

Characterization and adsorption mechanism of Pb (II) removal by insolubilized humic acid in polluted water

Ming-guang Ma, Yun-xia Wei*, Guo-hu Zhao, Fang Liu, Yan-Rong Zhu

Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education, Lanzhou City University, Lanzhou 730070, China

Email address:

Weiyx07@lzu.edu.cn (Yun-xia Wei)

To cite this article:

Ming-guang Ma, Yun-xia Wei, Guo-hu Zhao, Fang Liu, Yan-Rong Zhu. Characterization and Adsorption Mechanism of Pb (II) Removal by Insolubilized Humic Acid in Polluted Water. *International Journal of Environmental Protection and Policy*. Vol. X, No. X, 2014, pp. 230-235. doi: 10.11648/j.ijepp.20140206.16

Abstract: The removal of Pb^{2+} in the aqueous solutions by adsorption onto insolubilized humic acid (IHA) is investigated. The equilibrium isotherms were determined at pH 3.5 under constant ionic strength and at different temperatures. At the same time, the paper has also analyzed the adsorption experimental data by using three different isotherm models: Langmuir, Freundlich and Linear isotherm. As the result, it has obtained the optimal correlation for Freundlich isotherm equations. In addition, the paper has calculated the thermodynamic quantities ΔH in accordance with the Clausius-Clapeyron's theory. It means that the type of adsorption of Pb^{2+} onto IHA is physisorption, rather than by chemical bonding. And finally, the adsorption equilibrium gained around 12 hours and a high and stable removal of heavy metals on insoluble humic acid has been obtained almost under the neutral conditions.

Keywords: Water Contamination, Insolubilized Humic Acid, Adsorption, Modification

1. Introduction

Heavy metal water pollution is an area of major concern today in both developed and developing countries. Common anthropogenic sources include agricultural activities, atmospheric deposition, road run off, discharges from industrial plants and sewage works, acidic mine effluents and building of reservoirs^[1,2]. Lead is toxic priority pollutants that commonly interfere with the beneficial use of wastewater for irrigation and industrial applications producing kidney and blood diseases among with other health disorders^[3,4]. It is therefore mandatory to reduce their levels in water and wastewater. Some national and international health authorities such as USA Environment Protection Agency (EPA) and the World Health Organization (WHO, 2004) have drawn up that the maximum contaminant levels of Pb^{2+} is 0.0015 mg.L^{-1} in drinking water^[5].

Many processes for the removal of the heavy metals from water have been investigated such as filtration, reverse osmosis, chemical precipitation, ion-exchange, and electro-deposition. However, these technologies are ineffective or expensive when heavy metals are present in the wastewater at low concentration so that they are unsustainable in developing countries due to high costs for maintenance and

chemicals necessary for removal of heavy metals. Adsorption is an alternative technology because of its high effect, low cost and easy operation among the physicochemical treatment processes. Recently numerous alternative materials as adsorbents, which are good adsorbents and inexpensive, have increased much concern in sorption of heavy metals from wastewater including activated carbon^[6], activated slag^[7], iron oxide coated sand^[8], bagasse fly ash^[9], carbon nanotubes^[10], natural silicate minerals^[11], natural zeolites^[12], agricultural wastes^[13], microbial and plant derived biomass^[14], lignite^[15], wood sawdust^[16], chitin and chitosan^[17]. However, these materials are limited due to low efficiency, high cost or other shortage for practical application. Hence, currently it is still necessary to find out new economical and effective adsorbents.

Organic matter in the environment can be divided into two classes of compounds: non-humic material and humic substances^[18]. Humic substances have their functional groups, such as carboxyl and phenyl groups, therefore, they can replace the synthesized agents to bind cations and form complexes^[5]. As HA has strong chelating capacity with metals and obvious adsorption capacity on organic compounds, it cannot be used as an adsorbent due to its high solubility in chelating formation^[19]. However, some researchers have studied the adsorption effects of

insolubilized humic acid on metals and organic contaminants [20-21]. Insolubilized humic acid (IHA) is a material that is insoluble in aqueous media even at alkaline conditions, and is obtained through a process developed by Seki and Suzuki [21]. Because of its simplicity and effectiveness, an increasing interest has recently been given to insolubilization [23-24], and the obtained material, IHA, can provide an inexpensive substitute for the treatment of wastewaters containing heavy metal ions. The sorption processes being used for the removal and recovery of heavy metal ions from wastewaters are generally based on ion-exchange and complex formation mechanisms, and the medium pH is an of prime importance aspect in the optimization of such processes. In evaluating the sorption characteristics of heavy metal ions on humic acid-based sorbents, it is a common sense to derive adsorption isotherms on the basis of data obtained from concentration studies that performed at a fixed pH value. Besides, the sorption characteristics are generally discussed for the neutral and slightly acidic conditions and the sorption characteristics under strongly acidic conditions are usually disregarded. However, the adsorption isotherms derived from data obtained at different strongly acidic conditions can give an important idea about the tendency of specific and nonspecific interactions between heavy metal ions and humic acid-based sorbents. In this way, the optimization of sorption processes, especially those being performed under column conditions, can be constructed on a more reasonable basis. Hence, the present study aims at evaluating sorption phenomenon of Pb(II) ions on IHA at different medium pH values, and the obtained results are believed to be useful for removal, recovery and preconcentration of Pb(II) from strongly acidic wastes by using IHA as a sorbent.

2. Experimental

2.1. Chemicals and Reagents

A Shimadzu analytical balance, Model AW 120, was used (± 0.0001 g). A Memmert WB 22 water bath-shaker equipped with a digital thermostat was used in batch adsorption experiments. A Metrohm pH meter, Model 525A, was used for pH measurements. The concentration of Pb(II) was determined by flame atomic absorption spectrophotometry (Beijing, China). Humic acid (A.R.) was purchased from Shanghai Julan Science and Technology Ltd. All chemicals used in the study were of analytical grade. All solutions used were prepared with distilled water.

2.2. Preparation of Insolubilized Humic acid

Insolubilized humic acid (IHA) was prepared by heating HA at 330°C for 1 h after HA was pretreated with 2 M CaCl_2 solution and converted from sodium salt to calcium [25]. Additionally, HA could cause a rapid dehydration and condensation between acidic groups in the heating process. The obtained IHA was grounded and repeatedly washed with 1 M HNO_3 solution at first and then with distilled water. Finally, the IHA was converted from the hydrogen form to sodium form with 1 M NaNO_3 solution, and rinsed with

distilled water prior to drying at 80°C . Then the converted IHA was stored in an airtight glass bottle to remain insoluble in aqueous phase at pH less than 10.

2.3. Adsorption Experiments

The adsorption trends of Pb(II) on the IHA in aqueous solution were investigated as a function of contact time, pH, initial lead ion concentration and competing metal ions.

Batch adsorption experiments were conducted by introducing exact volume (25.00 mL) of Pb(II) with the known initial concentration into flasks containing 0.5 g of the IHA. The Pb(II) concentrations ranging from $5\text{ mg}\cdot\text{g}^{-1}$ to $300\text{ mg}\cdot\text{g}^{-1}$ had the ionic strength remained in 0.1 M NaNO_3 solution. The flasks were shaken at a constant temperature and pH until adsorption equilibrium was established. All experiments were performed at three different temperatures: 25 , 45 and $65\pm 0.1^{\circ}\text{C}$, respectively. The adsorbent was then removed from liquid phase by filtration and subsequent centrifugation. The equilibrium concentrations of Pb(II) were determined by flame atomic absorption spectrophotometry. All experiments were carried out in duplicate, but only mean values are presented in the paper. The sorbed amounts of Pb(II) were calculated by utilizing the difference between the initial and final concentration in aqueous phase, meanwhile, blank samples without adding Pb(II) were also prepared to determine a total loss of solute resulting from adsorption on flasks walls and other error sources.

3. Results and Discussion

3.1. IR Spectroscopy Analysis of HA and IHA

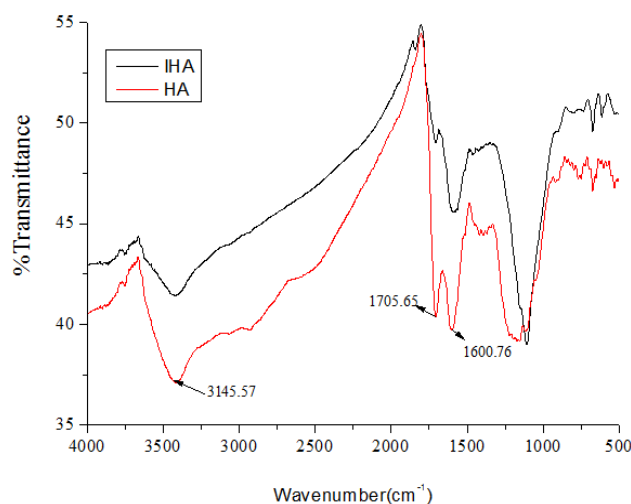


Fig. 1. FTIR spectra of nature and insolubiled humic acid

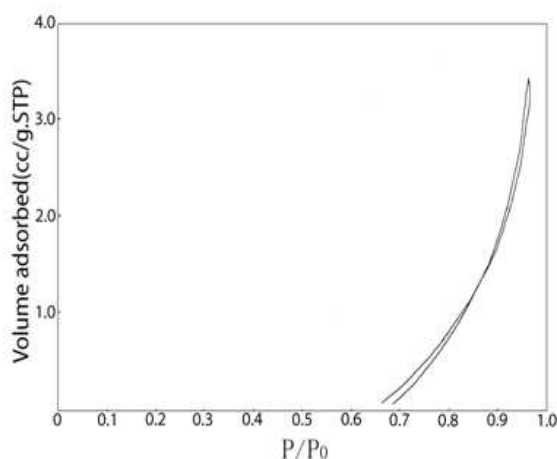
The FTIR spectra of HA and IHA gave more insights of structural changes in the humic acid evolution, recorded for $4000\text{--}500\text{ cm}^{-1}$, and displayed in Figure 1. The extremely strong polar group OH^- easily forms association reactions. Thus the peak of O-H stretching vibration with association of OH groups could be formed at $3500\text{--}3300\text{ cm}^{-1}$, and at $1720\text{--}1700\text{ cm}^{-1}$ for C=O stretching of carboxylic groups.

The absorption band at 1,580–1,650 cm^{-1} was assigned for C=C stretching of aromatic groups^[26]. Within the spectra of modified HA shown in Figure 1, the peak shape and location of the C=C stretching of aromatic groups only changed little. Compared to HA, the peak of C=O and O–H stretching vibration in the modified HA became weaker, showing that dehydration and decarboxylation might occur in the heating process. Since the humic macromolecules contain both hydrophobic (aromatic, aliphatic) and hydrophilic (carboxylic, phenolic, proteinic, and polysaccharidic) moieties^[27], the sponge-like structure of HA seemed to expose more polar groups on the solid-water interfaces. After being heated, HA might lose some 25% of acidic groups through the condensation reaction. As a result, IHA decreased its hydrophilicity and hydrophobicity increased^[28].

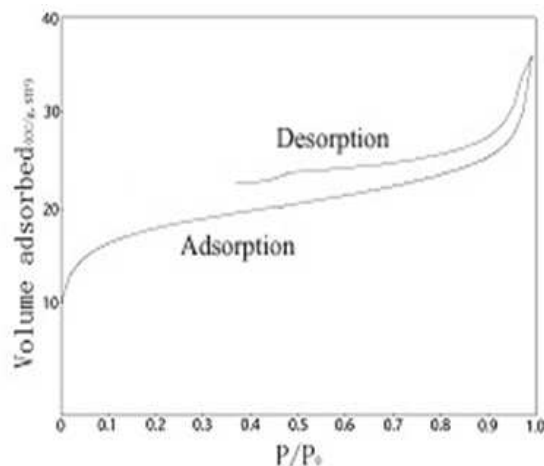
3.2. Nitrogen Adsorption Isotherms and Porous Structure

Samples of 50 to 100 mg were degassed in vacuum (133.3 9 10⁻⁵ Pa) at 350°C prior to the adsorption of gaseous nitrogen, and the curves of adsorbed volume versus relative pressure (P/P₀) are shown in Figure 2 (a,b), respectively. However, it was impossible to calculate the specific surface and pore volume of HA by the nitrogen adsorption-desorption curves shown in Figure 2a because much physisorbed and zeolite water existed in the structure of HA.

Thus, the adsorption and desorption curves were overlapped so closely that the hysteresis loop could not be distinguished. The adsorption of IHA shown in Figure 2b exhibits a Type II adsorption isotherm according to IUPAC classification with a sharp pore condensation step at the high relative pressure^[29]. As the amount of adsorbed nitrogen increased very slowly under the relative pressure between 0.2 and 0.5, it suggested that IHA had the insignificant microporous and small mesoporous feature. The adsorption gradually increased under the certain relative pressure ranging between 0.5 and 0.95, indicating that an adsorption process took place on a solid with primarily mesoporous or macroporous structure. The obvious adsorption and condensation of nitrogen occurred at a pressure range between 0.95 and 1.0 in correspondence to pores sizes larger than 40 nm. The adsorption/desorption hysteresis loop could be observed in the region of higher relative pressures, which proved that IHA pore structures had mesoporous and macroporous characteristics. The adsorption isotherms were analyzed by the Brunauer–Emmett–Teller (BET) equation to estimate the apparent surface area^[30], also, the microporous volume and external surface areas were estimated with the t-plot method based on the Harkins–Jura equation. The porous structure parameters of IHA samples are listed in Table 1.



(a) Natural humic



(b) Modified humic acid

Fig. 2. Nitrogen adsorption-desorption isotherms of HA and IHA

Table 1. Specific surface, pore volume and pore distribution of insolubilized humic acid

S _{BET}	S _t	S _{mic}	V _t	V _{mic}	V _{mac+mes}	pore size distribution (%)				
(m ² /g)	(m ² /g)	(m ² /g)	(ml/g)	(ml/g)	(ml/g)	30-20 nm	20-10 nm	10-3 nm	3-2 nm	2-1 nm
62.02	56.01	41.07	0.05823	0.02492	0.03331	33.59	37.20	21.98	5.01	3.4

3.3. Time of Equilibrium

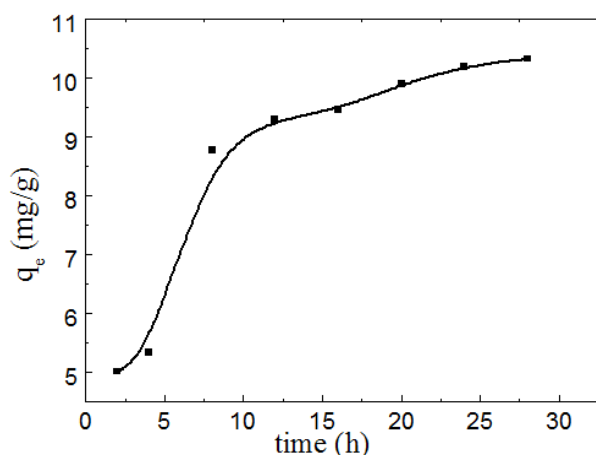


Fig. 3. Effect of time on adsorption of Pb^{2+} onto IHA in 0.1M $NaNO_3$ at pH 3.5

The relationship between reaction time and sorption amounts at the initial Pb(II) concentrations of 400 mg.L^{-1} was presented in Figure 3. The results showed the adsorption of Pb(II) onto IHA was very rapid with increase in contact time from 2 to 480 min, and sorption equilibration was not achieved within experiment time, followed by a constant adsorption rate with further shaking time. The initial rapid step of Pb(II) sorption might be due to the surface physical sorption because of large surface area, around $62.02 \text{ m}^2.\text{g}^{-1}$, obtained from BET test and chemical reactive sorption because of a facilely immediate interaction between Pb(II) and the reactive groups (i.e. $-OH$, $C=O$, $-COO^-$) on the surface of the nano-adsorbent. However, the subsequent slow step might be attributable to the reactive sorption within the polymer chain segments. Besides, the Pb(II) adhered on the surface of the nano-adsorbent would further hamper the diffusion of other Pb(II), resulting in a rather long time to reach the equilibrium. In fact, a 720-min reaction time is sufficient to achieve satisfactory reaction efficiency on the whole, although the equilibrium has not reached. At the same time, with the consideration of the total operation time, the reaction time was set at 720 min.

3.4. Effect of Initial Concentration and Temperature

Figure 4 shows the impacts of concentration of Pb(II) and temperature on Pb(II) sorption. It appeared that with the increase of initial concentration, the adsorption capacity at equilibrium time was promoted by the increased drive force, resulting from the concentration variance of Pb(II) between solution and the IHA. Nonetheless, the removal percentage of Pb(II) with the increase of Pb(II) concentration from 10 to 300 mg/L decreased from 85.7% to 48.0%, 86.9% to 52.3%, 92.0% to 62.3%, at the temperature of 25, 45, and $65 \pm 0.1^\circ\text{C}$, respectively. These results indicate that the initial Pb(II) concentration plays an important role in the adsorption of Pb(II). Also, the temperature had significant effects on Pb(II) adsorption capacity which essentially increased with increasing temperature. This phenomenon suggests that the process is endothermal, indicating that higher temperature is more favorable for the adsorption of Pb(II).

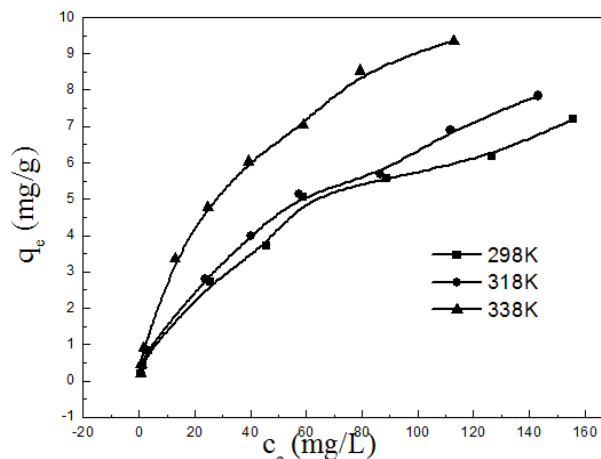


Fig. 4. Adsorption isotherms of Pb(II) on IHA in 0.1M $NaNO_3$ at pH=3.5 under different temperatures

3.5. Effect of pH

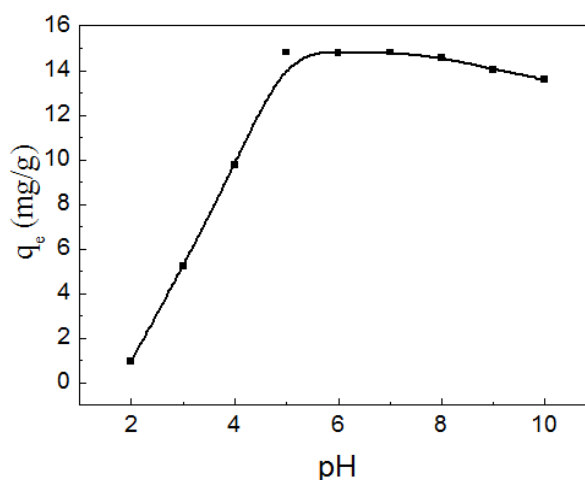


Fig. 5. Effect of pH on adsorption of Pb^{2+} onto IHA in 0.1M $NaNO_3$ at pH 3.5

The effect of pH on Pb(II) removal was investigated in the pH ranges of 2.0–10.0 at $25 \pm 0.1^\circ\text{C}$ for 12h as shown in Figure 5, it is apparent that the adsorption capacity of Pb(II) increased by increasing the pH value. Solution pH affects both IHA surface metal binding sites and the metal chemistry in water. At low pH value, the surface of the adsorbent is closely associated with the hydronium ions and repulsive forces limit the approach of the metal ions; when pH increases, more protons are greatly combined with OH^- to produce H_2O ; Pb(II) and $Pb(OH)^+$ species are present in the solution. The increase in adsorption of Pb(II) is probably due to cation hydrolysis such as $Pb(OH)^+$, since hydroxy complexes are adsorbed preferentially over uncomplexed cations. The basic structural units of humic acid are aromatic rings and alkyl chains contain a wide variety of functional groups ($-COOH$, $-COH$, $-NH_2$, etc.). These groups can bind strongly to metals and give humic acid a high adsorption capacity for metals; at higher pH the IHA surface starts to acquire a net negative charge, creating a situation electrostatically favorable for higher adsorption of lead ions

due to the increase in the concentration of hydroxyl ions. From the corresponding data, an increase in pH corresponds to an increase in adsorption, reaching the maximum adsorption capacity at pH 7. The higher the pH, the greater will be the dissociation of the functional groups $-\text{COOH}$ and $-\text{COH}$ to $-\text{COO}^-$ and $-\text{CO}^-$. When the solution pH varied from 2.0 to 7.0 the adsorption of Pb(II) increased from 0.9791 to 14.81mgg^{-1} .

3.6. Adsorption Isotherms

A comparison of adsorption models, with a linear experimental isotherm constant obtained from the sorption of Pb(II) onto the IHA at pH3.5 and at different temperature is presented in Table 2. The Freundlich isotherm appeared to be linear within the whole concentration range with high correlation coefficient, which certified that the Freundlich isotherm could excellently describe the monolayer adsorption processes when the equilibrium adsorption amount (q_{max}) and adsorption constant (k) were found to increase with the

increase of temperature. Thermodynamic evaluation of adsorption process the type of adsorption can be determined through thermodynamic quantities as ΔH_{ads} and ΔS [31]. The adsorption process is composed of two contributions, i.e., enthalpic and entropic, which characterize whether the reaction is spontaneous or not. From the Freundlich isotherm model, adsorption heating of Pb(II) on to IHA can be calculated from the temperature dependence of the equilibrium adsorption constant (K) by the Clausius–Claperyon’s equation:

$$\frac{\partial \log K}{\partial (1/T)} = \frac{-\Delta H_{\text{ads}}}{2.303R} \quad (1)$$

Here, a plot of $\log k$ versus $1/T$ should be linear with slope $-\Delta H/2.303R$ and with intercept $\Delta S/2.303R$. These quantities are related via

$$-RT \ln K = -\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S \quad (2)$$

Table 2. Isothermal adsorption equations of Pb^{2+} onto insolubilized humic acid

T/°C	Linear		Freundlich		Langmuir				
	$C_s = a + kC_e$		$C_s = kC_e^n$		$C_s = q_{\text{max}}C_e/(C_e + 1/k)$				
<i>a</i>	<i>k</i>	<i>r</i> ²	<i>k</i>	<i>n</i>	<i>r</i> ²	<i>k</i>	$q_{\text{max}}/(\text{mg}\cdot\text{g}^{-1})$	<i>r</i> ²	
25	1052.1761	44.1997	0.907 8	315	0.6419	0.9901	25.5618	8.3236	0.9603
45	997.1452	53.1642	0.939 1	326	0.6602	0.9810	24.4953	9.2782	0.9479
65	1461.2066	83.0912	0.895 1	472	0.6777	0.9714	35.5287	11.2585	0.9750

Examination (Table 2) revealed that ΔH_{ads} and ΔS values calculated by the Langmuir equilibrium constants were relatively equal to 8.338 J/mol and $75.3321\text{ J}\cdot\text{K}^{-1}$ when ΔG_{ads} values were -14.25, -15.30 and $-17.30\text{ kJ}\cdot\text{mol}^{-1}$ at 25, 35 and 45°C , respectively. The positive ΔH values implied that the adsorption process showed the endothermic nature in the present system. At the three different temperatures, the ΔH_{ads} values were smaller than the lower limit of chemisorption of 42.0 kJ/mol, which means that the sorption of Pb(II) on IHA was affected by physisorption, rather than chemical bonding. However, the free energy values (ΔG_{ads}) appeared to be very small and negative, indicating that the reaction appeared to be spontaneous.

4. Conclusions

Our research was dealt with conversion of humic acid into insolubilized humic acid by heating at 330°C that was certified to be the optimal temperature for modifying HA. The sorption of Pb(II) on IHA was performed at the different temperatures and the experimental results showed that IHA is a potentially efficient absorbent to purify water from the heavy metal contaminants. The experimental adsorption data obtained in IHA– Pb(II) system excellently obeyed to Freundlich isotherm equation. It was evident that the capacity of adsorption was strengthened with the increase of temperatures. On basis of Freundlich isotherm model, the relevant thermodynamic quantities of ΔH , ΔS and ΔG could be calculated. The experimental results

verified that Pb(II) adsorption onto IHA appeared to be spontaneous, and mainly was a physical process. The results obviously gave a suggestion that IHA, as a potential efficient absorbent, can be utilized to purify water contaminated by heavy metals.

Acknowledgments

We are grateful for the open fund for Key Laboratory of Eco-Environment-Related Polymer Materials (KF-13-02), the High School Tutor Foundation of Gansu Province (1212-04) and the Starting Fund for Doctoral Research of Lanzhou City University.

References

- [1] Flora, S., Saxena, G., Gautam, P., Kaur, P., Gill, K. (2007). Response of lead-induced oxidative stress and alterations in biogenic amines in different rat brain regions to combined administration of DMSA and MiADMSA. *Chemico-Biological Interactions*, 170 (3), 209–220.
- [2] Telišman S, Čolak B, A Pizent, Jurasović J. (2007). Reproductive toxicity of low-level lead exposure in men. *Environmental Research*, 105(2), 256–266.
- [3] Yangho K, Byung-Kook L (2012). Associations of blood lead, cadmium, and mercury with estimated glomerular filtration rate in the Korean general population: Analysis of 2008–2010 Korean National Health and Nutrition Examination Survey data. *Environmental Research*, 118, 124–129.

- [4] Massó, E., Corredor, L., Antonio, M. (2007). Oxidative damage in liver after perinatal intoxication with lead and/or cadmium. *Journal of Trace Elements in Medicine and Biology*, 21(3), 210–216.
- [5] Frantisek, K. (2004), WHO Guidelines for Drinking-Water Quality. National Institute of Public Health.
- [6] Rao M., Ramana, D., Seshaiiah, Wang, K., Chien, S. (2009), Removal of some metal ions by activated carbon prepared from *Phaseolus aureus* hulls. *Journal of Hazardous Materials*, 166 (2-3), 1006–1013.
- [7] Hammamini, A., González, F., Ballester, A., Blázquez, M., Muñoz, J. (2007), Biosorption of heavy metals by activated sludge and their desorption characteristics. *Journal of Environmental Management*, 84 (4), 419–426.
- [8] Kundu, S, Gupta, A. (2006), Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization. *Chemical Engineering Journal*, 122 (1-2), 93–106.
- [9] Ho, Y., McKay, G (1999), Comparative sorption kinetic studies of dye and aromatic compounds onto fly ash. *J. Environ. Sci. Health A*, 34(5), 1179–1204.
- [10] Li, Y., Ding, J., Luan, Z., Di Z., Zhu, Y., Xu, C., Wu, D., Wei, B. (2003), Competitive adsorption of Pb^{2+} , Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes. *Carbon*, 41(14), 2787–2792.
- [11] Venditti, F., Andrea, C., Palazzo, G., Colafemmin, G., Lopez, F. (2007), Removal of chromate from water by a new CTAB-silica gelatin composite, *Journal of Colloid and Interface Science*, 310(15), 353–361.
- [12] Purna, G, Rao, C., Satyaveni, S., Ramesh, A., Seshaiiah, K., Murthy, K., Choudary, N. (2006), Sorption of cadmium and zinc from aqueous solutions by zeolite 4A, zeolite 13X and bentonite. *Journal of Environmental Management*, 81(3), 265–272.
- [13] Orhan, Y., Büyükgüngör, H. (1993), The Removal of Heavy Metals by Using Agricultural Wastes. *Water Science & Technology*, 28(2), 247–255.
- [14] PAN, J., LIU, R., TANG, Hong. (2007), Surface reaction of *Bacillus cereus* biomass and its biosorption for lead and copper ions. *Journal of Environmental Sciences (China)*, 19 (4), 403–408.
- [15] Guo, X., Zhang, S., Shan, X. (2008), Adsorption of metal ions on lignin. *Journal of Hazardous Materials*, 151(1), 134–142.
- [16] Ofomaja AE (2010), Intraparticle diffusion process for lead (II) biosorption onto mansonina wood sawdust. *Bioresource technology*, 101(15), 5868–5876.
- [17] Wong, Y., Szeto, Y., Cheung W., McKay, G (2004), Adsorption of acid dyes on chitosan—equilibrium isotherm analyses. *Process Biochemistry*, 39(6), 695–704.
- [18] M.H.B. Hayes, in: G. Davies, E.A. Ghabbour (Eds.), *Humic Substances, Structures, Properties and Uses*, J. Gordon and Breach Science, New York, 1998, p. 1.
- [19] Li, L., Huang, W., Peng, P., Sheng, G., Fu, J. (2003), Chemical and molecular heterogeneity of humic acids repetitively extracted from a peat. *Soil Sci Soc Am J*, 67(3), 740–746.
- [20] Baker, H., Khalili, F. (2004), Analysis of the removal of lead(II) from aqueous solutions by adsorption onto insolubilized humic acid: temperature and pH dependence, *J. Analytica Chimica Acta*, 516 (1–2), 179–186.
- [21] Chen, H., Berndtsson, R., Ma, M., Zhu, K. (2009), Characterization of insolubilized humic acid and its sorption behaviors. *Environmental Geology*, 57(8), 1847–1853.
- [22] Hideshi, S., Akira, S. (1995), Adsorption of heavy metal ions onto insolubilized humic acid. *Journal of Colloid and Interface Science*, 171(2), 490–494.
- [23] Bassam, E., Fawwaz, K. (2006), Adsorption of Cu(II) and Ni(II) on solid humic acid from the Azraq area, Jordan. *Journal of Colloid and Interface Science*, 299(2), 497–503.
- [24] Gezici, O., Kara, H., Ersöz, M., Abali, Y. (2005), The sorption behavior of a nickel-insolubilized humic acid system in a column arrangement. *Journal of Colloid and Interface Science*, 292 (2), 381–391.
- [25] Chen H, Berndtsson R, Ma M, Zhu K (2009). Characterization of insolubilized humic acid and its sorption behaviors. *Environmental geology*, 57:1847–1853.
- [26] Fu, H., Quan, X. (2006), Complexes of fulvic acid on the surface of hematite, goethite and akaganeite: FTIR observation. *Chemosphere*, 63(3), 403–410.
- [27] Negrea, M., Leone, P., Trichet, J., Defarge, C., Boero, V., Gennari, M. (2004), Characterization of model soil colloids by cryo-scanning electron microscopy. *Geoderma*, 121(1–2), 1–16.
- [28] Bigalke M, Weyer S, Wilcke W. (2010), Copper Isotope Fractionation during Complexation with Insolubilized Humic Acid. *Environmental science & Technology*, 44 (14), 5496–5502
- [29] Sing, K., Everett, D., Haul, R., Moscou, L., Pierotti, R., Rouquerol, J., Siemieniowska, T. (1985), Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl Chem*, 57(4), 603–619.
- [30] Bambrough, C., Slade, R., Williams, R. (1998), Synthesis of a large pore phenyl-modified mesoporous silica and its characterization by nitrogen and benzene sorption. *J Materials Chem*, 8(3), 569–571.
- [31] Kara M, Yu zer H, Sabah E, Celik M. (2003), Adsorption of cobalt from aqueous solutions onto sepiolite. *Water Res*, 37(1), 224–232.