Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

p-ISSN: 0972-6268
e-ISSN: 2395-3454

Vol. 16 No. 2 pp. 639-642 2017

Original Research Paper **Open Access**

Kinetic and Thermodynamic Studies on the Adsorption of Zinc Ions from Aqueous Solution by the Blast Furnace Slag

Muqing Qiu*† and Pu Huang**
*College of Life Science, Shaoxing University, Shaoxing, 312000, P.R. China
**Environmental Protection Agency of Dinghai District Zhoushan, Zhoushan, 312000, P.R. China
†Corresponding author: Muqing Qiu

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 03-04-2016
Accepted: 24-05-2016

Key Words:
Kinetic studies
Adsoption
Zinc
Blast furnace slag

ABSTRACT

In this work, the adsorption ability of the blast furnace slag to adsorb Zn^{2+} ions in aqueous solution was investigated. The experimental results are discussed in detail. The adsorption kinetic studies showed that the adsorption of Zn^{2+} ion from aqueous solution by the blast furnace slag better fits to pseudo second order kinetic model. It implies that the predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent. The adsorption isotherm studies showed that Langmuir adsorption isotherm model was more suitable for the Zn^{2+} ion from aqueous solution than the Freundlich adsorption isotherm model. It was also suggested that the adsorption process was homogeneous adsorption. The thermodynamic parameters of ΔG^0, ΔH^0 and ΔS^0 are -0.04 kJ/mol, 51.35 kJ/mol and 165.42 $J \cdot mol^{-1} \cdot K^{-1}$ respectively. It implied that the adsorption process is an endothermic reaction and chemical adsorption process.

INTRODUCTION

The presence of metal ions in municipal or industrial wastewater and their potential impact has been a subject of scientific environmental research for a long time, because of their extreme toxicity even at low concentrations and their tendency to accumulate in the food chain (Stankovic et al. 2009). It is known that the industrial effluent is discharged into environment directly or indirectly, such as metallurgical, electrical and electronics, mining and smelting, metal plating industry, resulting in extensive damage to the ecosystem (Sprynskyy et al. 2006, Ugurlu et al. 2009). Zinc ion is essential in small quantity, but when exceeds the prescribed limit it has also a detrimental effect on human health. The World Health Organization has set a provisional limit of 5 mg/L for zinc ion in aqueous solution (Mishra & Patel 2009).

Therefore, there is an urgency to remove those toxic heavy metals from wastewater. Although heavy metal removal from aqueous solutions can be achieved by conventional methods, including chemical precipitation, oxidation, reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange and membrane technologies (Dabrovski et al. 2004, Veres et al. 2012, Zhong et al. 2012), they may be ineffective or cost expensive, especially when the metal ion concentrations in solution are in the range of 1 mg/L to 100 mg/L (Wu et al. 2011). Scientists have begun to make their further researches with the unique aim of getting more economically viable and more environmentally sustainable technology that could provide the lowest level of heavy metal ions in a treated effluent that will be low enough to be safely discharged in a surface water stream (Anirudhan & Sreekumari 2011, Krishnan et al. 2011, Gao et al. 2013). The adsorption method is preferred for the removal of heavy metals from wastewater because of its lower cost and high efficiency. In nature, there are so many materials which possess the properties of ion exchange and adsorption (Sreejalekshmi et al. 2009, Bouhanmed et al. 2012). Some materials are already in use even for commercial purposes. Some of the examples are zeolite, apatite, bentonite, etc. Similarly, many waste materials like fly ash, red mud and blast furnace slag are also used to remove the heavy metals from wastewater (Foo & Hameed 2010, Hansen et al. 2010).

The aim of the researches has been to determine the adsorption ability of the blast furnace slag to adsorb the zinc ions in aqueous solution. The adsorption kinetics and the equilibrium are also discussed in detail.

MATERIALS AND METHODS

Materials: The blast furnace slag was obtained from a power plant in Zhejiang Province. It was washed with water, then dried at 105°C for 12 h and sieved into 100 mesh for adsorption experiments.

Adsorption experiments: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing the blast furnace slag and 100 mL of zinc ions with initial concentrations in aqueous solution. The pH in solution was adjusted by (1+1) HCl and 10% NaOH. The flasks were placed in a shaker at a constant temperature and 160 rpm. The samples were then filtered and the residual concentration of zinc ion was analysed.

Analytical methods: The value of pH was measured by using a digital pH meter according to APHA standard method. The zinc ion concentration in aqueous solution was measured by using the atomic absorption spectrophotometer. The adsorption capacity of zinc ion was calculated by using the mass balance equation for the adsorbent:

$$Q_t = \frac{(C_0 - C_t)\times V}{m} \qquad ...(1)$$

Where, Q_t (mmol/g) is the amount of zinc ions uptake per unit mass of the adsorbent, *m* (g) is the dry mass of the adsorbent, *V* (L) is the volume of the test solution, C_0 (mmol/L) and C_t (mmol/L) represent the initial and final concentration of zinc ions.

Statistical analyses of data: All experiments were repeated in duplicate and the data of results were the mean and the standard deviation (SD). The value of the SD was calculated by the Excel software. All error estimates given in the text and error bars in figures are standard deviation of means (mean±SD). All statistical significance was noted at $\alpha=0.05$ unless otherwise noted.

RESULTS AND DISCUSSION

Adsorption kinetics: Kinetic studies are necessary to optimize different operating conditions for the absorption. To investigate the possible mechanisms that control the adsorption process and potential rate controlling steps, the pseudo first order and pseudo second order models were used to interpret the experimental data.

The pseudo first order kinetic model has been widely used to predict the sorption kinetics. The equation of the model was represented as follows (Bouhanmed et al. 2012):

$$\ln(q_e - q_t) = \ln q_e - K_1 t \qquad ...(2)$$

Where q_e (mg/g) and q_t (mg/g) are the amounts of the heavy metal Zn^{2+} ion adsorbed on the modified montmorillonite at equilibrium and at any time, *t* (min), respectively. K_1 (min^{-1}) is the pseudo first order adsorption rate constant. The plots of $\ln(q_e - q_t)$ versus *t* give the K_1 and q_e values.

The pseudo second order equation expressed is by:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad ...(3)$$

Where, K_2 ($g\cdot mg^{-1}\cdot min^{-1}$) is the adsorption rate constant of pseudo second order model. The constant K_2 and q_e can be obtained from a linear regression plot of (t/q_t) versus *t*.

In order to investigate kinetic studies, the following tests were carried out. The adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 1.5 g of the blast furnace slag and 100 mL of 100 mg/L zinc ions in aqueous solution. The flasks were placed in a shaker at a constant temperature of 308 K and 160 rpm. The samples were then filtered and the residual concentration of zinc ion was analysed. The effect of contact time on the adsorption capacity of zinc ions in aqueous solution by the blast furnace slag is shown in Fig. 1.

As shown from Fig. 1, the adsorption capacity of Zn^{2+} ions increased when the contact time increased at first stage. When the contact time reached 100 min, the adsorption capacity of Zn^{2+} ions reached to the equilibrium process slowly. This may be due to the fact that initially the adsorbent sites were vacant and the solute concentration gradient was high. Later, the Zn^{2+} ion uptake rate by adsorbent was decreased significantly, due to the decrease in number of adsorption sites as well as Zn^{2+} ion concentration.

According to the data of Fig. 1, the kinetic parameters can be calculated by the equation (2) and equation (3). The kinetic parameters are listed in Table 1.

From Table 1, it can be confirmed that the adsorption of Zn^{2+} ion from aqueous solution by the blast furnace slag better fits to pseudo second order kinetic model. It implies

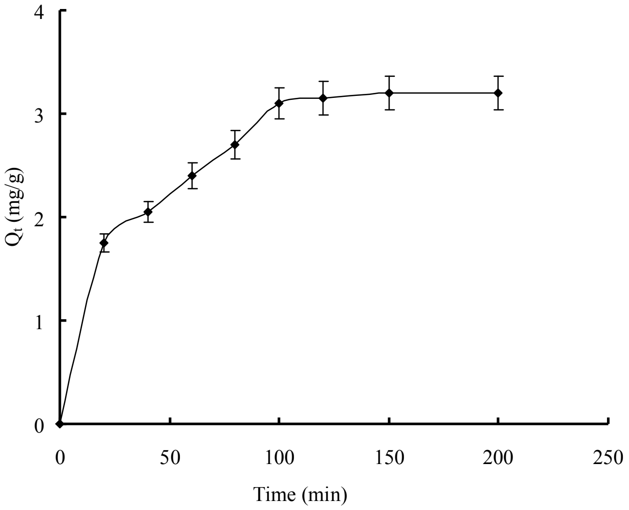

Fig. 1: The effect of contact time on the adsorption capacity of Zn^{2+} in aqueous solution by the blast furnace slag.

Table 1: The kinetic parameters for the adsorption of Zn^{2+} onto the blast furnace slag.

Pseudo first order		Pseudo second order	
k_1 (min^{-1})	R^2	k_2 ($g \cdot mg^{-1} \cdot min^{-1}$)	R^2
0.025	0.912	0.01	0.998

that the predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent.

Adsorption isotherms: To examine the relationship between adsorbent and adsorbate at equilibrium, and to search for the maximum sorption capacity of adsorbent, two adsorption isotherm models including Langmuir and Freundlich were applied. The Langmuir model and Freundlich model of linear forms (Liu & Zhang 2011) are :

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad ...(4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad ...(5)$$

Where, C_e (mg/L) is the equilibrium concentration in the solution, q_e (mg/g) is the adsorbate adsorbed at equilibrium, q_{max} (mg/g) is the maximum adsorption capacity, n is the Freundlich constant related to adsorption intensity, K_L (L/mg) and K_F ($(mg/g)^{1/n}$) are the adsorption constants for Langmuir and Freundlich models respectively.

Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 1.5 g of the blast furnace slag and 100 mL of zinc ions with initial concentrations (50, 100, 150 mg/L) in aqueous solution. The flasks were placed in a shaker at a constant temperature of 308 K and 160 rpm. According to the experimental data, the adsorption parameters were obtained from the Langmuir adsorption isotherm and Freundlich adsorption isotherm. They are listed in Table 2.

It was shown that the Langmuir adsorption isotherm model was more suitable for the Zn^{2+} ion from aqueous solution than the Freundlich adsorption isotherm model. It was also suggested that the adsorption process was homogeneous adsorption. The Zn^{2+} ion from aqueous solution adsorption on the blast furnace slag was monolayer adsorption.

Effect of temperature and thermodynamic parameters: The thermodynamic parameters of free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were used to describe thermodynamic behaviour of the adsorption of bromate ions onto the modified activated carbon. These parameters were calculated from the following equations (Duan et al. 2012).

$$\Delta G^0 = -RT \ln K_a \quad ...(6)$$

$$\ln K_a = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad ...(7)$$

$$K_a = \frac{q_e}{C_e} \quad ...(8)$$

Where, T is the solution temperature (K), K_a is the adsorption equilibrium constant, R is the gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$), q_e is the amount of adsorbate adsorbed per unit mass of adsorbate at equilibrium (mg/g) and C_e is the equilibrium concentration of the adsorbate (mg/L).

Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 1.5 g of the blast furnace slag and 100 mL of zinc ions with initial concentrations (100 mg/L) in aqueous solution. The flasks were placed in a shaker at a constant temperature (298 K, 308 K and 318 K) and 160 rpm. The contact time was 100 min. According to the experimental data, the thermodynamic parameters of ΔG^0, ΔH^0 and ΔS^0 can be calculated by the equation (6), (7) and (8). The thermodynamic parameters are listed in Table 3.

As seen from Table 3, it can be concluded that the value of ΔG^0 increased when the temperature increased. It also can be concluded that temperature would be beneficial to adsorb the Zn^{2+} ion in aqueous solution. The positive value of ΔH^0 suggested that the adsorption process of Zn^{2+} ions in aqueous solution by the blast furnace slag was endothermic reaction. The high temperature will be beneficial to improve the capacity ability of Zn^{2+} ion in aqueous solution. The adsorption process is also a chemical adsorption process according to the value of ΔS^0.

CONCLUSIONS

In this work, the adsorption ability of the blast furnace slag to adsorb the Zn^{2+} ions in aqueous solution was investigated. The adsorption kinetic studies showed that the adsorption of Zn^{2+} ion from aqueous solution by the blast furnace slag better fits to pseudo second order kinetic model. It implies that the predominant process is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent. The adsorption isotherm studies showed that Langmuir adsorption isotherm model was more suitable for the Zn^{2+} ion from aqueous solution than the Freundlich adsorption isotherm model. It was also suggested that the adsorption process was homogeneous adsorption. The thermodynamic parameters of ΔG^0, ΔH^0 and ΔS^0 are -0.04 kJ/mol, 51.35 kJ/mol and 165.42 $J \cdot mol^{-1} \cdot K^{-1}$ respectively. It implied that the adsorption process is endothermic reaction and chemical adsorption process.

Table 2: The adsorption parameters for Zn^{2+} ion from aqueous solution adsorption on the blast furnace slag by Langmuir adsorption isotherm and Freundlich isotherm.

Langmuir parameters			Freundlich parameters		
q_{max} (mg/g)	K_L (L/mg)	R^2	n	K_F	R^2
6.02	0.14	0.9867	3.56	1.59	0.9621

Table 3: The thermodynamic parameters for adsorption of Zn^{2+} ions on the blast furnace slag.

T(K)	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J·mol^{-1}·K^{-1})
298	2.45		
308	0.05		
318	-0.04	51.35	165.42

ACKNOWLEDGEMENTS

This study was financially supported by the project of science and technology plan in Shaoxing City (2013B70058). It was financially supported by the project of the education department in Zhejiang Province (Y201534144).

REFERENCES

Anirudhan, T.S. and Sreekumari, S.S. 2011. Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons. J. Environ. Sci., 23: 1989-1998.

Bouhanmed, F., Elouear, E. and Bouzid, J. 2012. Adsorptive removal of copper (II) from aqueous solutions on activated carbon prepared from Tunisian date stones: Equilibrium, kinetics and thermodynamics. J. Taiwan Inst. Chem. Eng., 43: 741-749.

Dabrovski, A., Habicki, Z., Podskocienly, P. and Robens, E. 2004. Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. Chemosphere, 56: 91-106.

Duan, X.H., Srinivasakannan, C., Qu, W.W., Wang, X., Peng, J.H. and Zhang, L.B. 2012. Regeneration of microwave assisted spent activated carbon: process optimization, adsorption isotherms and kinetics. Chem. Eng. Process., 53: 53-62.

Foo, K.Y. and Hameed, B.H. 2010. Insights into the modeling of adsorption isotherm systems. Chem. Eng. J., 156: 2-10.

Gao, Y., Yue, Q.Y., Gao, B.Y., Sun, Y.Y., Wang, W.Y., Li, Q. and Wang, Y. 2013. Preparation of high surface area-activated carbon from lignin of papermaking black liquor by KOH activation for Ni(II) adsorption. Chem. Eng. J., 217: 345-353.

Hansen, H.K., Arancibia, F. and Gutiérrez, C. 2010. Adsorption of copper onto agriculture waste materials. J. Hazard. Mater., 180: 442-448.

Krishnan, K.A., Sreejalekshmi, K.G. and Baiju, R.S. 2011. Nickel(II) adsorption onto biomass based activated carbon obtained from sugarcane bagasse pith. Bioresour. Technol., 102: 10239-10247.

Liu, Z.G. and Zhang, F.S. 2011. Removal of copper(II) and phenol from aqueous solution using porous carbons derived from hydrothermal chars. Desalination, 267: 101-106.

Mishra, P.C. and Patel, R.K. 2009. Removal of lead and zinc ions from water by low cost adsorbents. J. Hazard. Mater., 168: 319-325.

Sprynskyy, M., Buszewski, B., Terzyk, A.P. and Namiesnik, J. 2006. Study of the selection mechanism of heavy metal (Pb^{2+}, Cu^{2+}, Ni^{2+} and Cd^{2+}) adsorption on clinoptilolite. J. Collodi Interface Sci., 304: 21-28.

Sreejalekshmi, K.G., Anoop, K.K. and Anirudhan, T.S. 2009. Adsorption of Pb(II) and Pb(II) citric acid on sawdust activated carbon: kinetic and equilibrium isotherm studies. J. Hazard. Mater., 161: 1506-1517.

Stankovic, V., Božic, D., Gorgievski, M. and Bogdanovic, G. 2009. Heavy metal ions adsorption from mine waters by sawdust. Chem. Ind. Chem. Eng. Q., 15: 237-249.

Ugurlu, M., Kula, I., Karaoglu, M.H. and Arslan, Y. 2009. Removal of Ni(II) ions from aqueous solution using activated carbon prepared from olive stone by $ZnCl_2$ activtion. Environ. Prog. Energy, 28: 547-557.

Vereš, J., Lovás, M., Jakabský, S., Šepelák, V. and Hredzák, S. 2012. Characterization of blast furnace sludge and removal of zinc by microwave assisted extraction. Hudrometallurgy, 129-130: 67-73.

Wu, P.X., Zhang, Q., Dai, Y.P., Zhu, N.W., Dang, Z., Li, P., Wu, J.H. and Wang, X.D. 2011. Adsorption of Cu(II), Cd(II) and Cr(II) ions from aqueous solutions on humic acid modified ca-montmorillonite. Geoderma, 164: 215-219.

Zhong, Z.Y., Yang, Q., Li, X.M., Luo, K., Liu, Y. and Zeng, G.M. 2012. Preparation of peanut hull-based activated carbon by microwave-induced phosphoric acid activation and its application in Remazol Brilliant Blue R adsorption. Ind. Crops Prod., 37: 178-185.