Nature Environment and Pollution Technology
An International Quarterly Scientific Journal

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

Vol. 16 | No. 3 | pp. 867-871 | 2017

Original Research Paper | Open Access

The Adsorption Capacity and Influencing Factors of Cr^{3+} by the Modified Zeolite from Fly Ash

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

Received: 22-07-2016
Accepted: 24-08-2016

Key Words:
Adsorption
Cr^{3+} ion
Modified zeolite
Fly ash

ABSTRACT

In this study, the modified zeolite from fly ash was prepared and used as an adsorbent for removal of Cr^{3+} ion from aqueous solution. The characteristic of the modified zeolite was analysed. The adsorption capacity and influencing factors, such as contact time, pH in solution, the modified zeolite dosage, initial concentration of Cr^{3+} and temperature, were discussed in detail by the adsorption experiments. The experimental results showed that the modified zeolite from fly ash, own high adsorption capacity for Cr^{3+} ion in aqueous solution. The influencing factors had an important influence on the adsorption capacity. The removal efficiency of Cr^{3+} ion increased with the increase of the modified zeolite dosage. However, the removal efficiency of Cr^{3+} ion decreased with the increase of the initial concentration of Cr^{3+} ion in aqueous solution. The experimental results showed that the modified zeolite from fly ash has a strong potential ability for removal of Cr^{3+} ion in aqueous solution.

INTRODUCTION

The heavy metal Cr^{3+} ion in aqueous solution is one of the harmful metals for the environmental pollution. The trace concentration of Cr^{3+} ion is the necessary element for people (Anirudhan & Sreekumari 2011, Fu et al. 2016). However, the excessive Cr^{3+} ions in human body are harmful for the health, and lead to the carcinogenesis. It is urgent that Cr^{3+} ion is treated effectively (Sugashini & Begum 2015). The heavy metal wastewater often comes from the industries such as metallurgy, chemical, electroplating and so on (AL-Othman et al. 2012, Liu et al. 2014, Gottipati & Mishra 2016). Every day, large quantity of heavy metal wastewater is discharged into the environment. The wastewater containing heavy metals is very difficult to be biodegraded (Liu et al. 2010, Zou et al. 2015). At present, treatment methods of wastewater containing heavy metals are often ion exchange, chemical reaction, precipitation, adsorption, etc. In recent years, a lot of literature about the treatment of Cr^{6+} ion in aqueous solution has been generated (Gueye et al. 2014, Yang et al. 2015). However, the researches about the treatment of Cr^{3+} ion in aqueous solution are few. Its reason may be that the toxicity of Cr^{6+} ion is higher than Cr^{3+} ion and the Cr^{3+} ion in environment is easy to be changed into Cr^{6+} ion (Ahmadi et al. 2015). The Cr^{3+} ion in aqueous solution is easy to be transferred into the phase of soil because of the high adsorption ability of Cr^{3+} ion by colloid matter. In order to prevent the pollution from the Cr^{3+} ion, it is essential to treat the Cr^{3+} ion in aqueous solution (Varga et al. 2013, Lima et al. 2014).

The fly ash is a kind of a solid waste from the coal power plant. The 1 tonne of the fly ash is obtained from consumption of around 4 tonnes of coal. Every year, the production capacity of the fly ash is increasing quickly. The production capacity of the fly ash was one hundred million t in 2011 in China. The production capacity of the fly ash reaches four hundred million tonnes in 2013 in China. The high quantity of fly ash may lead to the environmental pollution problems, such as air pollution, water pollution and soil pollution. So, the resource utilization of fly ash was studied by more and more researchers (Ozdemir et al. 2011). One of the methods, about the resource utilization of fly ash, is the synthesis of the modified zeolite from the fly ash. In recent years, many researches on the synthesis of the modified zeolite from the fly ash applied in the treatment of wastewater were reported (Liu et al. 2012, Sun et al. 2013). The adsorbent is a grid structure, two-dimensional passage, and it can adsorb many ions from aqueous solution, such as K^+, Na^+, Ca^{2+}, Mg^{2+}, and so on. So, they can be applied in the treatment of wastewater widely (Giri et al. 2012, Zhang et al. 2015).

In this work, the synthesis of the modified zeolite from the fly ash was carried out with the method of the melted NaOH. The obtained adsorbent was also analysed by chemical methods. Then, the adsorption capacity and influencing factors of Cr^{3+} in aqueous solution by the modified zeolite were studied in detail by the adsorption experiments.

MATERIALS AND METHODS

Materials: The fly ash was obtained from a power plant in Hebei province. The 18 g of fly ash was mixed with the 21.6 g of NaOH in the quartz crucibles. Then, the mixture of fly ash and NaOH was put into the muffle furnace at 873 K for 3h. The mixture was added into the 250 mL flask containing 7 mL of distilled water. The flask was put into the thermostat water bath and agitated for 2 h at 353 K. Then, it was dried for 9 h at 383 K in the heating oven and washed with the distilled water into pH range of 7 to 9. The mixture was dried for 5 h at 383 K in the heating oven again and then ground and sifted into 100 meshes for adsorption experiment.

The wastewater of Cr^{3+} ion was prepared with the $CrCl_3.6H_2O$.

Experimental methods: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing the modified zeolite and 100 mL of Cr^{3+} ion solutions with various initial concentrations. The initial pH was adjusted with 1 mol/L HCl or 1 mol/L NaOH. The flasks were placed in a shaker at a constant temperature and 200 rpm. The samples were filtered and analysed.

Analytical methods: The textural characteristics of the modified zeolite, including surface area, pore volume, and pore size distribution were determined using standard N_2-adsorption techniques. The concentration of Cr^{3+} ion was analysed by atomic absorption spectrophotometry (AAS).

The amount of adsorbed Cr^{3+} ion q_t (mg/g) at different times was calculated as follows:

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

Where C_0 and C_t (mg/L) are the initial and equilibrium liquid-phase concentrations of Cr^{3+} ion, respectively. V (L) is the solution volume and m (g) is the mass of adsorbent used.

Statistical analyses of data: All the 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 the standard deviation of the means (mean±SD). All statistical significance was noted at α=0.05, unless otherwise specified.

RESULTS AND DISCUSSION

Characterization of the modified zeolite: The chemical composition of the modified zeolite from the fly ash was analysed (Table 1).

The textural characteristics of the modified zeolite, including surface area, pore volume and pore size distribution were determined using standard N_2-adsorption techniques. The surface area of the modified zeolite is 7.938 m^2/g. The pore volume and pore size distribution were 0.0727 cm^3/g and 9.16 nm, respectively.

Effect of pH: The value of pH in solution is an important factor affecting the adsorption experiment. Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 5 g/L of the modified zeolite and 100 mL of 500 mg/L Cr^{3+} ion solutions. The initial pH was adjusted with 1 mol/L HCl or 1 mol/L NaOH. The flasks were placed in a shaker at 293K and 200 rpm. The contact time was 100 min. The effect of pH on the adsorption is shown in Fig. 1.

From Fig. 1, it can be seen that the removal efficiency of Cr^{3+} ion in solution reached 63.04% at pH 2.0. The removal efficiency of Cr^{3+} ion increased when the value of pH in solution increased. The removal efficiency increased slowly above pH 6.0 in solution. It may be the reason that a lot of H^+ ions in solution were formed at lower value of pH. These H^+ ions were compared with the Cr^{3+} ions in solution. So, the removal efficiency of Cr^{3+} ions was lower. When the value of pH was above 7.0, Cr^{3+} ions in solution are easy to be precipitated with the OH^- ions in solution. The removal efficiency of Cr^{3+} ions in solution was high above pH 7.0.

Effect of the modified zeolite dosage: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing the modified zeolite and 100 mL of Cr^{3+} ion solutions with 500 mg/L of initial concentrations. The initial pH was adjusted to 5.0 with 1 mol/L HCl. The flasks were placed in a shaker at 293K and 200 rpm. The contact time was 100 min. The effect of the modified zeolite dosage is shown in Fig. 2.

From Fig. 2, it can be seen that the removal efficiency of Cr^{3+} ion in solution increased quickly along with the increase of the modified zeolite dosage. The removal efficiency of Cr^{3+} ion in solution reached 64.58% at 5 g/L of the modified zeolite dosage. The removal efficiency of Cr^{3+}

Table 1: Chemical composition of the modified zeolite from the fly ash (wt).

Composition	SiO_2	Na_2O	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	MnO	TiO_2
Content (%)	32.45	24.32	11.63	12.16	16.07	0.36	0.62	0.48	0.93

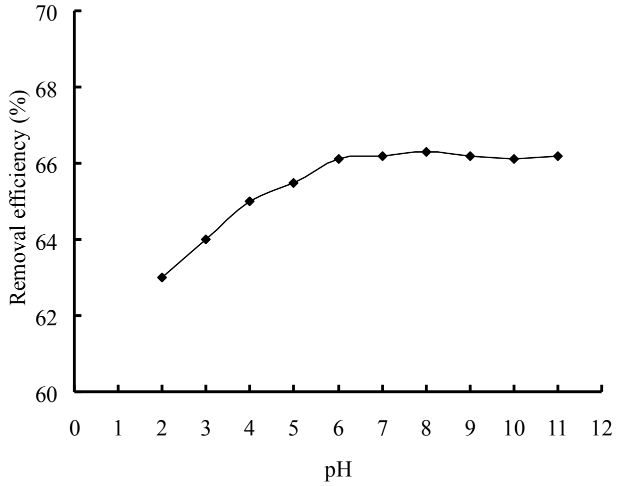

Fig. 1: Effect of pH on the Cr^{3+} ion in aqueous solution by the modified zeolite.

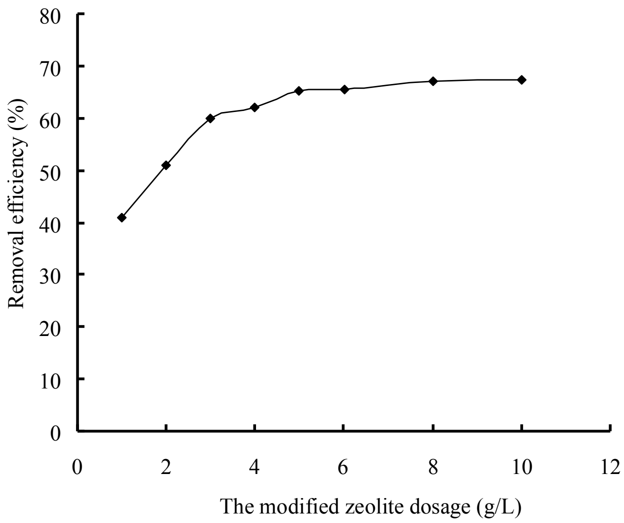

Fig. 2: The effect of the modified zeolite dosage on the adsorption process.

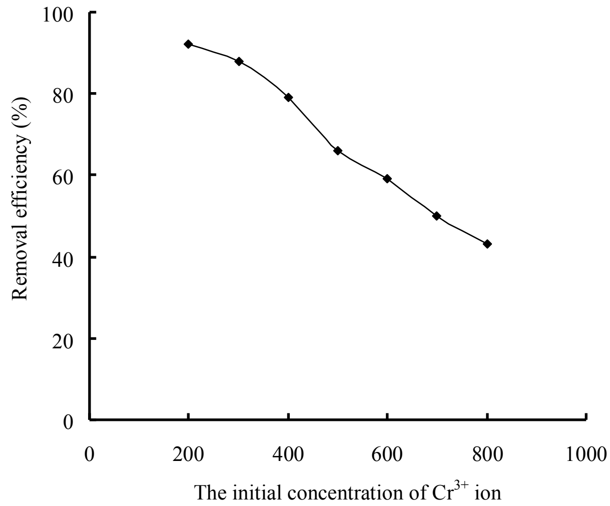

Fig. 3: The effect of the initial concentration of Cr^{3+} ion on the adsorption process.

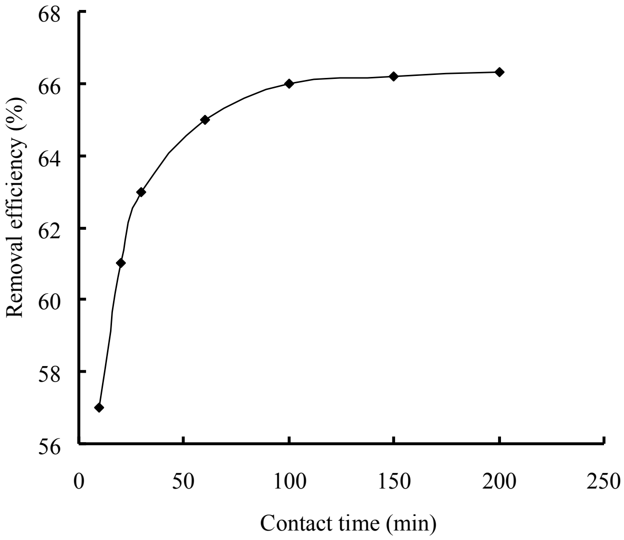

Fig. 4: The effect of contact time on the adsorption process.

ion in solution increased slowly above 5 g/L of the modified zeolite dosage.

Effect of the initial concentration of Cr^{3+} ion: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 5 g/L of the modified zeolite and 100 mL of Cr^{3+} ion solutions with various initial concentrations. The initial pH was adjusted to 5.0 with 1 mol/L HCl. The flasks were placed in a shaker at 293K and 200 rpm. The contact time was 100 min. The results of adsorption experiments are shown in Fig. 3.

From Fig. 3, it can be seen that the removal efficiency of Cr^{3+} ion decreased along with the increase of the initial concentration of Cr^{3+} ion. It may be the reason that the adsorption space of the modified zeolite from fly ash begun to decrease along with the increase of Cr^{3+} ion in aqueous solution.

Effect of contact time: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 5 g/L of the modified zeolite and 100 mL of 500 mg/L Cr^{3+} ion in solution. The initial pH was adjusted to 5.0 with 1 mol/L HCl. The flasks were placed in a shaker at 293K and 200 rpm. The effect of contact time on the adsorption process is shown in Fig. 4.

As shown from Fig. 4, it can be concluded that contact time is an important factor affecting the adsorption process of Cr^{3+} ion in aqueous solution by the modified zeolite from fly ash. When the contact time increased, the removal effi-

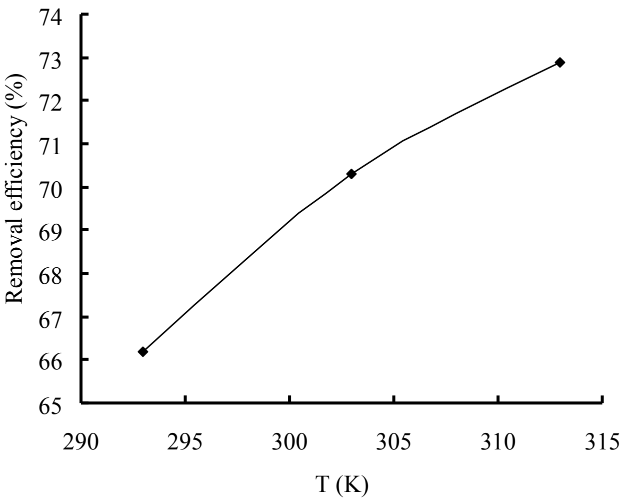

Fig. 5: The effect of reaction temperature on the adsorption process.

ciency increased quickly. The removal efficiency reached 65.86% at 60 min of contact time. The removal efficiency increased slowly above 60 min of contact time. It was also shown that the adsorption equilibrium would be reached at that time. The adsorption of Cr^{3+} ion in aqueous solution by the modified zeolite from fly ash begins to reach the saturation state.

Effect of temperature: Adsorption experiments were conducted in a set of 250 mL Erlenmeyer flasks containing 5 g/L of the modified zeolite and 100 mL of 500 mg/L Cr^{3+} ion in solution. The initial pH was adjusted to 5.0 with 1 mol/L HCl. The flasks were placed in a shaker at a constant temperature and 200 rpm. The contact time was 100 min.

The effect of temperature is shown in Fig. 5. It was found that the removal efficiency of Cr^{3+} ion in aqueous solution increased with increasing solution temperature from 293 K to 313 K. It also indicated that the adsorption process is an endothermic process. The enhancement in the adsorption capacity might be due to the chemical interaction between adsorbates and adsorbent, creation of some new adsorption sites or the increased rate of intraparticle diffusion of adsorbate molecules into the pores of the modified zeolite from fly ash at higher temperatures (Cho et al. 2011, Nethaji et al. 2013).

CONCLUSIONS

The synthesis of the modified zeolite from the fly ash was carried out with the method of the melted NaOH. The textural characteristics of the modified zeolite, including surface area, pore volume and pore size distribution were determined using standard N_2-adsorption techniques. Then, the adsorption capacity and influencing factors of Cr^{3+} in aqueous solution by the modified zeolite from fly ash were studied in details through the adsorption experiments. The experimental results showed that the modified zeolite from fly ash own high adsorption capacity of Cr^{3+} ion in aqueous solution. The influencing factors, such as contact time, pH in solution, the modified zeolite dosage, initial concentration of Cr^{3+} and solution temperature, had an important influence on the adsorption capacity.

ACKNOWLEDGEMENT

This study was financially supported by the project of science and technology plan in Shaoxing City (2013B70058).

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