

Competitive Adsorption of Heavy Metals Copper, Cadmium and Lead by Synthetic Zeolite

Xiao ZHANG
Jiangsu City Vocational College
Nanjing 210036, China

Ting CHENG
Jiangsu City Vocational College
Nanjing 210036, China
e-mail: wnchengting@sina.com

Chen CHEN*
School of Environmental and Chemical Engineering
Jiangsu University of Science and Technology
Zhenjiang 212003, China
e-mail: chenc@just.edu.cn

Abstract—The experiments are to study the competitive adsorption properties of three heavy metals of Cu^{2+} , Cd^{2+} and Pb^{2+} ions through synthesizing zeolite. The influencing factors and competitive adsorption kinetic modes are investigated. The results show that, with the increase of adsorbed dose, the removal rate of zeolite on the adsorption of three heavy metals all rise constantly, and the saturated adsorption capacity all drops gradually. When the value of initial concentration are 50 and 100 mg/L, the competitive adsorption sequence of zeolite on three heavy metal ions is: $\text{Pb} > \text{Cu} > \text{Cd}$. The removal rate of zeolite on the adsorption of three heavy metal ions all increases with the rise of the value of initial pH on the whole. During the competitive adsorption process, at various value of initial pH and concentration, the adsorption sequence of zeolite on three heavy metals remains still: $\text{Pb} > \text{Cu} > \text{Cd}$. The reaction time has an apparent effect on the removal rate of three heavy metals ions. The removal rate of zeolite increases gradually with the increase of reaction time, and the adsorption removal rate improves quickly within 2 hours. The value of equilibrium adsorption capacity of quasi second-class kinetic equation Q_{exp} is closer to the value of equilibrium adsorption capacity Q_{cal} according to experimental measurement. The adsorption behavior of synthetic zeolite materials on the adsorption of three heavy metal ions all fits for quasi second-class adsorption kinetic equation.

Keywords—Heavy metal, Copper, Cadmium, Lead, Fly ash, zeolite, Competitive adsorption

I. INTRODUCTION

With the rapid development of mining, smelting, chemical engineering, electroplating, electronics, leather and so on, the accidental emissions of heavy metal pollutions and the usage of too much fertilizer and pesticide make different kinds of heavy metal pollutions poured into the water [1-3]. The Lead pollution can not only affect human health, but also the growth of children's intelligence [1]. Cadmium is an extremely poisonous oxide and will accumulate in plants, animals and the inner side of human body. Besides, it is harmful to the health of plants and animals and human beings [4]. The heavy metal such as lead and cadmium and

its compounds have been listed as priority-control pollutants by the State Environmental Protection Administration of China. If the skin is exposed to the compounds of heavy metal copper, the skin would necrosis at high concentration. The treatment of heavy metal pollution in the water has become one of the problems widely concerned at home and abroad [5-7].

The treatments of heavy metal wastewater can be divided into two classes: one kind is to transform the resolvable heavy metal into the metal compounds that are unable or hard to dissolve so that it can be removed from the water, such as oxidation reduction, chemical precipitation, etc. The other one is conducting concentration and separation under the circumstance that the chemical form of heavy metals remain still, such as adsorption, reverse osmosis, ion exchange and so on. There are some other treatment methods such as air flotation, membrane separation and solution extraction and so on. In recent years, the research of the treatment of heavy metal wastewater by using new adsorbent has been widely focused, depending on the adsorption effect of active surface of adsorbent on heavy metal ions [3-5]. The essence of adsorption is the choice of adsorbents. There is too much research, which is the adsorption treatment on heavy metal wastewater by adsorbent and the research exploitation of economic, effective and easily-accessible adsorption materials has been hot spot.

Fly ash is one kind of clay-like volcanic material emitted from coal combustion. Fly ash contains porous vitreous body and carbon particle and honeycomb structure with large specific surface area. Besides, it contains active groups and extremely active adsorption properties. In recent years, the research of the removal of heavy metal in the water by using fly ash as adsorbent has been widely concerned [8,9]. Some industrial wastewater that contains toxic substances and industrial wastewater such as Cr^{3+} , Hg^{2+} , Pb^{2+} , F^- and phenols can be handled by fly ash. However, the adsorption effect in original state is not very satisfying.

Currently, the research about using fly ash to realize the synthesis of zeolite or some other adsorbent combinations to improve the adsorption ability of fly ash has broader

prospects[3,10]. There are a lot of equal holes and channels in the inner side of zeolite crystal, which make the zeolite a high specific surface area. The research indicates that the materials synthesized by using fly ash have excellent ability to remove the heavy metal ions in the water. However, currently, the majority of the research concentrates on adsorption properties of single heavy metal ions. But the research on the competitive adsorption of multiple heavy metal ions is not comprehensive enough.

This research uses fly ash as the basic material to realize the synthesis of zeolite adsorbent and studies its competitive adsorption effect on Pb^{2+} , Cd^{2+} , Cu^{2+} and adsorption mechanism. Study the adsorbed dose, the value of pH and the reaction time on the competitive adsorption of zeolite material about three heavy metals; then study the kinetic model of competitive adsorption of zeolite materials on Pb^{2+} , Cd^{2+} , Cu^{2+} on such basis. We look forward to obtaining highly effective heavy metal adsorption materials. In the meantime, we use wastes to deal with the wastes and turn the wastes into valuable substances so that we can provide technical references for the treatment technology of heavy metal wastewater.

II. EXPERIMENTAL

The experimental synthetic zeolite materials use fly ash as the raw material, the main chemical components of samples are: the mass fraction of silicon dioxide, lead dioxide, iron sesquioxide, calcium oxide, titanium oxide and magnesium oxide are 50.01%, 33.45%, 4.71%, 2.87%, 1.09% and 0.87% respectively. The Cu^{2+} aqueous solution, the Cd^{2+} aqueous solution and the Pb^{2+} aqueous solution is prepared through dissolving $Cu(NO_3)_2 \cdot 3H_2O$, $Cd(NO_3)_2$ and $Pb(NO_3)_2$ in DI water, respectively. All chemicals used in our experiment are analytical reagent and bought from China National Pharmaceutical Group Corporation.

The preparation for zeolite materials. The preparation process of zeolite materials is: put fly ash that weighs 2 gram into potassium Sodium hydroxide solution whose volume is 50ml and concentration is 8mol/L, keep reacting for 48 hours under the condition of 95°C. After finishing it, use deionized water to wash the obtained materials until it is neutral and dry it to the constant weight in the bake oven whose temperature is 105°C. After the synthetic reaction is done, the samples are identified by XRD and SEM, which makes sure that it is zeolite material.

The batch studies are conducted by mixing zeolite with Cu^{2+} , Cd^{2+} and Pb^{2+} metallic solutions prepared in the laboratory. The zeolite is mixed with heavy metal ions in 10 ml polypropylene tubes. The pH of solution is adjusted by 0.01mol/L NaOH and 0.01mol/L HNO_3 solutions. The tubes with mixtures are fixed in a water bath shaking box and shaken at 120rpm. The mixture is filtered through 0.45µm membrane filter using a vacuum pump after adsorption reaction. The filtrate is analyzed subsequently for heavy metal ions of Cu^{2+} , Cd^{2+} and Pb^{2+} content using AA240DUO atomic adsorption spectrophotometry (Agilent Technologies, Inc. USA). The pH of solution is determined by a PHS-3C pH

III. RESULTS AND DISCUSSION

A. Effect of Adsorbed Dose of Zeolite on Adsorption of Copper, Cadmium and Lead.

The effects of removal rate of adsorbed dose on the competitive adsorption of Pb^{2+} , Cd^{2+} , Cu^{2+} are shown in Fig.1 when the value of initial concentration of mixed heavy metals is 50mg/L. The initial value of pH is 6, the value of reaction time is 14 hours.

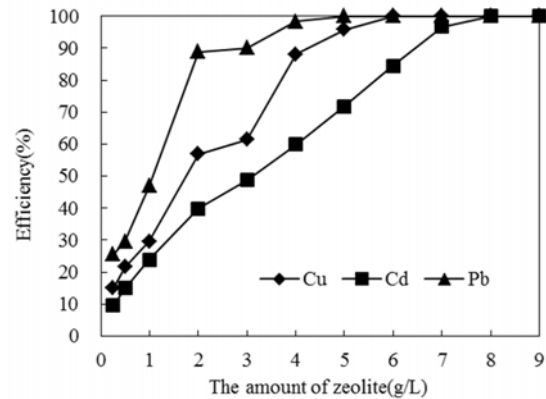


Figure 1. Influence of the amount of zeolite on heavy metal removal rate (the initial metal ions concentration 50 mg L⁻¹, contact time 14 h, pH value 6.0, temperature 35°C).

From the Fig. 1 we can know that adsorbed dose has a significant effect on the removal rate of zeolite on the adsorption of Pb^{2+} , Cd^{2+} , Cu^{2+} when the value of initial concentration is 50mg/L. When the value of adsorbed dose is 0.25~1g/L, the adsorption removal rate of zeolite on Pb^{2+} , Cd^{2+} , Cu^{2+} all have improved to some degree. The adsorption removal rate of zeolite on Cd^{2+} improves from 9.54% to 23.90%. The adsorption removal rate of Cu^{2+} improves from 14.91% to 29.53% and the adsorption removal rate of Pb^{2+} improves from 25.56% to 46.98%. When the value of adsorbed dose is larger than 2g/L, the adsorption removal rate of zeolite on Pb^{2+} , Cd^{2+} , Cu^{2+} all improve significantly. When the value of adsorbed dose is 2~7g/L, the removal rate on Cd^{2+} improves from 39.92% to 96.66%, the adsorption tends to be saturated after keeping raising adsorbed dose. When the value of adsorbed dose is 2~5g/L, the removal rate on Cu^{2+} improves from 56.90% to 96.01%. When the value of adsorbed dose is 2~4g/L, the removal rate on Pb^{2+} improves from 88.89% to 98.25%. When the value of adsorbed dose is larger than 7g/L, the rise of adsorbed dose has nothing to do with removal rate, the adsorption system tends to be saturated. We can also see from Fig. 1 that, during the whole adsorption process, competitive adsorption sequence of zeolite on Pb^{2+} , Cd^{2+} , Cu^{2+} is: $Pb > Cu > Cd$. When the heavy metal ions exist together, the adsorption removal rate of zeolite on Pb^{2+} behaves best. Cu^{2+} subsequently, and the removal rate of Cd^{2+} is worst.

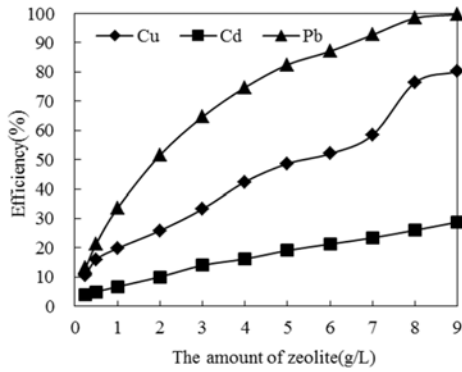


Figure 2. Influence of the amount of zeolite on heavy metal removal rate (initial metal ions concentration 100 mg L^{-1} , contact time 14 h, pH value 6.0, temperature 35°C).

B. The Effects of Saturated Adsorption Capacity of Adsorbed Dose of Zeolite on Adsorption of Heavy Metal

When the value of initial concentration is 100 mg/L , the effects of adsorbed dose of competitive adsorption removal rate of zeolite on Pb^{2+} , Cd^{2+} , Cu^{2+} are shown in picture 2. The adsorbed dose has a significant effect on the removal rate of zeolite on the adsorption of these three heavy metal ions. With the rise of adsorbed dose, the removal rate of zeolite on three heavy metal ions raises constantly, and competitive adsorption sequence of zeolite on the heavy metal ions remains still. When the value of adsorbed dose is $0.25\sim 1 \text{ g/L}$, the adsorption removal rate of zeolite on three heavy metal ions all rise to some degree. The removal rate on Cd^{2+} improves from 3.98% to 6.69%, the removal rate on Cu^{2+} improves from 10.58% to 19.82%, the removal rate on Pb^{2+} improves from 13.10% to 33.49%. When the value of adsorbed dose is $2\sim 9 \text{ g/L}$, the removal rate of zeolite on three heavy metals rises to various degree. The removal rate on Cd^{2+} improves from 10.07% to 28.81%, the removal rate on Cu^{2+} improves from 25.88% to 80.15%, the removal rate on Pb^{2+} improves from 51.51% to 99.68%.

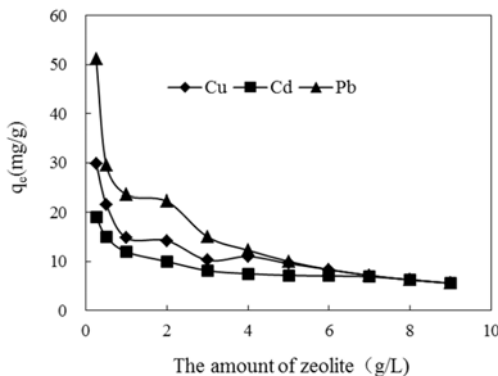


Figure 3. Effect of the amount of zeolite on q_e (heavy metal saturated extent of adsorption) (initial metal ions concentration 50 mg L^{-1} , contact time 14 h, pH value 6.0, temperature 35°C).

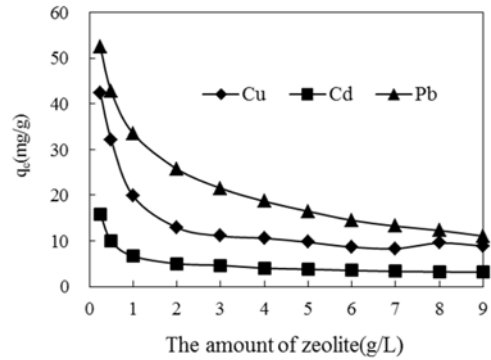


Figure 4. Effect of the amount of zeolite on q_e (heavy metal saturated extent of adsorption) (initial metal ions concentration 100 mg L^{-1} , contact time 14 h, pH value 6.0, temperature 35°C).

The effects of adsorbed dose of saturated adsorption capacity of zeolite on adsorption of Pb^{2+} , Cd^{2+} , Cu^{2+} are shown in picture 3 and picture 4. With the rise of adsorbed dose, the saturated adsorption capacity on three heavy metal ions keeps getting down, which is that the adsorption capacity of mass fraction adsorbent on the heavy metal ions drops constantly. When the value of adsorbed dose is $0.25\sim 1 \text{ g/L}$, the saturated adsorption capacity drops a lot with the rise of adsorbed dose when the value of initial concentration are 50 and 100 mg/L . The adsorption capacity of zeolite on Cd^{2+} drops from 19.08 mg/g to 11.95 mg/g when the value of initial concentration is 50 mg/L and the value of adsorbed dose is $0.25\sim 1 \text{ g/L}$, the adsorption capacity of zeolite on Cu^{2+} drops from 29.82 mg/g to 14.77 mg/g , the adsorption capacity of zeolite on Pb^{2+} drops from 51.11 mg/g to 23.49 mg/g . The adsorption capacity of zeolite on Cd^{2+} drops from 15.90 mg/g to 6.69 mg/g when the value of initial concentration is 100 mg/L and the value of adsorbed dose is $0.25\sim 1 \text{ g/L}$, the adsorption capacity of zeolite on Cu^{2+} drops from 42.34 mg/g to 19.82 mg/g , the adsorption capacity of zeolite on Pb^{2+} drops from 52.38 mg/g to 33.49 mg/g . The saturated adsorption capacity of zeolite on three heavy metal ions continues to decrease when the value of adsorbed dose continues to raise. After raising the value of adsorbed dose, the contact area between zeolite and mixed heavy metals in the water increases subsequently so that the utilization ratio of adsorbent reduces as a result.

C. The Effects of the Value of Initial pH of Zeolite on Adsorption of Copper, Cadmium and Lead

The effects of the removal rate of the value of initial pH about the zeolite on the adsorption of heavy metal ions are shown in Fig. 5 when the value of the concentration of heavy metal is 50 mg/L . The value of the adsorbed dose is 4 g/L , the value of reaction time is 14 hours. As is seen in Fig. 5, the value of pH has a significant effect on the removal effect of zeolite on the adsorption of three heavy metal ions. With the rise of the value of pH, the removal rate of three heavy metal ions all tend to increase. The competitive adsorption sequence of the zeolite on the heavy metal ions is:

Pb>Cu>Cd. When the value of pH is 2, the removal rate of zeolite on Cd²⁺ is 64.43%; when the value of pH rises to 4, the removal rate of zeolite on Cd²⁺ is 89.32%. When the value of pH is 6, the removal rate of zeolite on Cd²⁺ is 97%, then the process tends to be saturated. When the value of pH is 2~4, the removal rate of zeolite on Cu²⁺ rises from 77.88% to 97.20%. When the value of pH is 2, the adsorption removal rate of zeolite on Pb²⁺ arrives at 96.58%. All the evidence indicates that the removal effect of zeolite on Pb²⁺ is satisfying when three heavy metal ions exist together even if under the acid environment. Besides, it is better than the adsorption removal rate of Cu²⁺ and Cd²⁺.

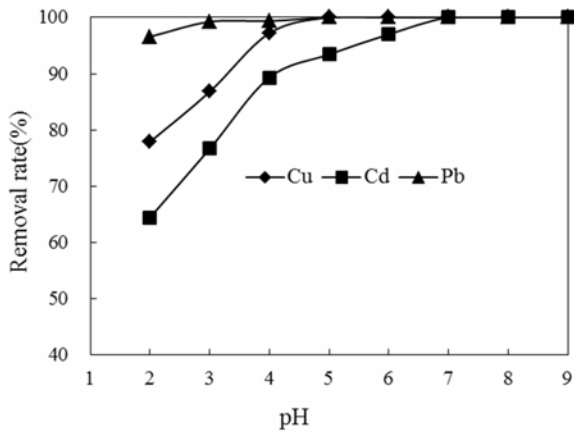


Figure 5. Effect of pH value on heavy metal efficiency (initial metal ions concentration 50 mg L⁻¹, the value of the adsorbed dose is 4 g L⁻¹, contact time 14 h, temperature 35°C).

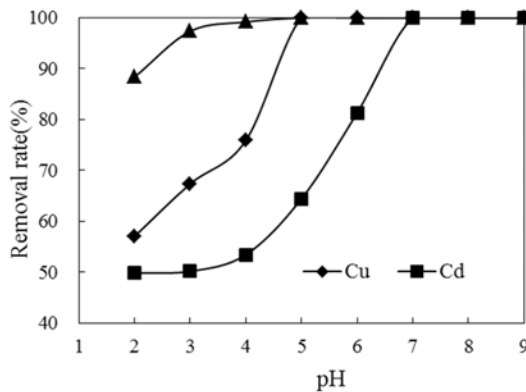


Figure 6. Effect of pH value on heavy metal efficiency (initial metal ions concentration 100 mg L⁻¹, the value of the adsorbed dose is 4 g L⁻¹, contact time 14 h, temperature 35°C).

When the value of concentration of mixed ions is 100mg/L, the effects of the removal rate of the value of initial pH of zeolite on the adsorption of Pb²⁺, Cd²⁺, Cu²⁺ are shown in picture 6. The value of adsorbed dose is 8g/L, the value of reaction time is 14 hours. The removal rate of zeolite on the adsorption of Pb²⁺, Cd²⁺, Cu²⁺ rises with the improvement of the value of initial pH on the whole. The

adsorption sequence of zeolite on three heavy metal ions remains still when the value of pH differs: Pb>Cu>Cd. When three heavy metal ions exist together, the removal rate of zeolite on Pb²⁺ behaves best, Cu²⁺ subsequently and the removal rate of Cd²⁺ is worst, which is consistent with the situation when the value of initial concentration is 50mg/L. When the value of pH is 2~6, the removal rate of zeolite on Cd²⁺ rises from 49.86% to 81.34%, then the process tends to be saturated. When the value of pH is 2~4, the removal rate of zeolite on Cu²⁺ rises from 57.06% to 75.90%. When the value of pH is 2, the removal rate of zeolite on Pb²⁺ is 88.35%; when the value of pH rises to 3, the removal rate of zeolite on the adsorption of Pb²⁺ increases to 97.34% quickly. As we can see from picture 5 and 6, when the value of pH is larger than 6, the removal rate of zeolite on three heavy metal ions all arrives at 100%. As is speculated, under the circumstance of the value of original pH, there are a lot of hydroxyl ions in the solution and generate precipitated substances with three kinds of heavy metal ions, which affects the process of adsorption reaction.

D. The Effects of Reaction Time of Zeolite on the Adsorption of Copper, Cadmium And Lead

The effects of removal rate of reaction time of zeolite on the adsorption of Pb²⁺, Cd²⁺, Cu²⁺ are shown in picture 7 (the value of initial concentration is 50mg/L) and picture 8 (the value of initial concentration is 100mg/L).

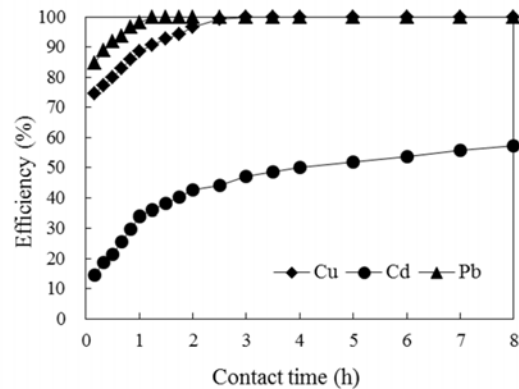


Figure 7. Effect of contact time on heavy metal efficiency (initial metal ions concentration 50 mg L⁻¹; the value of the adsorbed dose is 4 g L⁻¹, pH 6, temperature 35°C).

As we can see, with the lengthen of reaction time, the removal rate of zeolite on the adsorption of Pb²⁺, Cd²⁺, Cu²⁺ rises gradually. During the stage of initial reaction (0~2 hours), the removal rate of synthetic zeolite on the adsorption of Pb²⁺, Cd²⁺, Cu²⁺ changes much and improves quickly in this interval. When the value of initial concentration is 50mg/L, the removal rate of zeolite on Cd²⁺ increases from 14.56% to 42.74%; the removal rate of zeolite on Cu²⁺ increases from 74.58% to 96.73%; the removal rate of zeolite on Pb²⁺ is 98.28% when the value of reaction time is 1 hour. Then the removal rate of zeolite on three heavy metal ions changes little. When the value of initial concentration is 100mg/L, the

removal rate of zeolite on Cd^{2+} increases from 9.93% at 0.16 hour to 41.98% at 5 hours to 44.28% at 8 hours; the removal rate of zeolite on Cu^{2+} increases from 36.77% at 0.16 hour to 75.70% at 5 hours, then the lengthen of time can not improve the removal rate too much; the removal rate of zeolite on Pb^{2+} increases from 51.61% at 0.16 hour to 97.85% at 5 hours and the process tends to be saturated. From the picture 7 and picture 8, we can know that the competitive adsorption sequence of zeolite on three heavy metals remains still with the change of reaction time, which is $Pb > Cu > Cd$.

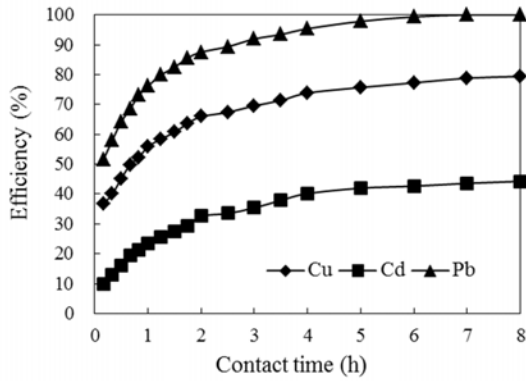


Figure 8. Effect of contact time on heavy metal efficiency (initial metal ions concentration 100 mg L⁻¹; the value of the adsorbed dose is 8 g L⁻¹, pH 6, temperature 35°C).

E. Competitive Adsorption Kinetics.

For general solid-liquid adsorption process, we usually use Quasi first-class and second-class kinetic equation to conduct kinetic simulation. The quasi first-class kinetic equation is:

$$\frac{dQ_t}{dt} = K_1(Q_e - Q_t) \quad (1)$$

Q_t means the adsorption capacity(mg/g) at the time of t, Q_e means equilibrium adsorption capacity(mg/g) of quasi first-class kinetic model, K_1 means the adsorption equilibrium speed constant of quasi first-class kinetic model.

Considering the border conditions: Q_t is equal to 0 when $t=0$; Q_t is equal to Q_e when $t=t$, we can draw the conclusion by integration:

$$\log(Q_e - Q_t) = \log Q_e - (K_1 / 2.303)t \quad (2)$$

The quasi second-class adsorption kinetic equation is:

$$\frac{dQ_t}{dt} = K_2(Q_e - Q_t)^2 \quad (3)$$

The meaning of Q_e and Q_t is consistent with what is referred in the previous contents, K_2 means the adsorption equilibrium speed constant/(mg·min) of quasi second-class kinetic model. By integration:

$$t / Q_t = 1/(K_2 Q_e^2) + (t / Q_e) \quad (4)$$

When the value of t is equal to 0, the initial adsorption speed can be expressed as:

$$h_0 = K_2 Q_e^2 \quad (5)$$

The equation 4 can be changed to:

$$t / Q_t = 1/h_0 + t / Q_e \quad (6)$$

Besides, we can judge which kind of first-class kinetic model can be fit for the experimental process by the value of R^2 . According to RMSE, we can make sure the differences between the adsorption capacity of adsorbents during the experimental process and calculated theoretical adsorption capacity. The smaller the difference of two squares is, the closer the practical adsorption capacity and theoretical adsorption capacity are, which means that the experiment fits kinetic model better. The formula of RMSE is:

$$RMSE = \sqrt{\sum_{i=1}^N (q_{exp} - q_{cal})^2 / N}$$

In this formula, q_{exp} means the practical adsorption capacity in the experimental process, q_{cal} means theoretical adsorption capacity of adsorbent, we can calculate and get the results by using the given formula.

F. The Simulation Result When the Initial Concentration of Mixed Heavy Metals is 50mg/L and 100mg/L.

Conduct the simulation of statistics of zeolite on the adsorption of three heavy metal ions of Cu^{2+} , Cd^{2+} and Pb^{2+} ions by using quasi first-class kinetic equation and quasi second-class kinetic equation, the results are shown in Tab.1.

TABLE I. THE CONSTANTS AND CORRELATION COEFFICIENTS OF QUASI FIRST-CLASS AND QUASI SECOND-CLASS KINETIC MODELS FOR ADSORPTION OF HEAVY METAL

Initial concentration (mg/L)	Metal	Q _{e, exp} (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
			Q _{e, cal} (mg/g)	K ₁	R ²	Q _{e, cal} (mg/g)	K ₂	R ²
50	Pb ²⁺	12.50	3.3602	5.8750	0.9571	12.7226	1.7161	0.999
	Cu ²⁺	12.50	5.4157	3.2352	0.9058	12.8205	0.5850	0.9977
	Cd ²⁺	7.38	4.9828	0.8351	0.9837	7.7821	0.1435	0.9975
	RMSE		9.1398			0.2226		
				7.0843			0.3205	
				2.3972			0.4021	
100	Pb ²⁺	12.50	6.2959	1.5142	0.9803	12.9198	0.2359	0.9988
	Cu ²⁺	10.20	4.9342	0.8721	0.9873	10.3950	0.2034	0.9984
	Cd ²⁺	5.78	4.1954	0.8684	0.9869	6.2617	0.1476	0.9967
	RMSE		6.2041			0.4198		
				5.2658			0.1950	
				1.5846			0.4817	

a. Note: Q_{e, exp} and Q_{e, cal} are the experimental and calculated values of q_e, respectively

From Tab.1, according to quasi first-class and quasi second-class kinetic calculation results, the value of quasi first-class kinetic simulation correlation coefficient R² are 0.9571,0.9058,0.9837 respectively when the value of initial concentration is 50mg/L, the value of quasi second-class kinetic simulation correlation coefficient R² are 0.999,0.9977,0.9975(all larger than 0.99) respectively. Compared to the value of RMSE, the value of quasi second-class kinetic RMSE of three heavy metal ions (0.2226,0.3205,0.4021)are smaller than the value of quasi first-class kinetic RMSE(9.1398,7.0843,2.3972), which means that the value of quasi second-class kinetic equilibrium adsorption capacity Q_{cal} is closer to the value of experimental measurement Q_{exp}.

When the value of initial concentration is 100mg/L, the value of quasi first-class kinetic simulation correlation coefficient of three heavy metal ions R² are 0.9803,0.9873,0.9869 respectively, the value of quasi second-class kinetic simulation correlation coefficient of three heavy metal ions R² are 0.9988,0.9984,0.9967 respectively, which means that the value of quasi second-class kinetic simulation correlation coefficient are larger than the value of quasi first-class kinetic simulation correlation coefficient. Compared to the value of RMSE, the value of quasi second-class kinetic RMSE of three heavy metal ions (0.4198, 0.1950, 0.4817) are smaller than the value of quasi first-class kinetic RMSE (6.2041, 5.2658,

1.5846). As we can see, the simulation degree of quasi first-class adsorption kinetics of zeolite on the adsorption of three heavy metal ions is terrible, the simulation degree of quasi second-class adsorption kinetics is just the opposite. When the value of initial concentration of mixed heavy metal ions are 50mg/L and 100mg/L respectively, the adsorption behavior of zeolite on the adsorption of three heavy metal ions all fits for quasi second-class adsorption kinetic equation.

IV. CONCLUSIONS

The adsorbed dose both has the significant effect on the removal rate and saturated adsorption capacity of zeolite on the adsorption of three heavy metal ions. With the increase of adsorbed dose, the removal rate of zeolite on the adsorption of three heavy metals all rise constantly. When the value of initial concentrations are 50 and 100 mg/L, the competitive adsorption sequence of zeolite on three heavy metal ions is: Pb>Cu>Cd. With the increase of adsorbed dose, the saturated adsorption capacity of zeolite on heavy metal ions all drops constantly, which is that adsorption capacity of the mass fraction zeolite adsorbent on three heavy metal ions decreases constantly. When the value of adsorbed dose is 0.25g/L~1g/L, the saturated adsorption capacity in the adsorption system whose initial concentration are 50mg/L and 100mg/L both drops a lot with the increase of adsorbed dose.

When the value of initial concentration are 50mg/L and 100 mg/L, the removal rate of zeolite on the adsorption of three heavy metal ions all increases with the rise of the value of initial pH on the whole. During the competitive adsorption process, at various value of initial pH and concentration, the adsorption sequence of zeolite on three heavy metals remains still: Pb>Cu>Cd. When the value of initial pH is larger than 6, the hydroxyl ions of adsorption system and three heavy metal ions both generate precipitation substances so that the process of adsorption reaction is affected.

The reaction time has apparent effect on the removal rate of zeolite on the adsorption of three heavy metal ions. The removal rate of zeolite increases gradually with the lengthen of reaction time. The adsorption removal rate of zeolite on the adsorption of three heavy metal ions improves quickly within 2 hours. With the change of reaction time, competitive adsorption sequence of zeolite on three heavy metals keeps still.

When the value of initial concentration of mixed heavy metal ions are 50mg/L and 100mg/L respectively, the value of quasi first-class kinetic simulation correlation coefficient of three heavy metal ions R^2 are smaller than the value of quasi second-class kinetic simulation correlation coefficient R^2 . Besides, compared to the value of RMSE, the value of quasi second-class kinetic equation RMSE are all smaller than the value of quasi first-class kinetic equation RMSE under different value of initial concentration, which means that the value of equilibrium adsorption capacity of quasi second-class kinetic equation Q_{exp} is closer to the value of equilibrium adsorption capacity Q_{cal} according to experimental measurement. The adsorption behavior of synthetic zeolite materials on the adsorption of three heavy

metal ions all fits for quasi second-class adsorption kinetic equation.

ACKNOWLEDGMENT

This work was financial supported by the Natural Science Foundation of China (NSFC) (Grant No. 21407068), Science Foundation of Jiangsu Colleges and Universities (Project No. 09KJB610004), 2016 University of Jiangsu Province Blue Project of young academic leader training objects, Open Fund Project of Jiangsu Provincial Key Laboratory of Environmental Engineering (Grant No. KF2014002, KF2015011), "13th Five-Year Plan" key subject of Jiangsu City Vocational College (Grant No. 16SSW-Z-001).

REFERENCES

- [1] F. Boudrahem, F. Aissani-Benissad and H. Ait-Amar, *J. Environ. Manage.***90**, 3031 (2009).
- [2] S. Noppadol and P. Pongsakorn, *Pol. J. Environ. Stud.***23**,853 (2014).
- [3] C. Chen, T. Cheng and Y. S. Shi, *Iran. J. Chem. Chem. Eng.***33**,29 (2014).
- [4] T. M. Alslaibi, I. Abustan and M. A. Ahmad, *J. Environ. Chem. Eng.***1**, 589(2013).
- [5] A. Papandreou, C. J. Stournaras and D. Panias, *J. Hazard. Mater.***148**,538 (2007).
- [6] S. H. Yao, X. X. Jiang and D. K. Shen, *Journal of Southeast University (Natural Science Edition)***45**, 515(2015). (in Chinese)
- [7] C. Chen, T. Cheng and Z. L. Wang, *J. Indian Chem. Soc.***91**,1 (2014).
- [8] A. Z. Kamel, S. A. Mohammad and B. H. Falah,*J. Hazard. Mater.***188**,414 (2011).
- [9] M. Ahmaruzzaman,*Prog. Energy Combust. Sci.***36**,327 (2010).
- [10] K. S. Hui, C. Y. H. Chao and S.C. Kot, *J. Hazard. Mater.***B127**,89 (2005).