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Application Research on the Adsorption of Cadmium Ion in Wastewater by Zeolite Molecular Sieve

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In this paper, the synthetic zeolite molecular sieve is used as the adsorbent to study the application of zeolite molecular sieves for the adsorption of cadmium ions in wastewater. It is found that the adsorption of cadmium ions in wastewater by zeolite molecular sieves reaches equilibrium at 90 min. In addition to the factor of time, temperature control is also the key to the adsorption of cadmium ions in wastewater by zeolite molecular sieves. In addition, the Langmuir model and the Freundilich model are used to describe the adsorption isotherm and it is discovered that the maximum adsorption capacity is 197.5 mg/g. When the pH value of the solution is 6, the adsorption capacity of cadmium ions in the wastewater by zeolite molecular sieves reaches the maximum value. In addition, the removal rate of cadmium ions in the wastewater will increase with the temperature. In summary, zeolite molecular sieves can effectively adsorb cadmium ions in wastewater. Therefore, zeolite molecular sieves have important application prospects in the treatment of cadmium ions in wastewater.

1. Introduction

1.1 Literature review

For the purpose of global green industry construction and environmental protection, the adsorption property of zeolite molecular sieves has been widely applied in many fields such as chemical industry and environmental protection (Wan et al., 2014). In the construction of green chemical industry and environmental protection, the treatment of heavy metal pollution has always been an important strategy for the sustainable development in China (Wang, 2012). Among them, due to its non-degradability and transitivity in the water environment, the cadmium has become a major problem in the treatment of heavy metal pollution (Chen, 2018; Xi, 2018; Fang et al., 2012; Li, 2018). The cadmium ion is not an essential element of life and it is the main inducing factor for itaiitai disease. So far, the application of zeolite molecular sieves is one of the most effective methods for adsorbing cadmium ions in wastewater (Chen et al., 2012). In the 20th century, Barrre et al. completed the study of the phase transition of natural minerals in the salt solution of re and completed the synthesis of zeolite molecular sieves for the first time (Chen et al., 2017). The zeolite molecular sieve is the hydrous aluminosilicate mineral with interconnected channels in a shelf-like configuration. The special crystalline chemical structure enables zeolites to have multiple functions such as ion exchange, high-efficiency selective adsorption and catalysis, as well as environmentally friendly attribute, thereby improving the efficiency of ion pollution treatment in wastewater and reducing energy consumption. Tao Hong et al. found that molecular sieves have the advantages of low dosage, large area of wastewater treatment, high effectiveness, less time and low restriction for the applicable pH value of waste water in the treatment of cadmium ions in waste water (Yu et al., 2017). Zeolite molecular sieves have good thermal and hydrothermal stability, good ion exchange performance and unique positive ion selective adsorption performance. The positive ion in zeolite molecular sieves can be exchanged by some catalytically active metal ions, making them become effective catalysts and catalytic carriers (Wang et al., 2012). When using the natural clinoptilolite to treat the heavy metal ions in the wastewater, Zorpas et al., found that when the mass of zeolite accounted for a certain proportion of the wastewater, all cadmium ions in the wastewater can be removed. The stable property of zeolite molecular sieves can help cadmium ions to be concentrated and recovered, as well as realizing multiple recycling after

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decomposition and absorption, which has a broad application prospect in the treatment of heavy metal wastewater.

1.2 Research purposes

With the rapid development of the socio-economic and chemical industry, the pollution caused by the discharge of various heavy metal industrial wastewater has become more and more severe and has attracted great social attention (Sun et al., 2017). In recent years, with the widespread application of heavy metals in the chemical industry such as the pigment industry, cadmium battery manufacturing, and the nuclear industry, the waste gas and waste solid generated by heavy metals have caused severe pollution to the water environment, thereby affecting the health of life entities (Yu et al., 2010). The accumulation of cadmium ions in life entities can lead to various diseases. Therefore, how to effectively treat the pollution of cadmium ions in heavy metal elements in the wastewater and avoid the damage to the ecological environment and biology in the recycling of wastewater is an urgent problem to be solved for related industries in China. In this paper, cadmium (Cd) metal wastewater is selected as the pollutant target (Mao et al., 2016). The absorption of zeolite molecular sieves is analyzed through the adsorption experiment of Cd^{2+} on zeolite molecular sieves and the impact of variable indexes in the wastewater solution such as the concentration pH value, adsorption time, waste water volume and adsorbent dosage of cadmium ions on the absorption efficiency is discussed (Liu et al., 2010). In addition, zeolite molecular sieves are used as adsorbents for the treatment of heavy metal wastewater pollution. How to realize the re-utilization of wastewater resource and bring environmental and social benefits is also one of the main research purposes in this paper (Guang et al., 2011).

2. Concept of zeolite molecular sieves

The zeolite molecular sieve is a hydro silicate porous mineral crystalline material that possesses a regular microporous structure and unique crystal chemistry feature. In the middle of the 20th century, scientists discovered zeolites A and X for the first time and subsequently studied the synthesis of zeolite Y and its catalytic cracking through experiments. The application in the chemical industry was realized, which greatly promoted the green development of zeolite molecular sieves in the chemical industry and environmental protection (Yi et al., 2016). Artificially synthesized zeolite molecular sieves are the main method for the removal of heavy metal water pollution internationally in the current stage. Compared with natural zeolites, the artificially synthesized zeolite molecular sieves have better chemical and physical stability and contains no harmful substances, which avoids the re-pollution of the adsorbed water area. Silicon, aluminum and their matched oxygen atoms are the basic framework elements of the zeolite molecular sieve. The TO4 tetrahedron is its primary structural unit and the T atom contains Si, Al, and P atoms. Zeolite molecular sieves possess the three-position empty skeletal framework, whose essence is crystalline aluminosilicate (Rong et al., 2012). It has strong acidity and high hydrothermal stability and thus it has been widely used in the adsorbing of heavy metals in wastewater.

Table 1: Molecular Sieve Models and Applications

Type	Chemical formula	Applications
3A	4K2O2Na2O 6AL2O312SiO2 27H2O	For building glass industry, gas refining, purification and petrochemical industry.
4A	2Na2O 2Al2O3 4Si O2 9H2O	For separation of liquids for natural gas and various chemical gases
5A	3CaO Na2O 4Al2O3 8 SiO2 9H2O	For the separation of isomers and other industrial and liquid drying and refining
10X	4CaO Na2O 5Al2O3 (14+1) SiO2(30-35) H2O	For paraffin refining
13X	5Na2O 5Al2O3 (14+1)5SiO2 (30-35) H2O	For gas drying, purification and catalyst liquids

Zeolite molecular sieves have adsorption property, ion exchange property and catalytic property. The adsorption property is a kind of “surface force” formed on the surface of the adsorbed object through molecular attraction (Ren et al., 2013). The specific surface area of zeolite is very large, which can reduce and eliminate heavy metal molecules in the fluid to the greatest extent and plays an important role in the environmental protection. The ion exchange property refers to the exchange of compensation positive ions outside the framework of zeolite molecular sieves. Under certain conditions (high temperature or aqueous solution), heavy metal ions are prone to migration (Ren et al., 2013). The catalytic property means that due to the specificity of the crystalline structure of zeolite molecular sieves, the pore structure of the size and shape is polarized by the Coulomb field to form an excellent catalyst. At present, the difference among various types of zeolite molecular sieves is significant, which leads to complex chemical composition. The chemical composition of the silicate zeolite molecular sieve is: $Mx/m[(AlO_2)x\cdot(SiO_2)y]\cdot zH_2O$. M represents positive ions; m represents the valence number; z represents the hydration number; and x and y are integers. After the activation of zeolite molecular sieves, the water molecules are removed and the remaining atoms form a cage structure with the pore size of 3 to 10 & Aring. In addition, the widely used methods for synthesizing zeolite molecular sieves mainly include hydrothermal synthesis, microwave-assisted synthesis, salting-in synthesis, dry gel method and mixed alkali vapor synthesis. Based on the different types of molecular sieve models and applications, the paper give the table 1 as below:

3. Specific application of zeolite molecular sieves in the adsorption of cadmium ions in wastewater

Cadmium is one of the sources of heavy metal pollution and the important reason for the cadmium pollution is the waste gas and pollutants produced by industries such as pigment industry, chemical industry and electric forging industry. If too much cadmium is accumulated in the body, it can cause a variety of diseases. Therefore, cadmium pollution is one of the key issues faced in the society (Fang et al., 2009). At present, the commonly used method for the treatment of cadmium ions is adsorption, which has the advantages of low cost, simple steps and quick results. Under the same pressure, the equilibrium absorption capacity of zeolite molecular sieves is much higher than that of activated carbon and silica gel. The ion exchange phenomenon is very likely to occur between the positive ions in the zeolite molecular sieve crystal such as Na^+ and K^+ and the heavy metal ions contained in solution. Also, the specific surface area of the zeolite molecular sieve is relatively large, which helps to enhance the physical adsorption capacity of metal ions. In addition, the zeolite molecular sieve also has good thermal stability, which will not cause secondary pollution to the environment after use. In summary, zeolite molecular sieves are effective adsorbents for the removal of cadmium ions in wastewater (Rong et al., 2009).

In this paper, through the actual experimental operation, the X zeolite molecular sieve prepared under the optimal synthesis conditions is selected to study the absorption application of cadmium ions in wastewater. The impact of adsorption time, ion concentration and different dosage of zeolite molecular sieves on the adsorption behavior is also investigated. This paper conducts the experimental analysis of the adsorption of cadmium ions in wastewater by zeolite molecular sieves.

3.1 Pretreatment of synthesis zeolite molecular sieves

In the adsorption experiment conducted in this study, the zeolite molecular sieve used is prepared from the alkali mixture product with bauxite and sodium hydroxide in the corresponding proportion with appropriate amount of ionized water under certain conditions. Considering that the high pH value will exert significant interference on cadmium ions in the treatment of cadmium ions in the wastewater. Therefore, before the experiment, the zeolite molecular sieve is washed with deionized water for several times and the pH is set to 6. It is dried at 100° C to be ready for use.

3.2 Specific experimental operation

In the experiment, according to the requirement, the stock solution of cadmium ion aqueous solution (1.00 g/L) is configured with cadmium nitrate at 25° C. Some zeolite molecular sieves are placed in several 250 mL conical flasks and 100 mL of cadmium ion aqueous solution of different concentrations is added. After that, it is placed in the thermostatic oscillator.

The computational formula of adsorption capacity is:

$$q=(C_0-C_e)\times V/m \tag{1}$$

In the above formula, C_o and C_e are the concentration of cadmium ion mass in the solution before and after the adsorption respectively; m is the adsorption mass; and V is the solution volume.

0.1g of cadmium ion-adsorbed zeolite molecular sieve is selected and added in a 100ml conical flask. 100ml of deionized water, tap water and seawater is added in the conical flask for shake and desorption for 1 day, 2 days, 5 days and 7 days respectively. It is then sampled respectively. The concentration of cadmium ions in the solution is analyzed and then the difference in the firmness of the adsorption of cadmium ions by zeolite molecular sieves based on different media is studied (Chun et al., 2010).

In a 100mL conical flask, suitable quantity of zeolite molecular sieve is put in and then 100 mL of NaCl solution in 5% concentration is added for shake and desorption for 2 hours. After that, it is sampled and the concentration of cadmium ions in the solution is analyzed. Then, the filtering separation is conducted and the

secondary distilled water is used to wash the zeolite molecular sieve water for multiple times. After that, it is dried. This process is repeated for 5 times (Chang et al., 2014).
When measuring the equilibrium adsorption capacity of cadmium ions in the wastewater by zeolite molecular sieves, the adsorption time is set to 90 min for full adsorption. At a constant temperature, when the adsorption process is in equilibrium state, the adsorption isotherm can be used to represent the relationship between the equilibrium concentration of the adsorbate in the solution and the adsorption capacity. Under different temperature environment, when the difference of adsorption equilibrium of zeolite molecular sieves is relatively small, it indicates that the zeolite molecular sieves has a strong adsorption capacity for cadmium ions (Sun et al., 2011).
As for the adsorption isotherm mode, the Langmuir model and the Freundilich model are widely used.
The formula of the Freundlich model is: $q_e = K_F c_e^{(1/n)}$. K_F and n are empirical constants, where the constant K_F represents the adsorption capacity and n represents the adsorption strength. The formula of Langmuir model is: $q_e=q_mK_fC_e/(1+K_lC_e)$ q_e is the equilibrium adsorption capacity (mg/g) of the adsorbate on the adsorbent of unit mass; Ce is the equilibrium concentration (mg/L) of the adsorbate in solution after the adsorption equilibrium; the constant q_m indicates the maximum adsorption capacity; the constant K_l indicates the affinity of the adsorbate for the adsorbent (Chun et al., 2016).
The Freundlich model is used to describe the adsorption isotherm and the data fitting is conducted on the isothermal adsorption equilibrium of cadmium ions on the X zeolite molecular sieve. The results are shown in Table 2.

Table 2: Freundlich model equation fitting parameters for the adsorption of cadmium ion on x zeolite molecular sieve

Temperature	Freundlich		
	K_f(mgg^{-1})	n	R^2
23	7.11	3.433	0.9261
46	7.52	3.359	0.8935
71	7.36	3.392	0.8857

The Langmuir model is used to describe the adsorption isotherm and the data fitting is conducted on the isothermal adsorption equilibrium of cadmium ions on the X zeolite molecular sieve (Chun et al., 2016). The results are shown in Table 3.

Table 3: Langmuir model equation fitting parameters for the adsorption of cadmium ion on x zeolite molecular sieve

Temperature	Langmuir		
	Q_m(mg/g)	K_L(L/mg)	R^2
23	182.6	1.34	0.9992
46	194.4	1.85	0.9978
71	197.5	2.35	0.9996

3.3 Discussion of experimental results

According to Table 2 and Table 3, the Langmuir model is used for fitting and the value of the coefficient of determination R^2 is all higher than 0.9978, indicating that the absorption of cadmium ions by X zeolite molecular sieve is more in line with the Langmuir model (Ren et al., 2014). The value of the coefficient of determination R^2 is all lower than 0.927 when the Frenundlich model is used for fitting, indicating that the absorption of cadmium ions by X zeolite molecular sieve is not in line with the Freundlich model (Ying et al., 2009). In addition, the absorption of cadmium ions by X zeolite molecular sieve is more in line with the Langmuir model when the temperature is 23°C. However, the maximum adsorption capacity value q_m increases with the temperature, indicating that the entire adsorption process of cadmium ions by the zeolite molecular sieve is an endothermic process (Hong et al., 2011).
With the increase of temperature, the aperture of zeolite molecular sieves will gradually increase, which in turn will promote the ions that have already been adsorbed on the surface of the zeolite to accelerate the motion. For zeolite molecular sieves, the increase in temperature will activate some of the inactivated absorption, giving rise to new adsorption sites, which has led to an increase in the adsorption capacity. It can be seen from the K_L value that all K_L values are relatively large under different temperature conditions, indicating that the zeolite molecular sieve has a significant role in adsorbing cadmium ions in the wastewater. The removal rate of cadmium ions in wastewater increases with the temperature. In addition, when the pH value of the

solution is 6, the adsorption capacity of zeolite ions in the wastewater by zeolite molecular sieves reaches its maximum.

4. Conclusion

In summary, the zeolite molecular sieve is a hydro silicate porous mineral crystalline material that possesses a regular microporous structure and unique crystal chemistry feature with adsorption property, ion exchange property and catalytic property. The zeolite molecular sieve is used to adsorb cadmium ions in wastewater. After desorption, the cadmium ion can be concentrated and recycled. With the increase of temperature, the aperture of zeolite molecular sieves will gradually increase, which in turn will promote the ions that have already been adsorbed on the surface of the zeolite to accelerate the motion. Also, the removal rate of cadmium ions in wastewater increases with the temperature. Therefore, the zeolite molecular sieve is of great important significance for the adsorption of cadmium ions in wastewater. It is believed that in the future, zeolite molecular sieves will be fully utilized in the adsorption cadmium ions in the wastewater.

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