

Adsorption mechanisms of purified attapulgite for Zn²⁺ in aqueous solution

Ling Tao, Yina Li, Yaqiong Zhao, Jun Ren*, Yijie Wang

School of Environmental and Municipal Engineering, Lanzhou Jiaotong University, Lanzhou, 730070, Gansu, P. R. China

Engineering Research Center for Cold and Arid Regions Water Resource Comprehensive Utilization, Ministry of Education, Lanzhou, 730070, P. R. China

*renjun@mail.lzjtu.cn

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Abstract. The adsorption capability, dynamics and thermodynamic of Zn²⁺ by purified attapulgite was studied in this research. The influences of adsorption time, initial concentration and temperature on the adsorption of Zn²⁺ were discussed. With the rising of initial concentration, temperature and adsorption time, the removal rate and adsorption capacity of Zn²⁺ by attapulgite was increased. The adsorption isotherms attapulgite could be described both by the Langmuir model and Freundlich model.

Introduction

The electrochemical separation precipitation, membrane filtration, ionic exchange and solvent extraction have been used for the sequestering of heavy metals from wastewater, however, these techniques are associated with problems such as excessive time requirements, high costs, inefficiency and energy use. For overcoming these drawbacks, some adsorbents have been developed in removal of heavy metal ions [1,2]. Attapulgite has been used for treating wastewater polluted by heavy metals[3]. Attapulgite is a natural clay mineral that is found in many places of the world. It is a crystalline hydrated magnesium silicate with a fibrous morphology, large specific surface area and moderate cation exchange capacity, and has been widely studied as an adsorbent for the removal of heavy metals from solutions[4]. However, the adsorption capability of natural attapulgite is very poor, some special treatments or modifications, such as heat treatment, acid treatment or graft reaction are needed to enhance its adsorption performance and selectivity[5]. In this study, purified attapulgite was made and used as adsorbents for Zn²⁺ adsorption from aqueous solution. The parameters influencing the adsorption capacity of Zn²⁺ onto attapulgite, such as contact time, initial concentration and temperature of solution were investigated. The adsorption kinetics and isotherms of the attapulgite toward Zn²⁺ were studied, and the adsorption mechanism was also discussed.

Experimental

Attapulgite was obtained from Gansu Shuangtai Attapulgite Co. Ltd.. The Zn²⁺ solutions were prepared by dissolving Zn (NO₃)₂·4H₂O in distilled water. Attapulgite underwent extrusion, drying and crushing. According to the dosing quantity 10 g/L, it was dispersed in 2mol/L H₂SO₄ for 18 h at room temperature. Then it went through deposition, impurity, centrifugal callback, and drying (105°C) resulting in attapulgite sample. The sample was then put through a screen to obtain particles of 200 meshes (0.075 mm). Samples were activated by calcination at 360°C for 2 h.

All batch adsorption experiments were carried out by mixing 0.5g of adsorbent with 50 mL of Zn²⁺ solution with the desired concentration and pH at value of 7.0 and then the mixture was shaken with a constant speed of 150r/min at the desired temperature and contact time. For equilibrium adsorption experiments, 50mL of various initial concentration (from 20 to 200 mg·L⁻¹) of Zn²⁺

solution was shaken at different temperature (from 298K to 333K) for 5h until the equilibrium was established.

The initial and the final concentration of Zn^{2+} in the aqueous solution were measured with ICP-AES. The adsorption capacity of attapulgite was calculated through the following equation:

$$q_e = \frac{(C_0 - C_e)V}{M} \quad (1)$$

Where q_e is the adsorption capacity of Zn^{2+} on adsorbent (mg/g), C_0 is the initial concentration of Zn^{2+} (mg/L), C_e is the equilibrium Zn^{2+} concentration in solution (mg/L), m is the mass of adsorbent used (g) and V is the volume of Zn^{2+} solution (L).

Results and Discussion

Adsorption kinetics. For examining the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and the pseudo-second-order kinetic models were used to evaluate the experimental data obtained from the Zn (II) removal experiments. The pseudo-first-order kinetic model was suggested by Lagergren for the adsorption of solid/liquid systems and its linear form can be formulated as [6]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

Where q_t is the adsorption capacity at time t (mg/g) and k_1 (min^{-1}) is the rate constant of the pseudo-first adsorption, was applied to the present study of Zn (II) adsorption.

The kinetic data were further analyzed using Ho's pseudo-second-order kinetics model. It can be expressed as [7]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

Where q_e and q_t respectively are the amount of Zn^{2+} adsorbed at equilibrium and time t (mg/g); k_2 ($\text{g/mg} \cdot \text{min}$) is the equilibrium rate constant of the pseudo-second-order adsorption.

The correlation coefficient for the intra-particle diffusion kinetics model over the whole time range is lower than those of the pseudo-first-order and the pseudo-second-order models. Moreover, the value of intercept C which reflects thickness of the boundary layer did not equal to zero, suggesting that all the linear line did not pass through the origin and the larger contribution of the surface adsorption in the rate controlling step. Some researchers reported that three adsorption stages occurred in the whole adsorption process. Firstly, in the initial stage, heavy metal ions migrate from liquid phase to the outer surface of adsorbent particles through film diffusion with very fast speed, it is called external mass transfer; secondly, the gradual adsorption stage, and the final equilibrium stage (Table 1).

Adsorption isotherms. It can be observed that temperature has a positive influence on the Zn^{2+} adsorption by the adsorbents, which is probably because high temperature provided more chances for metal ions to pass the external boundary layer, and produced the enlargement of pore volume and surface area enabling metal ions to penetrate further[8]. The most commonly used isotherm models for liquid-solid adsorption are Langmuir and Freundlich isotherms [9].

The Langmuir model is based on the assumption of a structurally homogeneous adsorbent where all sorption sites are identical and energetically equivalent [10]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{m1}} + \frac{1}{b \times q_{m1}} \quad (4)$$

where q_{m1} represents the maximal adsorption capacity to form a monolayer(mg/g) in the system. The essential feature of the Langmuir isotherm is R_L :

$$R_L = \frac{1}{1 + bC_0} \quad (5)$$

The value of R_L is indicator of the shape of adsorption isotherm to be favourable or unfavourable.

The Freundlich isotherm is applied for multilayer adsorption on heterogeneous adsorbent and it assumes that the adsorption sites increase exponentially with respect to the heat of adsorption and the Freundlich equation is an empirical equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

Where K_F (mg/g) and $1/n$ are Freundlich constants, related to adsorption capacity and adsorption intensity, respectively, and the other symbols are the same as defined above.

Table 1 The intra-particle diffusion kinetic model parameters for Zn^{2+} ions adsorbed on adsorbents.

T(K)	C_0 (mg/L)	q_e (exp) mg/g	k_i $\times 10^{-3}$ mg/g·min ^{-1/2}	C mg/g	r^2
298	20	0.8433	6.9488	0.7586	0.3850
	40	1.4831	30.3558	1.0892	0.5281
	60	2.0270	30.7515	1.6369	0.4544
	100	3.3634	34.8165	2.8783	0.5412
	150	4.4687	81.2785	3.4385	0.4917
	200	0.0938	63.8921	4.9536	0.2933
303	20	0.8540	9.9299	0.7156	0.7345
	40	1.3145	11.8855	1.1467	0.7804
	60	1.9875	34.5550	1.5151	0.8034
	100	3.3538	67.1264	2.4976	0.6524
	150	4.6615	130.5759	2.6504	0.9169
	200	5.9535	204.3233	2.7963	0.9300
313	20	0.8605	10.0358	0.7311	0.6577
	40	1.6175	21.7952	1.3334	0.6803
	60	2.4910	59.3811	1.6565	0.7959
	100	3.8590	126.7827	2.3091	0.6515
	150	4.7876	116.1338	3.2267	0.6872
	200	6.7878	269.4809	3.1031	0.7725
323	20	0.8585	8.8170	0.7329	0.6925
	40	1.6416	27.0719	1.2490	0.9268
	60	2.4913	68.2549	1.4227	0.8974
	100	3.9470	147.7977	1.5887	0.7671
	150	5.1770	248.4331	1.6852	0.7480
	200	6.7393	474.9443	1.0957	0.6610
333	20	0.8696	9.6345	0.7572	0.7821
	40	1.6444	25.8911	1.2887	0.7286
	60	2.4479	45.5098	1.6554	0.8487
	100	3.9965	18.4830	3.9049	0.0213
	150	5.1990	81.8673	4.7700	0.9059
	200	6.7198	79.9215	5.5973	0.7101

The isotherm models simulated the experimental data well, which is supported by the good value of correlation coefficients r^2 for the two equation in Table 4 (All r^2 are greater than 0.95), and the r^2 of Langmuir equation were higher than the other two isotherm values, which indicated the three isotherm correctly fitted the equilibrium data. It was seen from the Langmuir calculated results that the adsorption equilibrium capacity for Zn^{2+} onto attapulgite varied from 0.87mg/g to 7.28mg/g with the rising of temperature from 298K to 333K, this result indicates the higher temperature favour the adsorption of Zn^{2+} onto natural attapulgite. Obviously that the values of constant b 、 KL and K_f increase with the rising of the temperature support the above point (Table 2, 3).

Table 2. The constant parameters and correlation coefficients of Langmuir model

T(K)	$q_{ml}/mg/g$	$b/L/mg$	R_L	r^2
298	8.1833	0.0225	0.1818	0.8901
303	10.4058	0.0145	0.2561	0.6468
313	8.5179	0.0357	0.1230	0.8989
323	9.4073	0.0327	0.1325	0.9685
333	9.3284	0.0336	0.1294	0.9672

Table 3. The constant parameters and correlation coefficients of Freundlich model

T (K)	K_F (mg/g)(L/mg) $1/n$	$1/n$	r^2
298	0.3982	0.5904	0.9874
303	0.3624	0.6134	0.9351
313	0.6155	0.5563	0.9505
323	0.4844	0.6424	0.9782
333	0.5014	0.6326	0.9824

Conclusions

The attapulgite modified by acid and thermal was performed. Kinetics experiments showed that natural attapulgite offered fast kinetics for adsorption of Zn^{2+} and the adsorption processes reached equilibrium after 90min; the adsorption follow pseudo-second-order kinetics model suggesting chemisorptions is the rate-controlling step. Equilibrium data were well described by Langmuir and Freundlich isotherms model, and it seems Langmuir model is better than the other in representing indicating equilibrium data confirming the monolayer coverage of Zn^{2+} onto attapulgite. The maximum adsorption capacity was found to be 6.72 mg/g at pH of 7.0 and temperature at 333 K.

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