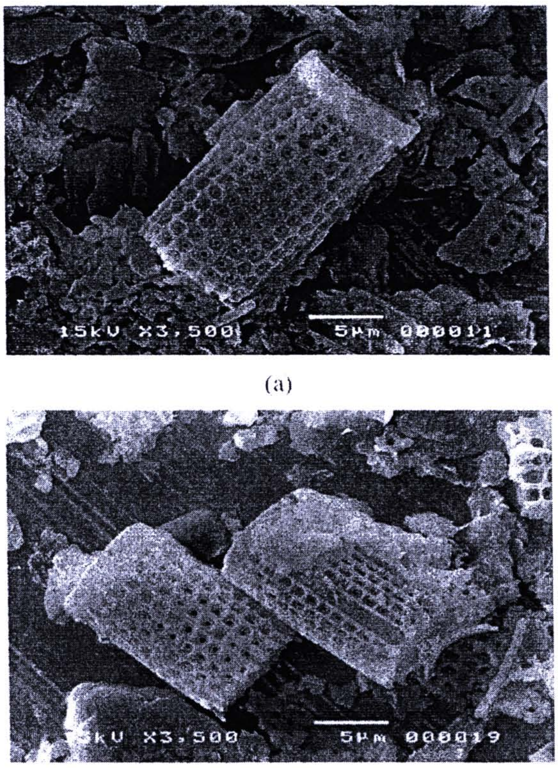
Diatomite ($SiO_2.nH_2O$) is a pale-colored and lightweight sedimentary rock composed principally of silica microfossils of aquatic unicellular algae. Diatomite consists of a wide variety of shape and sized diatoms in a structure containing up to 80–90% void. Diatomite's high porous structure, low density and high surface area results in a number of industrial applications such as filtration media for various inorganic and organic chemicals, absorbent, catalyst carrier, filler and so on. Regarding wastewater treatment a number of laboratory-scale studies have demonstrated that diatomite is a promising material for removing waterborne radio nuclides, heavy metal ions, and basic textile dyes. In aqueous solution diatomite particles are negatively charged, and possesses strong attract ability for positively charged species. Diatomite exists in large deposits around the world, and it has wide future applications in various industrial processes [1,2]. Chemical modification of diatomite is a common modification to enhance its adsorption capacity and to give it certain properties for desirable applications. The previously work reported the results of a purification and adsorption of natural and modified diatomite which treated in sodium hydroxide with manganese chloride [2], hydrochloric acid [3] and microemulsion [4]. This paper reported the adsorption of cadmium, lead, copper and zinc ions on modified diatomite from hydrothermal method with hydrochloric acid at 100 °C for 1h.

2. MATERIALS AND METHODS

Natural diatomite obtained through the natural resources in China. Natural diatomite was modified by treating with 1M hydrochloric acid at 100 °C for 1h then adjusted to pH 3 and 7 with deionized water, dried at 100 °C with hot air oven (Model 625G, Fisher Sciencetific, U.S.A.) overnight, desiccated and stored in tightly stoppered glass bottles. The morphology of modified diatomite was investigated by scanning electron microscope (JSM-5410LV, JEOL, Japan). The average pore size of modified diatomite was measured by surface area and pore size analyzer (Quantachrome Instrument, Autosorb-1MP, U.S.A.). All chemicals used were the analytical reagent grades. Standard Cd(II), Pb(II), Cu(II) and Zn(II) (1000 mg.dm^{-3}) solutions were prepared by dissolving $3CdSO_4.8H_2O$, $Pb(NO_3)_2$, $Cu(NO_3)_2.2.5H_2O$ and $Zn(NO_3)_2.6H_2O$ powders, respectively, in deionized water. Diluted standard metal ion solutions were prepared from the stock solutions (1000 mg.dm^{-3}). The adsorption percentage was determined by adding 1.0000 g of modified diatomite to 20 cm^3 of standard solutions with concentration of 150 mg.dm^{-3} for Cd(II), 20 mg.dm^{-3} for Pb(II), 200 mg.dm^{-3} for Cu(II) and 300 mg.dm^{-3} for Zn(II). The mixtures were shook and stood for 1h at room temperature. The decanted solutions were filtered with the final pH of solutions of 4 and 6, respectively. Metal ions were analyzed using atomic absorption spectrophotometer (AAnalyst 100, PerkinElmer, U.S.A.).

3. RESULTS AND DISCUSSION

Diatomite was modified by treating with hydrochloric acid for purification of silica on diatomite's surface and reduction of the contribution of undesirable aluminium, calcium, magnesium, iron and alkaline elements [3]. The active silica surface with large specific surface area is of great importance in adsorption and ion exchange applications. At the surface, the structure terminates in either siloxane group (Si–O–Si) or silanol groups (Si–OH) by the treatment of hydrochloric acid [5]. Figure 1 shows SEM micrograph of modified diatomite. The morphology of both modified diatomite at pH 3 and pH 7 were generally cylindrical in shape with the average particle size of 10 µm in width and 15 µm in length as shown in Fig. 1(a) and Fig. 1(b), respectively. The average pore size was measured by BET surface area technique as follows: modified diatomite at pH 3 and pH 7 of 0.25 µm and 0.35 µm, respectively.



(a)

(b)

Figure 1. SEM micrograph of modified diatomite at (a) pH=3 and (b) pH=7

Figure 2 shows the surface morphology of the modified diatomite. The high surface area of this diatomite was the main reason for choosing it as a potential adsorbent for heavy metals due to the negatively charged of silanol groups present on the surface structure. The silanol groups could be isolated (free silanol groups) as shown in Fig. 2(a), where the surface silicon atom has three bonds into the bulkstructure and the fourth to OH group and the vicinal or bridged silanols as shown in Fig. 2(b), where two isolated silanol groups attached to two different silicon atoms are bridged by H-bond. A third type of silanols called geminal silanols as shown in Fig. 2(c), consisting of two hydroxyl groups attached to one silicon atom. The geminal silanols are close enough to have H-bond whereas free silanols are too far separated. The silanol groups with lower p*Ka* value are believed to be isolated silanol groups with no hydrogen bonding with its neighbors. The fact for considering them as isolated silanol is due to the easy dissociation of hydroxyl hydrogen compared to other silanols coupled through hydrogen bond. Other type of silanols with higher p*Ka* value is believed to be those connected to each other through H-bonding directly or via the bridging water molecule. The previously reported results for silanol groups on the surface of silica sol particles, where isolated silanol and bridged silanols with p*Ka* values 5.5 and 9.0 had the surface population of 15 % and 85%, respectively [5].

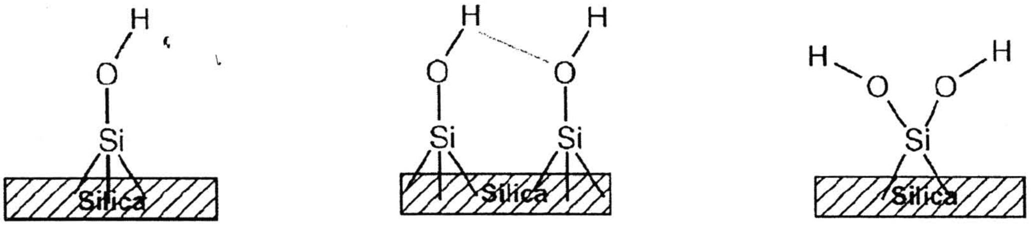


Figure 2. The structure of silanol groups (a) isolated silanol,
(b) vicinal silanol and (c) geminal silanol

The adsorption percentage of Cd(II), Pb(II), Cu(II) and Zn(II) solutions from the final pH of 4 and 6, on modified diatomite (at pH 3 and 7) were 83.0 %, 83.3%, 41.0 % and 84.5%, and 99.7%, 96.6%, 96.7% and 99.4%, respectively as shown in Figure 3.

The batch isotherm studies were conducted under slightly acidic conditions for two main reasons. Firstly, heavy metals normally start to precipitate (by forming metal oxides and hydroxides) under alkaline conditions. In these concentrations study, heavy metals are expected to precipitate at pH ≥ 8, therefore, a slightly acidic solution ensures that adsorption on diatomite is restricted to divalent ions rather than to highly adsorbable metal hydroxide species. In addition, heavy metals are usually found in a cationic form in wastewater. Secondly, diatomite powder is slightly unstable in higher pH conditions. It is known that silica containing materials precipitate when expose to alkaline solution [6].

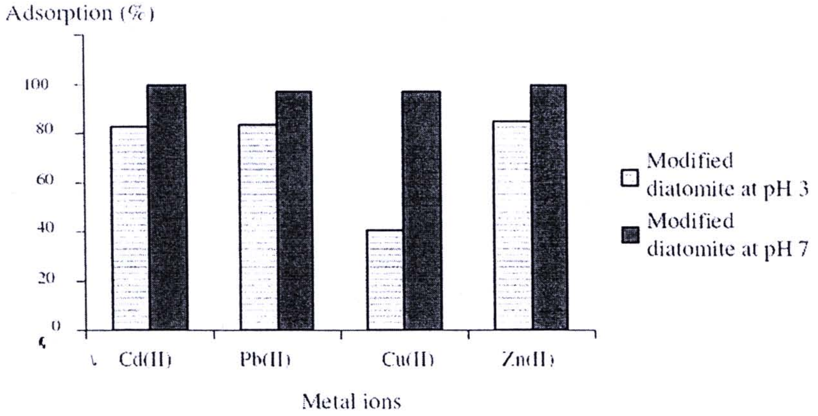


Figure 3. The adsorption percentage of standard solutions on modified diatomite

4. CONCLUSION

The morphology of both modified diatomite was generally cylindrical in shape with the average particle size of 10 μm in width and 15 μm in length. The average pore size was 0.25 μm and 0.35 μm of the modified diatomite at pH 3 and 7, respectively. The percentage adsorption range of metal ions from the final pH of solutions (pH 6 and 4) on modified diatomite at pH 7 was from 96.6 to 99.7 and higher than at pH 3 about 15 percent.

5. ACKNOWLEDGMENTS

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Manganese Chloride Modification of Natural Diatomite by Using Hydrothermal method

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Abstract

Natural diatomite was modified by manganese chloride via hydrothermal method. The characterization of natural and modified diatomite was investigated by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and specific surface area (BET) analysis techniques. The morphology of both diatomites was generally cylindrical in shape with the range of particle size of 5-6 μm in width and 10-12 μm in length. There are the energy peaks of silicon (Si) of 1.75 keV and oxygen (O) of 0.52 keV in their characteristic X-ray radiations and the extra peak of manganese (Mn) of 6.10 keV in that of modified diatomite. The surface areas of natural and modified diatomite were 60 and 33 $m^2.g^{-1}$, respectively. The adsorption of copper onto natural and modified diatomite was determined by atomic absorption spectrometry (AAS). The adsorptions capacity of both diatomites were 2.33 and 4.52 $mg.g^{-1}$, respectively. The element composition of both diatomites after adsorption of copper standard solution was measured by energy dispersive X-ray spectrometry (EDS). It was found that the energy level of copper was K_β 0.95 keV and K_α 8.04 keV, respectively.

Background

Diatomite ($SiO_2.nH_2O$) is a fine granulated siliceous sedimentary rock or unlithified sediment of biogenic origin. It is composed of amorphous silica, present in the form of opaline diatom skeletons or frustules. The structure of diatomite is quite complex and contains numerous fine microscopic pores, cavities and channels, and therefore the material has a large specific surface area, high absorption capacity and low density. Other intrinsic properties are low thermal conductivity, relatively high melting-point, chemical inertness and small grain size [1-2]. A number of studies were performed to investigate the potential application of diatomite as adsorbent for the removal of uranium [3] and heavy metal ions [2-5] and textile dyes [6] from wastewater. The results indicated that diatomite is a very suitable material in wastewater management. Many modification methods have been researched. The beneficiation processes comprise crushing, drying, calcinations and classification [7-8] or chemical treatment such as leaching with and without acid and/or heat [9]. The hydrothermal process in general progresses in a closed system at a high autogeneous pressure. By the benefit of the close system with high pressure, the required temperature for preparing ceramic powder can be greatly reduced because of enhanced reactivity of reactive species can be maintained. Hydrothermal method is a convenient process for preparing diatomite. It is able to produce fine particles, with high homogeneity and high purity [10].

The aim of this work is to examine the effectiveness of natural and diatomite modified by manganese chloride via the hydrothermal method for the removal of Cu (II) ion from standard solution. Furthermore, the characteristic of surface loading with Cu (II) ion on adsorbent structure and adsorption capacity were studied.

Materials and Methods

Adsorbent

Natural diatomite from China was washed with distilled water to remove fines and other adhered impurities, dried at 100 °C for 24h, desiccated and stored in tightly stoppered glass bottles.

Surface modification

Natural diatomite was modified by manganese chloride via hydrothermal method. 15 g of natural diatomite was immersed in 100 ml of 3M $MnCl_2.4H_2O$ and adjusted to pH 8 with 3M NaOH. The reaction temperature was maintained at 100 °C for 2h. The sample was then filtered and dried at 100 °C for 24h, desiccated and stored in tightly stoppered glass bottles.

Characterization of diatomites

The morphology of natural and modified diatomite was investigated by scanning electron microscope (SEM) (Jeol-JSM 5410LV, Japan). The chemical composition was analyzed by energy dispersive X-ray spectrometer (EDS) (Oxford-Inca 6647, England). The surface area was determined by specific surface area analyzer (Quantachrome-Autosorp 1MP, England).

Adsorption isotherms

Copper standard solution with 1000 ppm was prepared by dissolving in 1% HNO_3. Diluted solution was prepared from the stock copper solution (1000 ppm). The adsorption capacity for natural and modified diatomite was determined by adding 1.0000 g of adsorbent to 20 cm^3 of the standard solution in the range concentration from 20-400 ppm then shaking and standing for 1h at room temperature. The decanted solutions were filtered, diluted with 1% HNO_3. The concentration of copper was determined using atomic absorption spectrometer (PerkinElmer-AAnalyst100, U.S.A.). The adsorption isotherm of copper was studied at increased concentrations due to the high capacity of natural and modified diatomite.

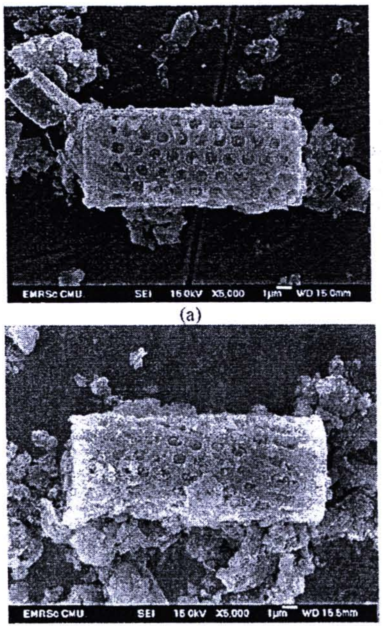
Characterization of diatomites after adsorption

The morphology of natural and modified diatomite after adsorption copper standard solution were studied by scanning electron microscope (SEM) (Jeol-JSM5410LV, Japan). The element composition was analyzed by energy dispersive X-ray spectrometer (EDS) (Oxford-Inca 6647, England).

Results and Discussion

Characterization of diatomites

Figure 1 shows SEM micrograph of natural and modified diatomite. The morphology of both diatomites was generally cylindrical in shape with the range of particle size of 5-6 μm in width and 10-12 μm in length. The average particle size and surface area of natural and modified diatomite as shown in Table 1.



(a)

(b)

Figure 1 SEM micrograph of (a) natural and (b) modified diatomite

Table 1 The average particle size and surface area of natural and modified diatomite

Properties	Diatomite	
	Natural	Modified
Average particle size (μm)	10	12
Surface area ($m^2.g^{-1}$)	60	33

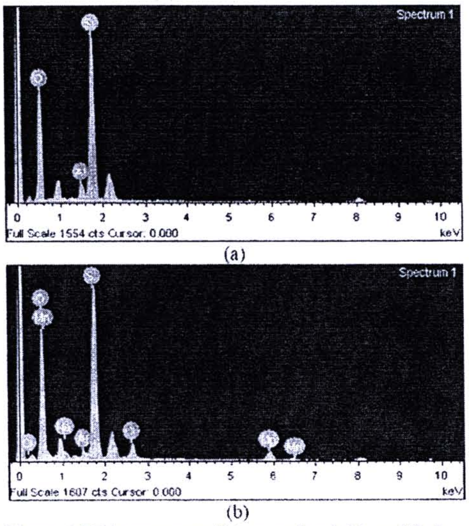
The active silica surface with large specific surface area is of great importance adsorption and ion exchange applications [4-5]. The chemical composition was analyzed by energy dispersive X-ray spectrometer (Oxford-Inca 6647, England). The characteristic X-ray radiation of natural diatomite showed silicon (Si) = 1.75 keV, oxygen (O) = 0.52 keV (Fig. 2(a)). The characteristic X-ray radiation of modified diatomite showed silicon (Si) = 1.75 keV, oxygen (O) = 0.52 keV and manganese (Mn) = 6.10 keV (Fig. 2(b)).

Adsorption isotherms

The diatomite has a large void volume, and a highly porous structure. The high porosity of this material was one of the main reasons for choosing it as a potential sorbent for heavy metals. It has previously been reported that structural Mn^{2-} can be desorbed from the surface during adsorption of heavy metals [11-12].

The Langmuir equation can be presented by the well-known equation [11]:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a}{K_L} C_e \tag{1}$$



(a)

(b)

Figure 2 EDS spectrum of (a) natural and (b) modified diatomite

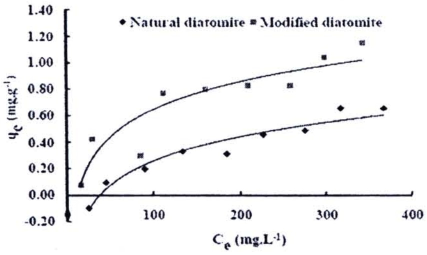


Figure 3 Adsorption isotherm of copper ion onto natural and modified diatomite

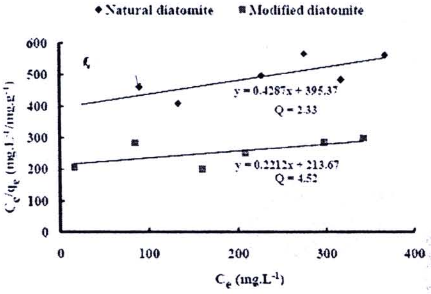


Figure 4 Langmuir isotherms of copper ion onto natural and modified diatomite

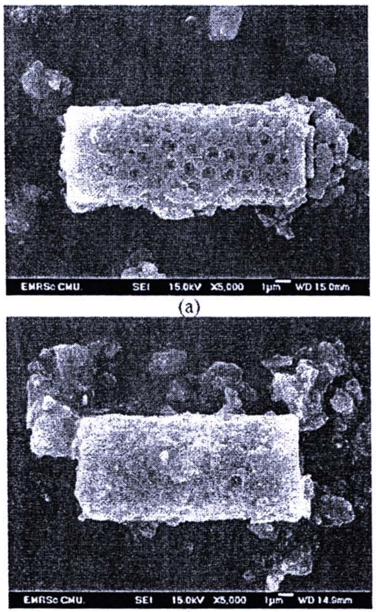
where C_e and q_e are the solution (mg.L^{-1}) and surface concentrations (mg.g^{-1}) for the adsorbate, respectively, and K_L and a are the isotherm constants for a particular solute solvent combination. K_L can be obtained from the interception of a plot of C_e/q_e versus C_e. The constant, a, is related to the energy of adsorption. The adsorption isotherms take the form of a typical 'H', or 'high capacity', isotherm, according to 'Giles' classification [13], or Type-2 Class L (Langmuir Type), according to the classification of adsorption isotherms in solution [14]. As shown, the quantity of metal adsorbed increases with increasing metal concentration until a maximum adsorption (*Q*) is established. A linear form of this equation is:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L}\right) + \left(\frac{1}{Q}\right) C_e \qquad (2)$$

Q can be obtained from the slope of a plot of C_e/q_e versus C_e. Adsorption isotherms of Cu (II) onto natural and modified diatomite are shown in Figure 3.

Typically, the sorption data were analyzed according to the linear form of the Langmuir isotherm (Eq. (2)). Plots of the specific sorption, C_e/q_e against the equilibrium concentration, C_e for natural and modified diatomite are shown in Figure 4. The saturation capacity (*Q*), indicating relative sorption in the equilibrium of Cu (II) concentration in the range 0-400 mg.L^{-1}was 2.33 mg.g^{-1} for natural diatomite and 4.52 mg.g^{-1} for modified diatomite. The modification processes of the diatomite changed the surface area, porosity, diffusion properties and accessibility to internal sites [12].

The comparison between previously reported adsorption capacities of investigated materials and the presented results is difficult due to different experimental conditions (pH, Cu^{2+} concentration range, solid to solution ratio, contact time, etc.) and the properties of the adsorbents. For example, adsorption capacities towards Cu^{2+} of 3.23 mg.g^{-1} [4] and 4.27 mg.g^{-1} [15], were reported for modified diatomite. In this work, significantly higher Cu^{2+} adsorption (4.52 mg.g^{-1}) was reported for modified diatomite.



(a)

(b)

Figure 5 SEM micrograph of (a) natural and (b) modified diatomite after adsorption of copper standard solution

Characterization of diatomites after adsorption

SEM micrograph of natural and modified diatomite after adsorption copper standard solution are shown in Figure 5. The morphology of both diatomites was generally cylindrical in shape with the range of particle size of 5-6 μm in width and 9-10 μm in length.

The EDS spectrum of natural and modified diatomite after adsorption copper standard solution are shown in Figure 6. Basically, the elemental chemical composition of silicon, oxygen, for natural diatomite and manganese for modified diatomite showed the characteristic X-ray energy

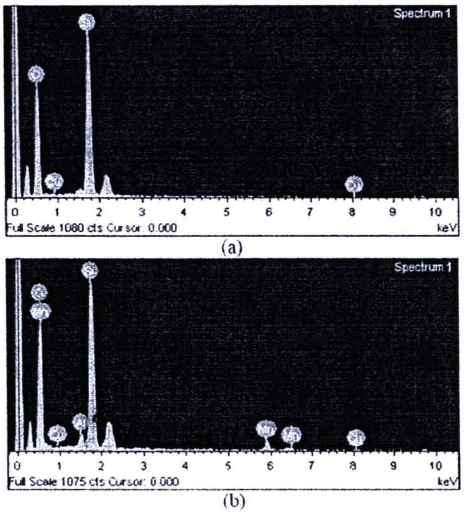


Figure 6 EDS spectrum of (a) natural and (b) modified diatomite after adsorption of copper standard

values. Moreover, the adsorption of copper onto both diatomites showed the characteristic X-ray energy values: K_β of 0.95 keV and K_α of 8.04 keV, respectively.

Conclusion

Diatomite was modified by manganese chloride via hydrothermal method. Morphology of modified diatomite was generally cylindrical in shape with the average particle size of diatomite 6x12 μm. The surface area was 33 $m^2.g^{-1}$. The characteristic X-ray radiation of modified diatomite showed silicon (Si), oxygen (O) and manganese (Mn). The adsorption capacity of modified diatomite was 4.52 $mg.g^{-1}$. The hydrothermal modification processes of the diatomite changed the surface area, porosity, diffusion properties and accessibility to internal sites. The increasing in sorption efficiency of modified diatomite was attributed to high negative surface charge on the modified surface.

Acknowledgements

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การดูดซับทองแดงอิออน โดยไดอะทอไมต์ที่ดัดแปรด้วยแมงกานีสคลอไรด์โดยวิธีไฮโดรเทอร์มอล

Adsorption of copper ion (II) by manganese chloride modified diatomite via hydrothermal method

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บทคัดย่อ: ทำการเตรียม การหาลักษณะเฉพาะและการศึกษาคุณสมบัติการดูดซับของไดอะทอไมต์จากธรรมชาติแฉะหลังการดัดแปร ทำการดัดแปรไดอะทอไมต์จากธรรมชาติโดยใช้แมงกานีสคลอไรด์ ผ่านวิธีไฮโดรเทอร์มอล ทำการวิเคราะห์หาองค์ประกอบทางเคมีและองค์ประกอบของธาตุของไดอะทอไมต์จากธรรมชาติและหลังการดัดแปร โดยเทคนิคเอ็กซเรย์ฟลูออเรสเซนต์ สเปกโทรสโคปี (XRF) และเทคนิคการกระจายพลังงานเอ็กซ์เรย์ สเปกโทรสโคปี (EDS) ทำการตรวจสอบลักษณะสัณฐานวิทยา การหาขนาดอนุภาคและพื้นที่ผิว โดยเทคนิคจุลทรรศน์อิเล็กตรอนชนิดส่องกราด (SEM) และเทคนิคการหาขนาดอนุภาคและพื้นที่ผิว (BET) ทำการศึกษาประสิทธิภาพการดูดซับทองแดงของไดอะทอไมต์ โดยเทคนิคอะตอมมิกแอ็บซอร์พชัน สเปกโทรสโคปี (AAS)

Abstract: The preparation, characterization and adsorption properties of natural diatomite and modified diatomite were investigated. Modified diatomite was prepared by adding manganese chloride to natural diatomite via hydrothermal method. The chemical compositions of both diatomites were determined by X-ray fluorescence spectroscopy (XRF) and energy dispersive X-ray spectroscopy (EDS). The morphology, particle size and surface area were investigated by scanning electron microscopy (SEM) and Brunauer Emmett Teller (BET). The adsorption efficiency of copper onto diatomite was studied by atomic absorption spectroscopy (AAS).

Introduction: The presence of heavy metals in the environment has been of great concern because of their increased discharge, toxic nature and other adverse effect on receiving water bodies. The potential sources of Cu(II) in industrial effluents include metal cleaning and plating baths, pulp, paper and paper board mills, fertilizer industry, etc. Excessive intake of copper results in an accumulation in the lever and may produce gastrointestinal catarrh. It is also toxic to aquatic organisms even at very small concentrations in the natural waters[1]. Low-cost sorbents are needed for the adsorption of heavy metal ions. Natural materials that are available in high reserves, or certain waste products from agricultural or industrial operations, may have potential as low-cost sorbents. Diatomite is fine-grained, low-density biogenic sediment, which consists essentially of amorphous silica ($SiO_2.nH_2O$) derived from opalescent frustules of diatoms. Due to the presence of silanol groups that spread over the matrix of silica, diatomite can react with many polar functional groups[2]. It has been commonly used in water purification, filtration of commercial fluids, clarifications of liquors and juices and for separation of various oils and chemicals[3]. A number of studies were performed to investigate the potential application of diatomite as adsorbent for the removal of uranium[4], and heavy metal ions[5-8] and textile dyes[9] from wastewater. The results indicated that diatomite is a very suitable material in wastewater management. Many modification methods have been researched. The beneficiation processes comprise crushing, drying, calcinations and classification[10-11] or chemical treatment such as leaching with and without acid and/or heat[12]. In water treatment, diatomite was modified by Mn oxides to increase the surface area for adsorbing lead and dye[6,13]. Moreover, hydrous manganese dioxide has been described as a good adsorbent for heavy metals such as Co, Ni, Cu, Zn, Pb and Cd from aqueous solutions[14]. Commonly, the surface charge of manganese oxides is negative, and they can be used as adsorbents to remove heavy metals from wastewater[15]. The hydrothermal process in general progresses in a closed system at a high autogeneous pressure. By the benefit of the close system with high pressure, the required temperature for preparing ceramic powder can be greatly reduced because of enhanced reactivity of reactive species can be maintained. Hydrothermal method is a convenient process for preparing diatomite. It is able to produce fine particles, with high homogeneity and high purity[16]. The aim of this research is to examine the effectiveness of natural and diatomite modified by manganese chloride via the hydrothermal method for the removal of Cu (II) ion from standard solution.

Methodology: Diatomite was obtained from China. It was washed with distilled water to remove fines and other adhered impurities, dried at 100 °C for 24h, desiccated and stored in tightly stoppered glass bottles. Surface modification was accomplished by manganese chloride via hydrothermal method. 15 g of natural diatomite was immersed in 100 ml of 1M $MnCl_2.4H_2O$ and adjusted to pH 7 with 3M NaOH. The reaction temperature was maintained at 100 °C for 2h. The sample was then filtered and dried at 100 °C for 24h, desiccated and stored in tightly stoppered glass bottles. The chemical compositions of natural and modified diatomite were determined using an X-ray fluorescence spectrometer (XRF) (Bruker-SRS3400, Germany) and element composition was analyzed by energy dispersive X-ray spectrometer (EDS) (Oxford-Inca 6647, England). Moreover, the morphology of natural and modified diatomite was investigated by scanning electron microscope (SEM) (Jeol-JSM 5410LV, Japan). The surface area was determined by specific surface area analyzer (Quantachrome-Autosorp 1MP, England). Copper standard solution with 1000 $mg.L^{-1}$ was prepared by dissolving $Cu(NO_3)_2.2.5H_2O$ in deionized water. Diluted solution was prepared from the stock copper solution (1000 $mg.L^{-1}$), batch sorption experiments were conducted using 0.5000 g natural diatomite (I), 0.5000 g modified diatomite (II), 1.0000 g natural diatomite (III) and 1.0000 g modified diatomite (IV) immersed in 20 ml of the standard solution in the range concentration from 100-500 $mg.L^{-1}$ then shook and stood for 1h at room temperature. The decanted solutions were filtered, diluted with 1% HNO_3. The concentration of copper was determined using flame atomic absorption spectrometer (AAS) (PerkinElmer-AAnalyst100, U.S.A.).

Results, Discussion and Conclusion: Chemical compositions of natural and modified diatomite were obtained by X-ray fluorescence spectrometer. The chemical compositions of natural diatomite show that the silicone dioxide (SiO_2) as the main component (62.78%) and the metal oxides (Fe_2O_3, Al_2O_3 and Na_2O) are the minor constituents. Based on chemical analyses data it could be concluded that there are certain differences in chemical compositions of modified diatomite. The analysis showed that higher content of MnO (11.86 %) than the natural diatomite and lower content of other present oxides, respectively as shown in Table 1.

Table 1. Chemical compositions of natural diatomite and modified diatomite

Composition	Natural diatomite (I) (%)	Modified diatomite (II) (%)
SiO_2	62.8	46.1
Fe_2O_3	11.4	9.1
Al_2O_3	9.7	7.3
MnO	< 0.01	11.9
Other oxide	7.1	5.1
Cl	<0.01	6.9
Loss on Ignition (LOI)	9.3	13.6

Diatomite is regarded as a mineral of organic origin, where the silica of fossilized diatom skeleton resembles opal or hydrous silica in composition ($SiO_2.H_2O$)[3]. It is not pure hydrous silica but rather contains other associated elements: other oxides and alkali metals shown in Table 1. The silica surface contains silanol groups that spread over the matrix of the silica as shown in Figure 1. The silanol group is a very active group, which can react with many polar organic compounds and various functional groups[9]. The high silanol group of this material was one of the main reasons for choosing it as a potential sorbent for heavy metals[17].

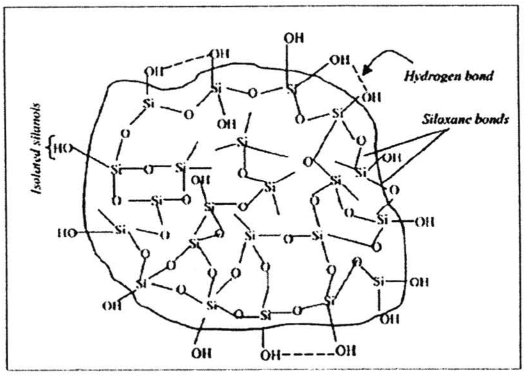
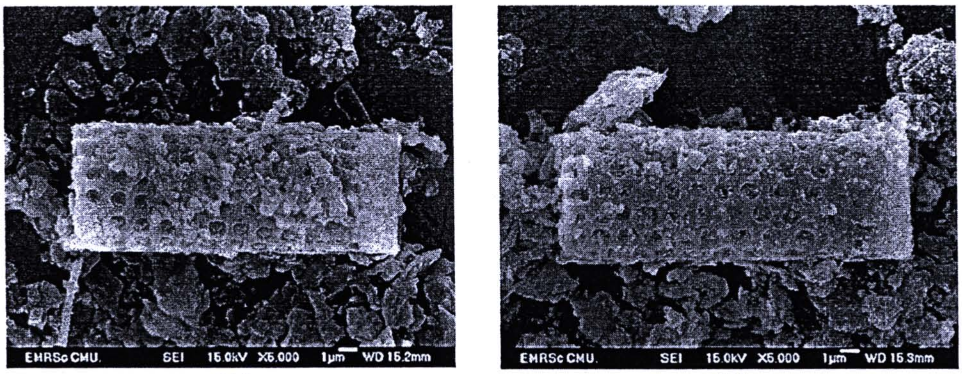


Figure1. Structure of silica surface depicting the various types of bonds and silanol groups present

The morphology of natural and modified diatomite was investigated by scanning electron microscope (SEM). Figure 2 shows SEM micrograph of natural and modified diatomite. The morphology of both diatomites was generally cylindrical in shape with the range of particle size of 5-6 μm in width and 15-16 μm in length. The average particle size and surface area of natural diatomite and modified diatomite were obtained by Brunauer Emmett Teller (BET). Surface area and average particle size distribution of natural and modified diatomite are shown in Table 2. The surface area of modified diatomite composite was smaller than that of natural diatomite and the average particle size of modified diatomite composite increased. This implies that the modified diatomite is deposited on the surface of diatomite, which decreases the surface area of diatomite. The average particle size of natural diatomite and modified diatomite were 10 and 12 μm, respectively, corresponding with the SEM micrograph as shown in Figure 2. The surface areas of natural and modified diatomite were found to be 60 and 32 $m^2.g^{-1}$, respectively.



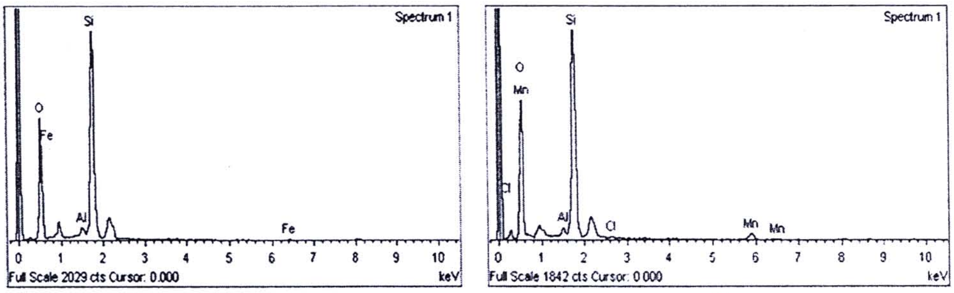
(A) (B)

Figure 2. SEM micrograph of (A) natural and (B) modified diatomite

Table 2. The average particle size and surface area of natural diatomite and modified diatomite

Properties	**Natural diatomite (I)**	**Modified diatomite (II)**
Average particle size (µm)	10	12
Surface area ($m^2.g^{-1}$)	60	32

The chemical composition was determined by energy dispersive X-ray spectrometer. The characteristic X-ray radiation of natural diatomite showed silicon (Si) K_α = 1.75 keV and oxygen (O) K_α = 0.52 keV (Fig. 3 (A)). The characteristic X-ray radiation of modified diatomite showed silicon (Si) K_α = 1.75 keV, oxygen (O) K_α = 0.52 keV and manganese (Mn) K_α = 5.90 keV and L_α = 0.64 keV (Fig. 3 (B)), respectively.



(A) (B)

Figure 3. EDS spectrum of (A) natural and (B) modified diatomite

The materials under investigation are diatomite in its natural and modified forms. Diatomite impregnated by manganese oxides (MOMD) was an effective adsorbent for removing heavy metals from aqueous solution. Manganese oxides are regarded as a good scavenger of heavy metal ions to the extent that it has been considered as a sink for heavy metals[6]. Manganese oxides are important materials in terrestrial, marine geochemistry and in sediments. The birnessite-type ($Na_4Mn_{14}O_{27}.9H_2O$) or (δ-MnO_2) is one of the most active and common forms of mineralised manganese in soil, sediments and water. It is a strong adsorbent of mineral ions and acts as a scavenger in marine and freshwater environments[5,18]. The surface area modified diatomite was decreasing as mean particle size increased as shown in Table 2. For this reason, the resultant surface charge offered by the formation of the manganese oxides on the modified diatomite surface. Manganese oxides surface charge in solution is normally higher than other oxides due to the large acidity constant of the manganese oxide surface. This means that the surface ionizes at a low pH and carries a net negative charge greater than that of other oxides[6].

Table 3. The adsorption percentage of copper standard solution onto natural diatomite and modified diatomite

Concentration (mg.L^{-1})	% Adsorption			
	Natural diatomite[a]		**Modified diatomite[b]**	
	I	**III**	**II**	**IV**
100	67.1	87.3	98.9	99.8
200	48.5	72.1	95.1	99.5
300	37.1	61.0	82.0	99.2
400	30.7	55.1	71.7	98.5
500	26.8	51.7	63.3	96.4

[a] (I) 0.5000 g natural diatomite and (III) 1.0000 g natural diatomite

[b] (II) 0.5000 g modified diatomite and (IV) 1.0000 g modified diatomite

In this research, optimum conditions were determined for the adsorption percentage of Cu(II) ions from copper standard solution. The concentration of copper standard solution and amount of adsorbent were studied. The effect of concentration of copper standard solution on the diatomites surface on adsorption ability was investigated. Table 3 shows the adsorption percentage of copper standard solution onto natural diatomite and modified diatomite. At the concentration of copper standard solution of 100 mg.L^{-1}, modified diatomite (II, IV) show higher adsorption percentage than natural diatomite (I, III). And, the adsorption percentage of natural diatomite (III) was higher than natural diatomite (I). As the amount of both diatomites increased, the adsorption percentage of both diatomites increased. In the range concentration of copper standard solution of 100-500 mg.L^{-1}, natural diatomite (I, III) showed the range adsorption percentage of 67.1-26.8 and 87.3-51.7 and modified diatomite (II, IV) showed the range adsorption percentage of 98.9-63.3 and 99.8-96.4, respectively. As the concentration of copper standard solution increased, the adsorption percentage of both diatomites decreased.

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Keywords: adsorption, diatomite, hydrothermal method, modified diatomite

Adsorption of Copper Ions onto Natural and Modified Diatomite from Aqueous Solutions

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Keywords Adsorption, diatomite, hydrothermal method, modified diatomite

Introduction

Water pollution has become a serious problem nowadays. Both the environment and human beings are exposed to hazards of different pollutants (organic pollutants, metal ions, etc.) from waste and potable water. The enormous damage caused by water pollution have led to numerous investigations having as their object the protection of the threatened environment and living creatures through new methods (Yardim et al., 2003). As representative of heavy metal cations Cu(II) was chosen in this research. This element is one of the principle heavy metals responsible for causing degradation of the environment, and although essential for leaving in low concentrations, both acute and chronic exposure to excess copper is associated with various health effects (Stern et al., 2007). Moreover, low-cost sorbents are needed for its application. Natural materials that are available in high reserves, or certain waste products from agricultural or industrial operations, may have potential as low-cost sorbents (Gürü et al., 2008). One material under investigation is diatomite in its natural and modified forms. Diatomite a pale, soft, lightweight rock composed principally of the silica microfossils of aquatic unicellular algae. It has a unique combination of physical and chemical properties such as high porosity, high permeability, small particle size, and large surface area, which makes diatomite suitable for a wide range of industrial applications, such as use as a filter aid or filler (Inglethrope, 1992). Diatomite impregnated by manganese oxides modified diatomite (MOMD) was an effective adsorbent for removing lead ions from aqueous solution. Manganese oxides are regarded as a good scavenger of heavy metal ions to the extent that it has been considered as a sink for heavy metals (Al-degs et al., 2001). Moreover, Many researchers demonstrated that the mobility and bioavailability of these metals and their complexes in any natural system are most likely controlled by sorption-desorption reactions on the surface of colloidal materials containing oxides-hydroxides of iron, aluminum and manganese (McLaren et al. 1998, Criscenti and Sverjensky, 2002). The hydrothermal process has attracted great interest because it is a promising route to produce highly crystallized, weakly agglomerated powders having a narrow size distribution. The process has some advantages in controlling particle size, morphology and other characteristics by adjustments to the reaction temperature, time, additives and other factors (Pookmanee et al., 2004). Hydrothermal method is a convenient process for preparing diatomite. It is able to produce fine particles, with high homogeneity and high purity (Pookmanee et al., 2008). The aim of this research is to examine the effectiveness of natural and diatomite modified by manganese chloride via the hydrothermal method for the removal of Cu(II) ion from aqueous standard solution.

Experimental Details

Diatomite was obtained from China. It was washed with distilled water to remove fines and other adhered impurities, dried at 100 °C for 24h, desiccated and stored in tightly stoppered glass bottles. Surface modification was accomplished by manganese chloride via the hydrothermal method. 15 g of natural diatomite was immersed in 100 ml of 1M $MnCl_2.4H_2O$ and adjusted to pH 7 with 3M NaOH. The reaction temperature was maintained at 100 °C for 2h. The sample was then filtered and dried at 100 °C for 24h, desiccated and stored in tightly stoppered glass bottles. The chemical compositions of natural and modified diatomite were determined using an X-ray fluorescence spectrometer (Bruker, Germany) and element composition was analyzed by energy dispersive X-ray spectrometer (Oxford-Inca 6647, England). Moreover, Copper standard solution with 1000 $mg.L^{-1}$ was prepared by dissolving $Cu(NO_3)_2.2.5H_2O$ in deionized water. Diluted solution was prepared from the stock copper solution (1000 $mg.L^{-1}$). The adsorption percentage of copper standard solution onto natural diatomite and modified diatomite were conducted using (I), (III), (V) and (VII) of natural diatomite from 0.2500 g to 1.0000 g (interval amount of 0.2500 g) and (II), (IV), (VI) and (VIII) of modified diatomite from 0.2500 g to 1.0000 g (interval amount of 0.2500 g) immersed in 20 ml of the standard solution in the range concentration from 100-500 $mg.L^{-1}$ then shook and stood for 1h at room temperature. The decanted solutions were filtered, diluted with 0.2M HNO_3. The concentration of copper was determined using atomic absorption spectrometer (PerkinElmer-AAnalyst100, U.S.A.). The adsorption capacity of both diatomites loaded with different quantities of (III) and (IV) was estimated by equilibrating 0.5000 g of adsorbent to 20 ml of the standard solution of varying concentration 100-500 $mg.L^{-1}$.The quantity of Cu(II) adsorbed was determined from the difference between the equilibrium and initial concentrations.

Results and Discussion

Base on chemical analyses data it could be concluded that there are certain differences in chemical composition of diatomite depending on the surface. Chemical compositions of natural and modified diatomite were obtained by X-ray fluorescence spectrometer. The chemical compositions of natural diatomite show that the silicone dioxide (SiO_2) as the main component (62.8%) and the metal oxides (11.4% Fe_2O_3 and 9.7% Al_2O_3) are the minor constituents. Chemical compositions of modified diatomite was showed that higher content of MnO (11.86 %) than the natural diatomite and lower content of other present oxides (46.1% SiO_2, 9.1% Fe_2O_3 and 7.3% Al_2O_3), corresponding with the data from the energy dispersive X-ray spectrometer.

Table 1 The adsorption percentage of copper standard solution onto natural diatomite and modified diatomite.

Concentration ($mg.L^{-1}$)	% Adsorption							
	Natural diatomite				Modified diatomite			
	I	III	V	VII	II	IV	VI	VIII
100	53.9	67.1	78.1	87.3	82.0	98.9	99.4	99.8
200	37.9	48.5	59.7	72.1	59.2	95.1	98.8	99.5
300	29.1	37.1	47.5	61.0	42.3	82.0	89.7	99.2
400	25.5	30.7	39.4	55.0	40.1	71.6	78.4	98.5
500	23.3	26.8	34.0	51.7	36.9	63.3	69.8	96.4

Table 1 and Figure 1 show the adsorption percentage of copper standard solution onto natural diatomite and modified diatomite. At the concentration of copper standard solution of 100 $mg.L^{-1}$, modified diatomite (II, IV, VI, VIII) show higher adsorption percentage than natural diatomite (I, III, V, VII). And, this concentration the amount of natural diatomite (VII) and modified diatomite (VIII) were higher adsorption percentage than the amount of natural diatomite (I, III, V) and modified diatomite (II, IV, VI), respectively. The amount of both diatomites increased, the adsorption percentage of both diatomites increased. In the range concentration of copper standard solution of 100-500 $mg.L^{-1}$, natural diatomite (I, III, V, VII) showed the range adsorption percentage of 53.9-23.3, 67.1-26.8, 78.1-34.0 and 87.3-51.7 and modified diatomite (II, IV, VI, VIII) showed the range adsorption percentage of 82.0-36.9, 98.9-63.3, 99.4-69.8 and 99.8-96.4, respectively. As the concentration of copper standard solution increased, the adsorption percentage of both diatomites decreased.

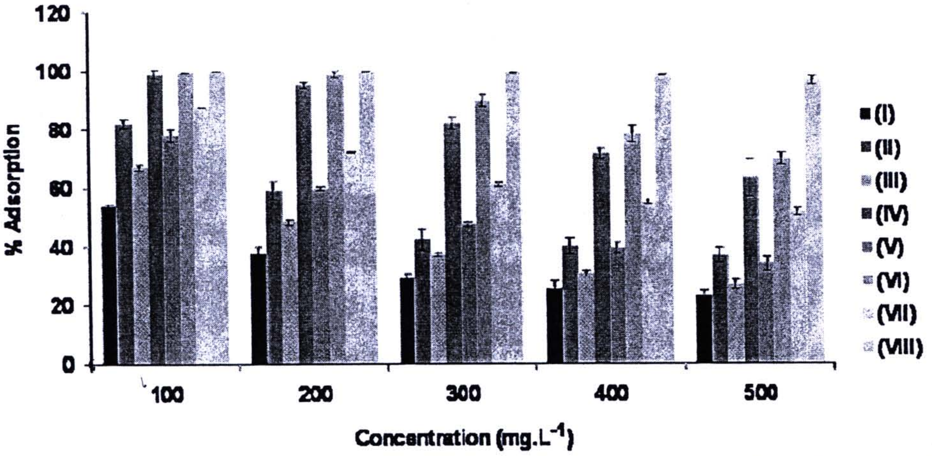

Fig. 1 The adsorption percentage of copper standard solution onto natural and modified diatomite; (I) natural diatomite (mass of adsorbent = 0.2500 g), (II) modified diatomite (mass of adsorbent = 0.2500 g), (III) natural diatomite (mass of adsorbent = 0.5000 g), (IV) modified diatomite (mass of adsorbent = 0.5000 g), (V) natural diatomite (mass of adsorbent = 0.7500 g), (VI) modified diatomite (mass of adsorbent = 0.7500 g), (VII) natural diatomite (mass of adsorbent = 1.0000 g) and (VIII) modified diatomite (mass of adsorbent = 1.0000 g).

The Langmuir equation can be presented by the well-known equation (Khraisheh et al., 2004):

$$\frac{C_e}{q_e}=\left(\frac{1}{K_L}\right)+\left(\frac{1}{Q}\right)C_e \qquad (1)$$

where C_e is the equilibrium concentration for Cu(II) (mg.L^{-1}), q_e the surface concentration for Cu(II) on the solid surface (mg.g^{-1}), K_L the Langmuir constant (L.mg^{-1}), K_L can be obtained from the interception of a plot of C_e/q_e versus C_e and Q the saturation capacity for Cu(II) on the solid surface (mg.g^{-1}) , Q can be obtained from the slope of a plot of C_e/q_e versus C_e. Adsorption isotherms of Cu(II) onto natural and modified diatomite are shown in Figure 2.

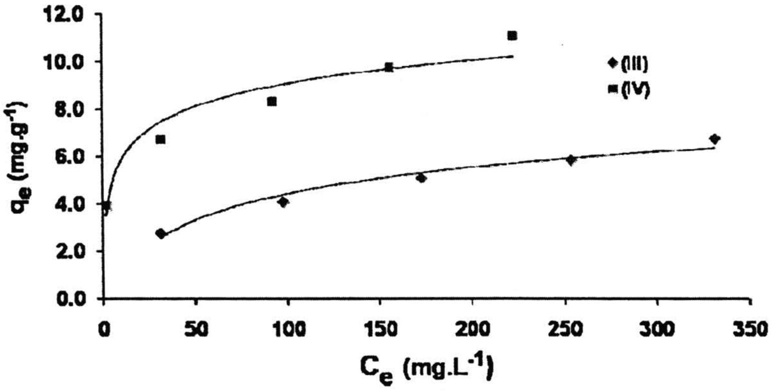

Fig. 2 Adsorption isotherm of copper ions onto natural and modified diatomite; (III) natural diatomite (mass of adsorbent = 0.5000 g) and (IV) modified diatomite (mass of adsorbent = 0.5000 g).

Figure 3 show the saturation capacity, indicating relative sorption intensities in the equilibrium of Cu(II) concentration range 100-500 mg.L^{-1}, was 8.0 and 11.4 mg.g^{-1} for natural and modified diatomite, respectively. It is evident that chemical modification enhanced the sorption of Cu(II) significantly. This may be attributed to modified diatomite surface charge offered by the formation of the manganese oxides on the diatomite surface (Catts and Langmuir, 1986). The negative charge on the disperse forms of manganese dioxide is significant in such fields as the scavenging of heavy metals in soils and in the oceans, the removal of metal ions from industrial and civic effluents, and the stability of colloidal sols in surface waters (McKenzie, 1979).

Conclusion

Diatomite was modified by manganese chloride via the hydrothermal method. The saturation capacity of Cu(II) was 8.0 and 11.4 mg.g^{-1} for natural and modified diatomite. The adsorption efficiency of Cu(II) onto modified diatomite is better than natural diatomite. The amount of diatomite increased, the adsorption percentage increased.

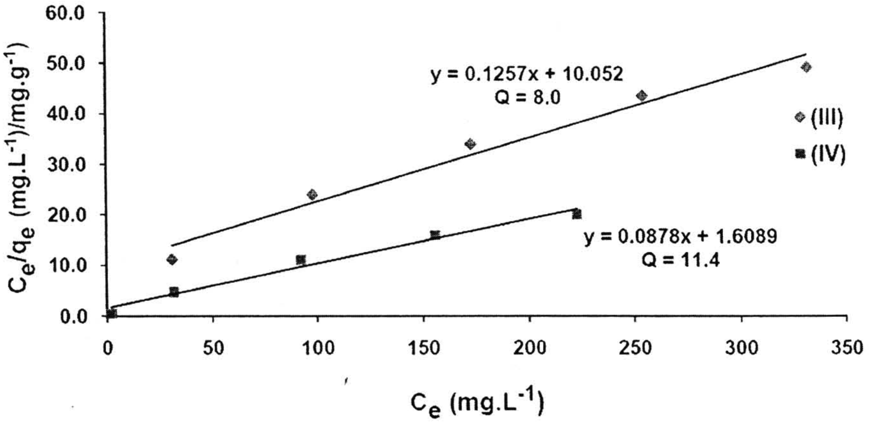

Fig. 3 Langmuir isotherms of copper ions onto natural and modified diatomite; (III) natural diatomite (mass of adsorbent = 0.5000 g) and (IV) modified diatomite (mass of adsorbent = 0.5000 g).

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