Treated Clay for Adsorption of Mercury(II) Ions

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In this work, natural clays (bentonite, china clay and ball clay) from Thailand were acid activated and chemically treated using sulfur compounds (sodium sulfide, thiourea and 2-mercaptobenzothiazole). They were characterized and used for adsorption of mercury from aqueous solution and drilling mud samples obtained from oil platforms in the Gulf of Thailand. Variations in the quantity of adsorbed mercury(II) ions as a function of pH, ionic strength and type of treatment were studied. The highest adsorption levels, 312, 270 and 263 μg/g respectively, were observed in 2-mercaptobenzothiazole treated bentonite, china clay and ball clay at pH 6 and at a temperature of 33^{o}C. Desorption of mercury from the adsorbent was done with hydrochloric acid. The adsorption efficiency of the clays for mercury(II) was 77-96%.

Key words: mercury, clay, adsorption, sulfide, thiourea and 2-mercaptobenzothiazole.

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เคลย์ที่ดัดแปรสำหรับการดูดซับไอออนปรอท (II)

วิมลรัตน์ ตระการพฤกษ์ และ ณาฐวรา จิรันดร (2548)
วารสารวิจัยวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย 30(2)

ในงานวิจัยนี้ ได้ทำการกระตุ้นเคลย์ที่ได้จากธรรมชาติ (เบนโทไนต์ ไชน่าเคลย์ และบอลเคลย์) ในประเทศไทยด้วยกรด และดัดแปรสมบัติโดยทำปฏิกิริยากับสารประกอบซัลเฟอร์ (โซเดียมซัลไฟด์ ไทโอยูเรีย และ 2-เมอร์แคพโทเบนโซไทอาโซล) ลักษณะของเคลย์ที่ดัดแปรได้รับการตรวจสอบ และนำมาใช้ในการศึกษาการดูดซับปรอทจากสารละลายชนิดน้ำ และตัวอย่างโคลนจากแท่นขุดเจาะน้ำมันในอ่าวไทย ทำการศึกษาการแปรผันของปริมาณไอออนปรอท(II) ที่ถูกดูดซับเป็นฟังก์ชันของพีเอช ความแรงไอออน และประเภทของการดัดแปร จากการทดลองพบว่าความสามารถในการดูดซับของเคลย์ชนิด เบนโทไนต์ ไชน่าเคลย์ และบอลเคลย์ที่ผ่านการดัดแปรด้วย 2-เมอร์แคพโทเบนโซไทอาโซล ที่พีเอช 6 และอุณหภูมิ 33 องศาเซลเซียส มีค่าสูงสุดเท่ากับ 312, 270 และ 263 ไมโครกรัม/กรัม ตามลำดับ การชะปรอทออกจากตัวดูดซับทำได้โดยใช้กรดไฮโดรคลอริก ประสิทธิภาพของการดูดซับปรอท (II) ของเคลย์มีค่า 77- 96%

คำสำคัญ ปรอท เคลย์ การดูดซับ ซัลไฟด์ ไทโอยูเรีย 2-เมอร์แคพโทเบนโซไทอาโซล

INTRODUCTION

Mercury (Hg) is one of the heavy metals of concern to environmentalists 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.(1) The tolerance limit for discharging Hg(II) into inland surface waters is 10 μg/l and for drinking water it is 1 μg/l (Bulgarian Standard Institution). Various types of technology are available for removing Hg from water including chemical precipitation,(2) reverse osmosis,(3) ion-exchange(4) and adsorption.(5) Some waste materials used as adsorbents, such as sawdust(6) and coconut husk,(7) have been reported. Mixed oxide gels and polymer grafted lignocellulosic materials(8) have also been used.

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.(9) Impregnation of organic molecules on a solid surface is a physical process, while organofunctionalization or grafting of organic molecules on a solid surface is a chemical process. Using the impregnation method, adsorbents are more easily prepared. Clay minerals are considered very important adsorbents in natural water systems because of their high specific surface area. Their pore structures are more flexible than that of a molecular sieve since usually the interlayer space can expand to accommodate the guest species. Some examples of treated clays which are used for the removal of heavy metals from water samples include: clay treated with 2-mercaptobenzothiazole,(10) 2-mercaptobenzimidazole clay(11) and thiol-functionalized montmorillonite clay.(12)

In this work, we impregnated sulfur containing compounds on natural clays (bentonite, china clay and ball clay) and used them in the removal of Hg(II). The major objective of this work was to investigate the potential of these treated clays as adsorbents for removing mercury from water and drilling mud samples. We analyzed the effects of various parameters, such as initial sorbate concentration, pH, ionic strength, and temperature, in optimizing the adsorption process. Desorption of Hg (II) from the adsorbent was also studied to evaluate the potential of such material in mercury ion removal and environmental cleanup technology.

EXPERIMENTAL

Materials and instruments

All reagents were of analytical grade and used without further purification. Natural clays used were obtained from sources in Thailand (Donated from Cernic International Co. Ltd). The surface areas of raw clays and treated clays were measured by the nitrogen adsorption method and calculated using the Brunauer-Emmett-Teller (BET) method. The Si/Al ratios were determined by X-ray fluorescence (XRF). Powder X-ray diffractogram was obtained by Rigagu diffractometer equipped with a rotating anode using Ni filtered Cu-Kα radiation. Cation exchange capacity (CEC) was determined by the copper bis(ethylenediamine) method, *i.e.* adding copper complex solution to the clay, stirring for 30 minutes, then centrifuging. The concentration of copper in the filtrate was determined by using a visible spectrophotometer at 548 nm. Hg(II) ion concentrations remaining in the solution were measured by cold vapor, Flow Injection Mercury System Atomic Absorption Spectrometer (FIM-AAS), model FIMS Perkin Elmer, which has a detection limit of 0.04 μg/l. The mercury cold vapor generator is a reaction cell where a solution under analysis reacts with an acid solution (5M HCl) and a reducing solution (0.3% $NaBH_4$ aqueous solution). Hg(II) was reduced to Hg(0) and vaporized. In the absorption cell, absorbance was measured at 253.7 nm.

Clay sample preparations

Clay was activated by heating at 150°C for 5 h, then treated with 0.5 M solution of potassium permanganate and sulphuric acid solution (6 M). 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 clay was immersed in 0.1M acetone solution of sodium sulfide, or 5 M acetone solution of thiourea or 2-mercaptobenzothiazole (MBT), stirred for 4 h and the solvent evaporated. The material was washed with deionized water to remove any non-adsorbed reagent and was dried at 80°C.

Mercury(II) adsorption experiments

Mercury(II) solution

A stock solution of 1000 mg/l Hg(II) was prepared from $HgCl_2$ in deionized water. This solution was diluted to obtain a standard solution containing 100 µg/l Hg(II).

General procedure of adsorption measurement

About 0.01 g of clay was mixed with 50 ml of Hg(II) solution at different concentrations. The pH of the solution was adjusted to the desired value using 0.1 M NaOH and HCl. The mixture was stirred at 500 rpm at 33 ± 1°C and the samples were taken at specific time intervals. The amount of Hg(II) ions in the supernatant was measured. The amount of Hg(II) adsorbed was calculated. All experiments were run in triplicate, the errors of resulting data were within ± 5%, and the mean values were used to establish the adsorption isotherms.

Effect of pH

The effect of pH on the Hg(II) adsorption was studied by varying pH from 3 to 8 with MBT treated bentonite (0.05 g) and 25 ml of 100 µg/l Hg(II). They were mixed and stirred for 30 minutes, at 33 ± 1°C.

Kinetics and equilibria of adsorption

Two important physico-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 10 to 100 µg/l. A fixed adsorbent weight of 0.01 g was added to 50 ml of Hg(II) solution. The uptakes of Hg(II) over time (0-90 min) at pH of 6 for different initial concentrations of Hg(II) ion were measured.

The study of adsorption isotherms is useful for determining the maximum adsorption capacity for a given adsorbent. Langmuir adsorption isotherms were studied using different initial concentrations of Hg(II) 10-100 µg/l and a fixed adsorbent dose of 0.01g per 50 ml Hg(II) solution at pH of 6. The Langmuir equation was used for the calculation.

Effect of ionic strength

The effect of ionic strength was studied using the same conditions as above except that pH was controlled at 6 and solutions of various concentrations of sodium chloride (0.05-1.0 M) were added.

Adsorption of Hg(II) from real samples from oil platforms in the Gulf of Thailand

Gas and condensate produced from natural gas fields have been found to contain significant amounts of mercury. The presence of mercury in the gas and condensate causes both processing and environmental concerns. Produced waters from gas and oil wells may contain significant amounts of mercury. It must be cleaned to meet Thailand's strict discharge specifications before disposal, or it can be transported to a nearby platform where it can be injected into a disposal well. In addition, in the drilling operation, some drilling wastes (mud) contain mercury. They are either dumped overboard or transported to the shore for further treatment and disposal.

Produced water, discharged water and drilling mud from platforms in the Gulf of Thailand were sampled. These were prepared according to the standard method(13) and we studied the adsorption of mercury using 0.05 g of MBT treated bentonite and 50 ml of the samples.

Desorption studies

After the adsorption, desorption was examined as follows: 1 g of Hg-adsorbed clay was stirred with 25 ml of hot water or 6 M hydrochloric acid for 24 h. The concentration of Hg(II) desorbed into the solution was analyzed.

RESULTS AND DISCUSSION

Chemical composition of clays

The results of the chemical composition of raw clays are given in Table 1.

It is evident that clay contains silica and alumina as major constituents while other oxides of metals are present in lesser amounts. Bentonite has more silica and metal content than ball clay and china clay. The higher cation exchange capacity is also consistent with this.

The chemical treatments applied to the clay samples changed the composition and the surface areas as shown in Table 2.

Table 1. Chemical composition of raw clays.

Clay	SiO_2 %	Al_2O_3 %	CaO %	Fe_2O_3 %	Na_2O %	K_2O %	LOI %	SE	CEC
Bentonite	63.6	17.6	3.0	3.1	3.4	0.5	5.8	59	0.76
Ball clay	51.5	23.0	0.8	1.4	0.2	0.9	19.6	32	0.22
China clay	44.8	37.9	0.1	1.0	0.1	1.2	14.0	25	0.22

LOI = loss on ignition
SE = surface area (m^2/g)
CEC = cation exchange capacity (meq/g)

Table 2. Chemical composition of acid activated clays.

Clay	SiO_2 %	Al_2O_3 %	SE
Bentonite	66.8	11.2	64
Ball clay	55.0	20.4	37
China clay	54.3	30.0	31

On acid activation, the alumina content of the raw clay was decreased and the surface area was increased as shown in Table 2. It was observed that acid treatment increased surface area and the material becomes more porous.(14) After impregnation with sulfur compounds, all treated clays showed a decrease in surface area (49, 26 and 22 for bentonite, ball clay and china clay, respectively) indicating that most of the interlamellar sites are clogged with sulfur compounds which block the passage of N_2 gas (used as an adsorbate in the surface area analysis) into the interior portion of the clay.

Powder X-ray diffraction

The XRD patterns of the natural clays also revealed the presence of quartz impurity as a common composition of the natural clay.(15) Table 3 summarizes the characteristic peaks of the main constituents of the clays (montmorillonite in bentonite, and kaolinite in ball clay and china clay) and their chemically treated counterpart. Representative XRD patterns and basal spacing (d_{001}) of bentonite and treated bentonite are presented in Figure 1.

Table 3. Characteristic XRD peaks of clays before and after chemical treatments.

Clay	d_{001} (Å)			
	Raw	Sodium sulfide	Thiourea	2-mercapto-benzothiazole
Bentonite	12.69	12.96	13.63	13.50
Ball clay	7.14	7.15	7.20	7.17
China clay	7.15	7.20	7.21	7.21

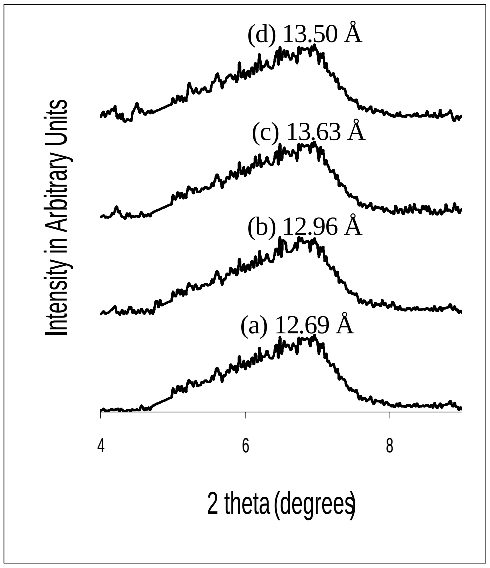

Figure 1. XRD patterns and basal spacing (d_{001}) of (a) bentonite (b) bentonite treated with sodium sulfide (c) bentonite treated with thiourea (d) bentonite treated with 2-mercaptobenzothiazole.

The powder X-ray diffractograms (XRD) of 2-mercaptobenzothiazole treated clay shows a shift of peak toward the lower diffraction angle (or larger d spacing), suggesting a slight expansion of the interlayer space upon chemical treatment. However, such an increase does not allow the accommodation of the arrangement of the sulfur compound. It may be tilted into the interlayer space. We also observed a stacking disorder, seen in the broadness of (001) peak, due to the presence of the organic molecules.(16) For ball clay and china clay, after chemical treatment, no change in diffraction peak was observed, this might be due to non-expansion of the clays.(17)

Adsorption isotherms

Effect of pH

The adsorption of Hg(II) was studied by varying pH between 3 and 8 using MBT treated bentonite. Contact time was 90 min. A plot of q_e, the amount of Hg(II) adsorbed at equilibrium (μg/g) versus at various pH is shown in Figure 2. At pH 3 or in 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 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 mercury(II) in pH range of 6-8 which is consistent with other work on kaolinite.(18) According to the theoretical calculation, Hg phases of 0.01 M Hg(II) solution in the presence of Cl^- at pH > 4, are Hg(II), and $Hg(OH)_2$.(19)

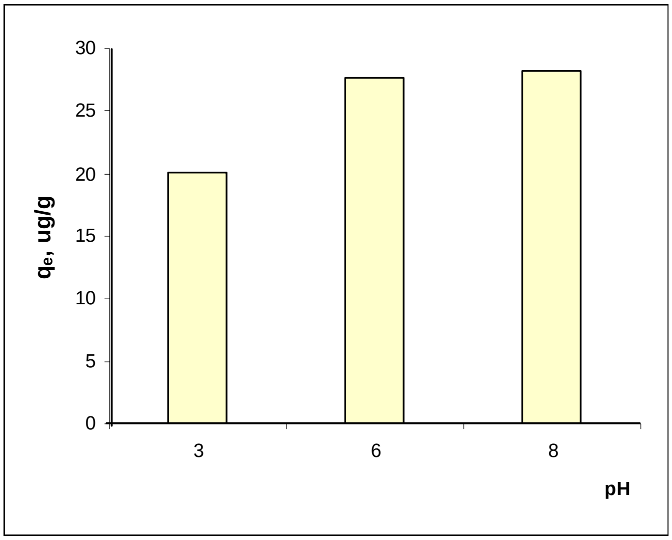

Figure 2. Adsorption efficiency at various pHs.

Effect of time and initial concentration

The adsorptions of Hg(II) on three types of clays treated with sodium sulfide, thiorea and MBT over time and at a pH of 6 for different initial concentrations of Hg(II) ion are shown in Figures 3-5. 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 30 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 physico-chemical processes. The mechanism of metal removal is thought to be complexation and ion exchange.(11)

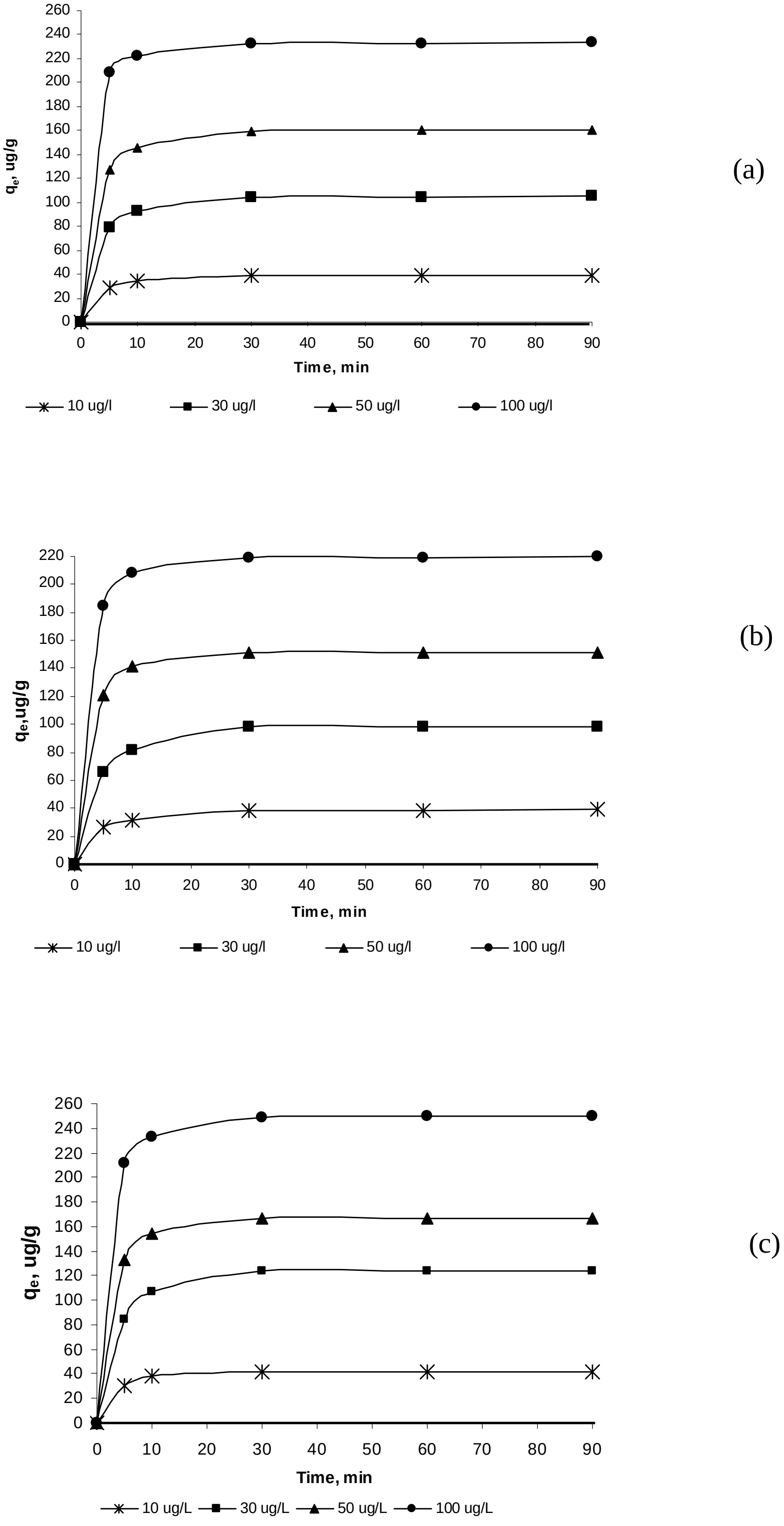

Figure 3. Kinetics curves on bentonite treated with (a) Sodium sulfide (b) Thiourea (c) MBT.

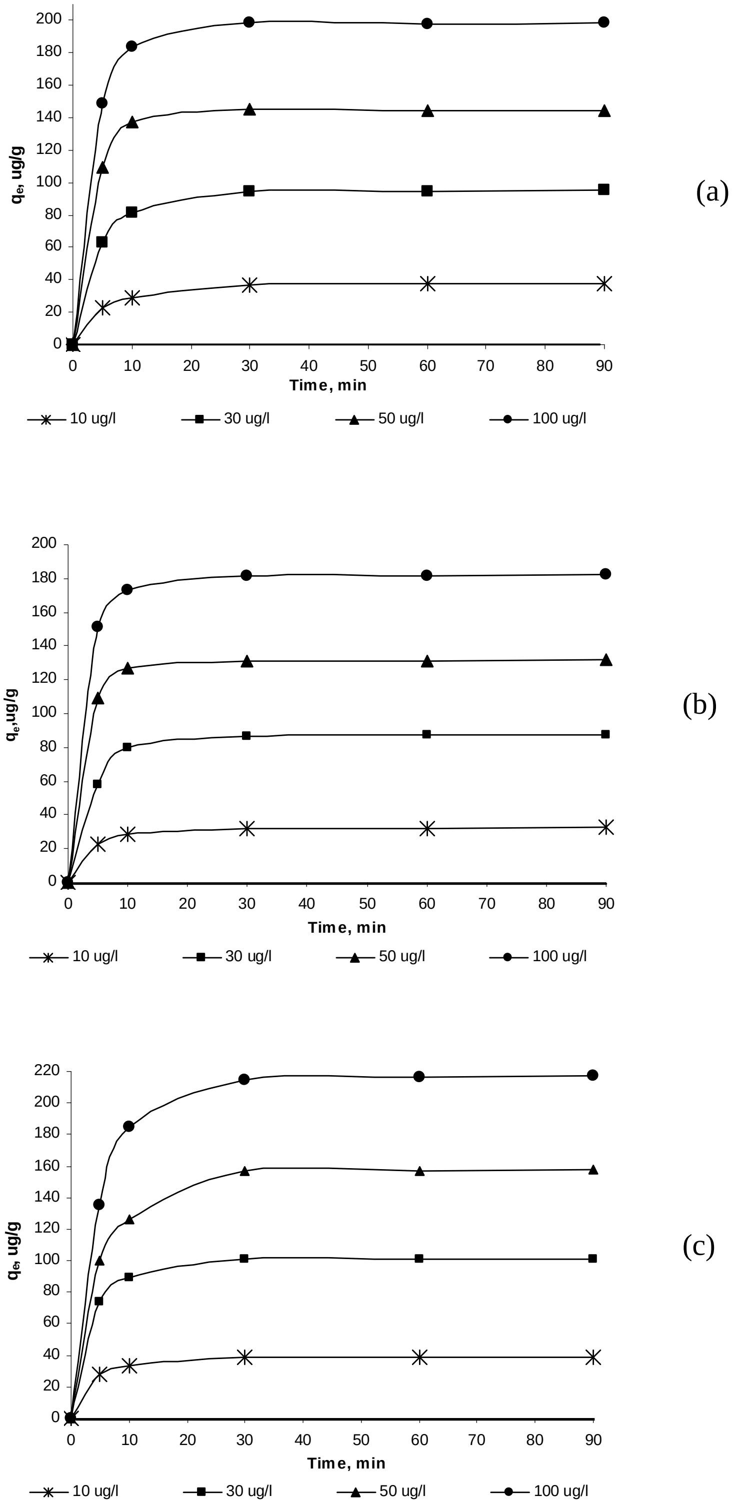

Figure 4. Kinetics curves on china clay treated with (a) Sodium sulfide (b) Thiourea (c) MBT.

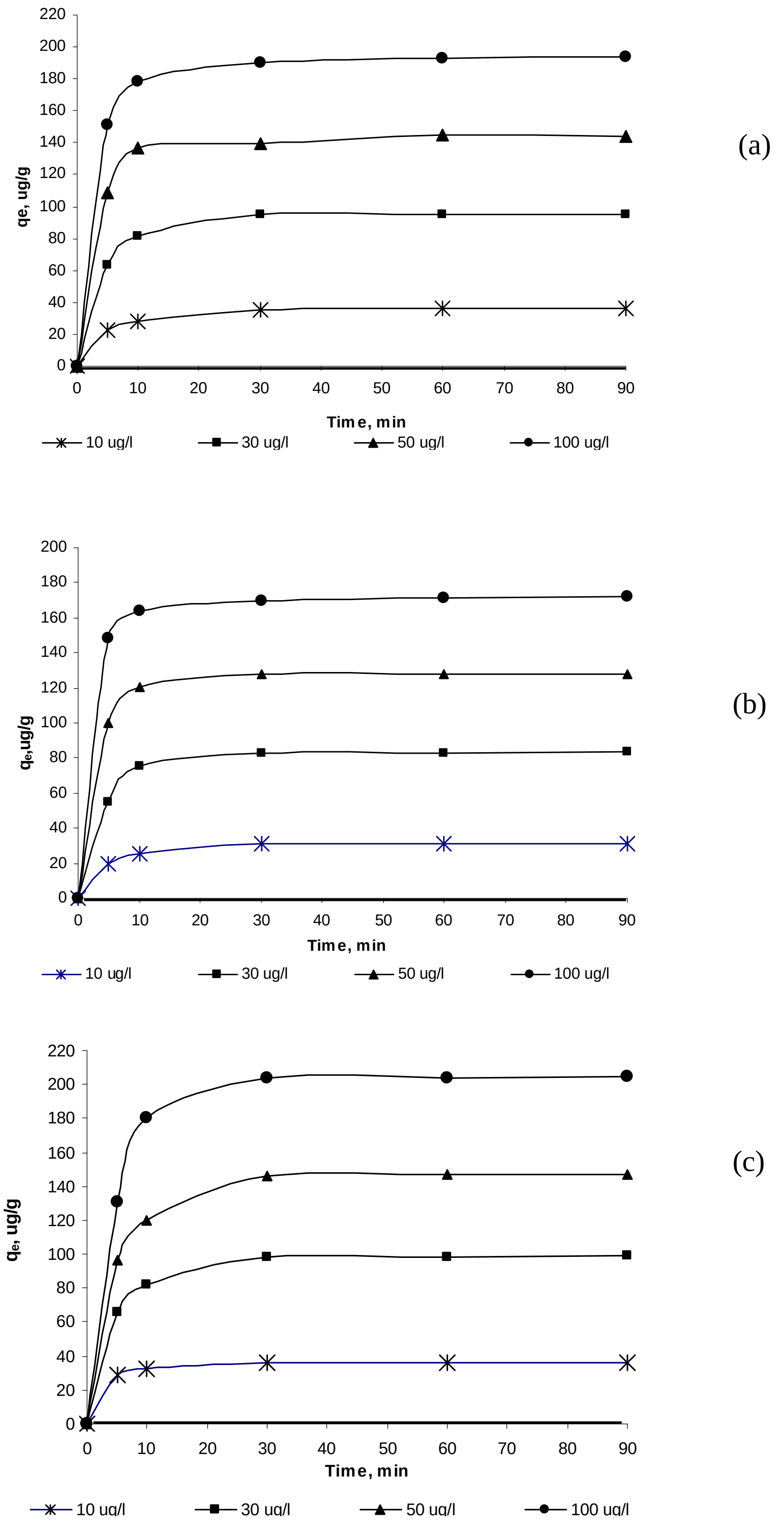

Figure 5. Kinetics curves on ball clay treated with (a) Sodium sulfide (b) Thiourea (c) MBT.

Langmuir equation was applied to study adsorption equilibrium.(20) It is based on the assumptions that the maximum adsorption corresponds to a saturated monolayer of adsorbate on the adsorbent surface. Langmuir equation is given in equation 1.

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \qquad \dots(1)$$

where C_e is the equilibrium concentration (µg/l), q_e the amount of Hg(II) adsorbed at equilibrium (µg/g), Q_0 and b the characteristic Langmuir constants related to maximum adsorption capacity and rate of adsorption, respectively. Plots of q_e versus C_e at pH 6 are shown in Figure 6.

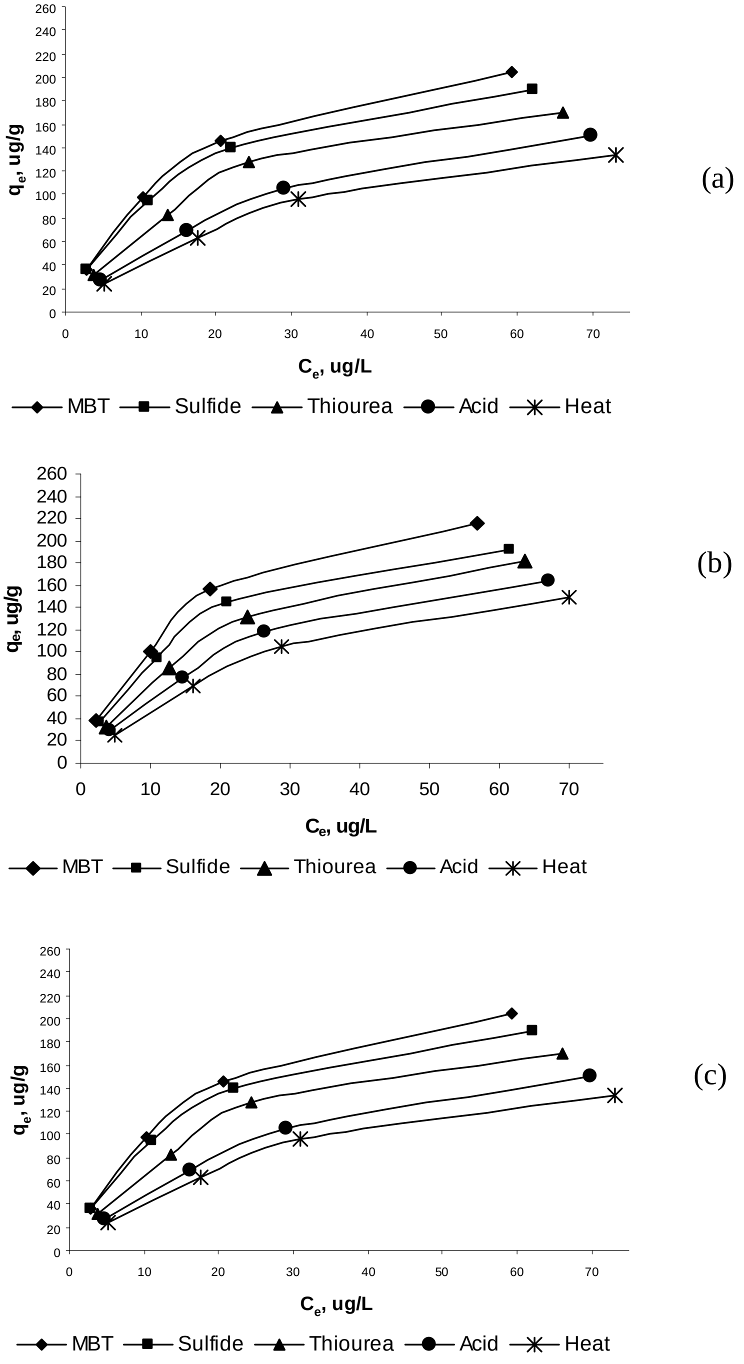

Figure 6. Isotherms for the adsorption of Hg(II) on treated clays (a) bentonite (b) china clay (c) ball clay.

All clays treated with sulfur compounds showed higher affinity to adsorb Hg(II) than untreated clays. Sulfur-functionalized adsorbents exhibited a specific binding toward mercury as a consequence of a soft Lewis acid-soft Lewis base interaction.(21) The high affinity of sulfur treated clays is explained by the Pearson rule because the sulfur compound and Hg(II) are soft base and soft acid, respectively. Hard acid prefers to co-ordinate with hard base and soft acid to soft base.

Comparing the three treatments, the highest adsorption of Hg(II) was found in MBT treated clay. This is explained by the structure of 2-mercaptobenzothiazole which is a multifunctional ligand.

The MBT treated bentonite, china clay and ball clay were compared for efficiency and the results are shown in Figure 7.

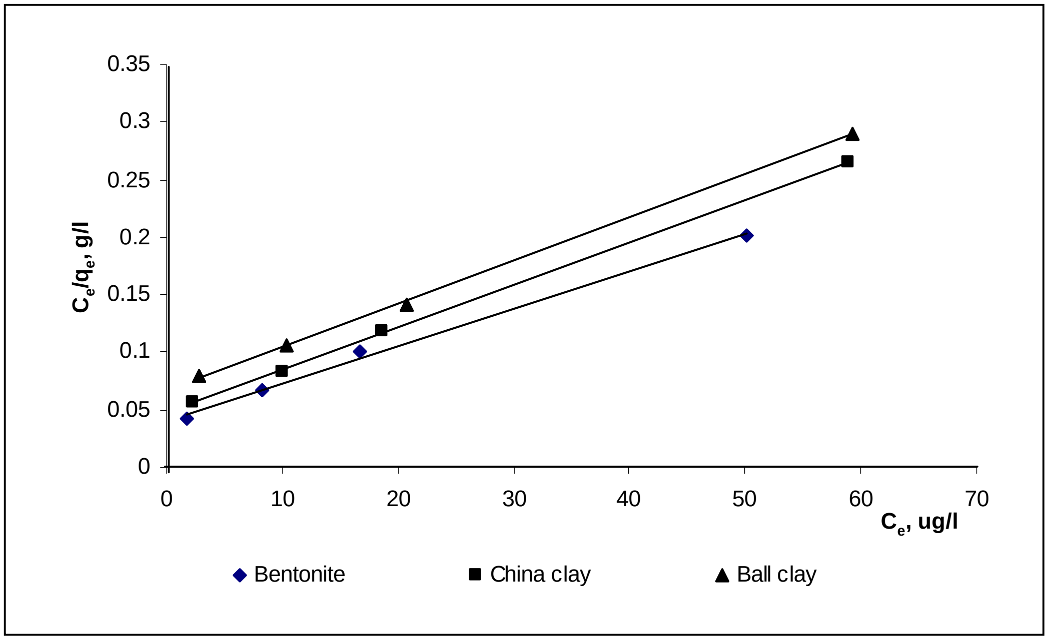

Figure 7. Langmuir plot for the adsorption of Hg(II) by MBT treated clays.

Linear plots of C_e/q_e versus C_e show that the adsorption follows the Langmuir isotherm model. The Q_0 and b values were determined from the slope and intercept of the plot. The isotherms for all of the MBT treated samples were well fitted (R = 0.9973 for bentonite, 0.9998 for china clay and 0.9994 for ball clay) by the Langmuir equation (1). The values of Q_0 determined are 312, 270 and 263 µg/g; b determined are 0.08, 0.08 and 0.06l l/µg, for bentonite, china clay and ball clay, respectively. This result shows that the chemical treatment of the clay influenced the adsorption activity by increasing the adsorbent surface area. In addition, different layer charges and location of the charges may have affected the metal adsorption. The location of layer charge determined the strength of the Lewis base of the clay. Bentonite is a 2:1 type clay with an excess negative charge; this tends to cause adsorption of positive Hg(II) ions. Ball clay and china clay (which are kaolinite) are 1:1 type clays with a neutral surface charge.(17)

Effect of temperature

Langmuir plot for adsorption of Hg(II) at various temperatures are shown in Figure 8.

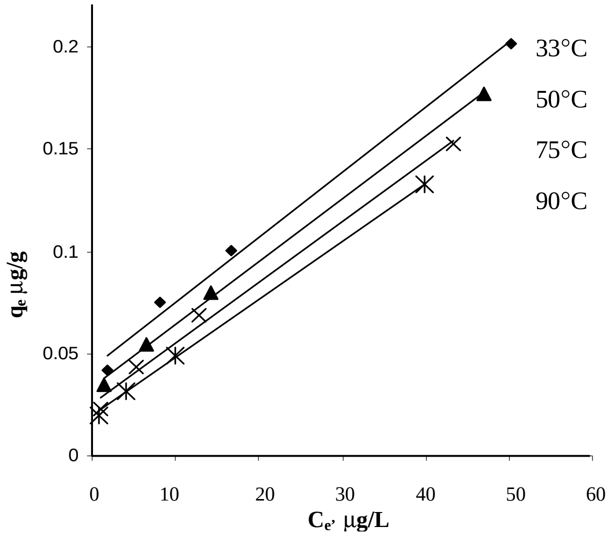

Figure 8. Langmuir plot for adsorption of Hg(II) at various temperatures.

It was observed that adsorption capacity of Hg(II) increased with increasing temperature, *i.e.* adsorption was endothermic in nature. This corresponds to prior results reported.(11) The Q_0 values determined from the slope of the plot are 312, 322, 333 and 344 µg/g, respectively, for a temperature of 33, 50, 75 and 90°C. This indicates that the affinity for Hg(II) ion is more favorable at high temperature. Based on Langmuir isotherm, at high temperature the adsorption sites are activated more than at low temperature.

Effect of ionic strength

Effect of ionic strength, using NaCl (0.05-1.0 M) are shown in Figure 9. In the presence of NaCl the adsorption of Hg(II) was strongly affected. It may be concluded that competitive adsorption takes place between Hg (II) and Na^+. Similar observations were made for mercury adsorption on silica and gibbsite surfaces.(21)

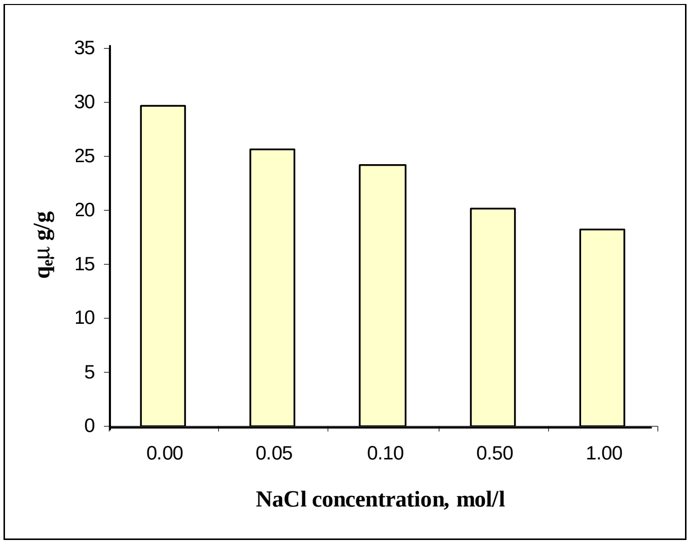

Figure 9. Adsorption of Hg(II) on clays as a function of ionic strength.

Adsorption of mercury(II) from real samples

Produced water, discharged water and drilling mud from platforms in the Gulf of Thailand were sampled and adsorption of mercury by treated and untreated clays was conducted. The results are shown in Table 4.

Table 4. Results of Hg(II) adsorption from real life water and mud samples by MBT treated and untreated clays.

Station	Sample type	pH	Depth (ft)	Hg content, µg/l		% Adsorption
				Before treatment	After treatment	
1	Discharged water	7.8	-	40.7	1.8	95.6
2	Produced water	6.7	-	68.7	3.5	94.9
3	Drilling mud	7.2	5000	167.0	33.8	79.7
4	Drilling mud	7.9	7000	345.8	70.7	79.6
5	Drilling mud	6.9	9000	656.9	146.7	77.7

The efficiency of Hg(II) removal in discharged waters, produced waters and drilling mud from the platforms was high (78-96% adsorption).

Desorption measurements

The forces acting between the clay surface and the Hg(II) ions are of two main types: physical and chemical. They give rise to physisorption and chemisorption, respectively. A study of the character of the adsorption onto the modified clay surface was carried out. When performing desorption of Hg(II) ions using hot water, %desorption is 5%, when using an acid solution to elute Hg(II) ions, desorption is 98%. These results show that a small fraction of Hg(II) ions are weakly adsorbed on the clay surface and most of the Hg(II) ions are chemically adsorbed.

CONCLUSION

Clays used in this work: bentonite, china clay and ball clay treated with sulfur compounds (sodium sulfide, thiourea and 2-mercaptobenzothiazole) have been shown to be effective adsorbents for Hg(II) at the pH range 6-8. Adsorption isotherms have been determined and data have been analyzed according to the Langmuir model. Adsorption capacity order for bentonite, china clay and ball clay treated with 2-mercaptobenzothiazole is: 312, 270 and 263 µg/g, respectively, at pH 6 and a temperature of 33^{o}C. Increasing temperature increased the adsorption, thus indicating the endothermic nature of the process. Besides the ion exchange capacity and the high surface area of clay, it is believed that bond formation between the metal and the sulfur atoms in the sulfur compound accounts for the high affinity of mercury. This is in accord with the Pearson rule. The objective of this work has been achieved by utilizing the adsorbent in removing mercury from discharged water, produced water and drilling mud samples obtained from oil platforms in the Gulf of Thailand. An advantage in using clay as sorbent is the abundance and low cost of natural clay and the easy preparation of modified clay.

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REFERENCES

1. Krishnamoorthi, C. R. and Vishwanathan, P. (1991) “Toxic metal in the Indian environment.” *New Delhi: Tata McGraw-Hill Publishing Co. Ltd.*
2. Patterson, W. and Passion, R. (1990) “Metals speciation-separation and recovery.” *Lewis Publishers*, New York.
3. Larson, A., (1992) “Liquid ion exchange for mercury removal from water over a wide pH range” *Ind. Eng. Chem. Res*., **31**, 2714-2723.
4. Chiale, S., Ratto, M. and Rovatti, M. (2000) “Mercury removal from water by ion exchange resins adsorption.” *Water Res*. **34**, 2971-2982.
5. Namasivayam, C. and Senthilkumar, S. (1997) “Recycling of industrial solid waste for the removal of mercury(II) by adsorption process.” *Chemosphere* **34**, 357-375.

6. Cox, M., El-Shafey, E. l., Pichugin, A. A. and Appleton, Q. (2000) "Removal of mercury(II) from aqueous solutions on a carbonaceous sorbent prepared from flax shieve" *J. Chem. Technol. Biotechnol.* **75**, 427-435.
7. Sreedhar, M. K., Madhukumar, A. and Anirudhan, T. S. (1999) "Evaluation of an adsorbent prepared by treating coconut husk with polysulphide for the removal of mercury from wastewater" *Indian, J. Eng. Mater. Sci.* **6**, 279-285.
8. Sreedhar, M. K. and Anirudhan, T. S. (2000) "Preparation of an adsorbent by graft polymerization of acrylamide onto coconut husk for mercury(II) removal from aqueous solution and chlor-alkali industry wastewater" *J. Polym. Sci..* **25**, 1261-1269.
9. Malakul, P., Srinivasan, K. R. and Wang, H. Y. (1998) "Metal adsorption and desorption characteristics of surfactant-modified clay complexes" *Ind. Eng. Chem. Res.* **37**, 296-301.
10. Filho, N. L., Polito, W. L. and Gushikem, Y. (1995) "Sorption and preconcentration of some heavy metals by 2-mercaptobenzothiazole-clay" *Tantala* **42**, 1031-1036.
11. Manohar, D. M., Krishnan, K. A. and Anirudhan, T. S. (2002) "Removal of mercury(II) from aqueous solutions and chlor-alkali industry wastewater using 2-mercaptobenzimidazole-clay" *Water Research* **36**, 1609-1619.
12. Lagacid, I. L., Mitchell, M. K. and Payne, B. D. (2001) "Highly effective adsorption of heavy metal ions by a thiol-functionalized magnesium phyllosilicate clay" *Environ. Sci. Technology*. **35**, 984-990.
13. (a) Method 7470A. Mercury in liquid waste (manual cold-vapor technique) *The United States Environmental Protection Agency*, 1994. (b) Method 7471A. Mercury in solid and semisolid waste (manual cold-vapor technique) *Environmental Protection Agency*, 1994.
14. Filho, N. L., Gushikem, Y. and Polito, W. L. (1995) "2-Mercaptobenzothiazole clay as matrix for sorption and preconcentration of some heavy metals from aqueous solution" *Analytica Chimica Acta.* **306**, 167-172.
15. Brigatti, F., Colonna, S., Malferrari, D., Medici, L. and Poppi, L. (2005) "Mercury adsorption by montmorillonite and vermiculite: a combined XRD, TG-MS, and EXAFS study" *Applied Clay Science* **28**, 1-8.
16. Whilton, N. T., Burkett, S. L. and Mann, S. (1998) "Hybrid lamellar nanocomposites based on organically functionalized magnesium phyllosilicate clays with interlayer reactivity" *J. Mater. Chem.* **8**, 1927-1932.
17. Miranda-Trevino, J. and Coles, C. (2003) "Kaolinite properties, structure and influence of metal retention on pH" *Applied Clay Science* **23**, 133-139.
18. Sarkar, D., Essington, M. E. and Misra, K. C. (2000) "Adsorption of mercury(II) by kaolinite" *Soil. Sci. Soc. Am. J.* **64**, 1968-1975.
19. Knocke, W. R. and Hemphill, L. H. (1981) "Mercury(II) sorption by waste rubber" *Water Research* **15**, 275-282.
20. Langmuir, I. (1918) "Adsorption of gases on plane surfaces of glass, mica and platinum" *J. Am. Chem. Sci.* **40**, 1361–1403.
21. Sarkar, D., Essington, M. E. and Misra, K. C. (1999) "Adsorption of mercury(II) by variable charge surfaces of quartz and Gibbsite" *Soil Sci. Soc. Am. J.* **63**, 1615-1617.

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