

The experimental study of the adsorption behavior of Cd^{2+} on manganese dioxides

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Abstract: The adsorption behavior of Cd^{2+} on manganese dioxides was studied in the paper, especially the influence factors of the adsorption behavior were concerned. The results showed that the adsorption equilibrium reached in about six hours. The adsorption amount of Cd^{2+} on the manganese dioxide increased with the increasing of the initial Cd^{2+} concentration, and the adsorption rate increased at first, then decreased. The adsorption isotherm curve accorded with Langmuir isotherm equation. The most influence factor on the adsorption properties of the manganese dioxide was pH value. After the addition of inorganic salts, only the ammonium bicarbonate could promote the adsorption of Cd^{2+} on the manganese dioxide, other inorganic salts inhibited the adsorption.

1. Introduction

The manganese oxide, as an important substance composition in the soils, is not only an importance source of manganese element in the flora and fauna, but also an important adsorption carrier of heavy metals, and a contact catalyst of chemical reactions and a subject of redox reactions [1, 2]. The content of manganese oxides is a little in the soils, but its existence is of a fundamental significance in environmental studies because of its low soil zero point charge (PZC), large specific surface area, high negative charge, active surface activity, high adsorptive performance, and the significant influences on the migration and sediment of anions and cations, heavy metal ions, and organic fat mixtures in the surface environment.

In recent years, a great deal of experimental and theoretical researches indicated that the manganese oxides could effectively adsorb heavy metal ions and then lowered the pollutant concentrations [3]. The adsorption behavior of Cd^{2+} on manganese dioxides was studied in the paper, especially the influence factors of the adsorption behavior were concerned.

2. The experimental method and process

(1) The 0.2g manganese dioxide powders and 50ml CdCl_2 solutions of Cd^{2+} mass concentration of 78.675mg/L were mixed. At the same time, two parallel samples were done, and time-samplings were taken respectively. For the experimental accuracy, two parallel samples in following experiments were done, then average values of the three samples were calculated and used.

(2) The 0.2g manganese dioxide powders were added respectively into the six 50ml CdCl_2 solutions of Cd^{2+} mass concentration of 15.735, 31.470, 33.933, 62.940, 78.675 and 157.350mg/L.

(3) The 0.2g manganese dioxide powders and 50ml CdCl_2 solutions of Cd^{2+} mass concentration of



78.675mg/L were mixed. The hydrochloric acids and sodium hydroxides were used to adjust the pH values of the solutions to 3.5, 4, 6, 7, 9 and 11, respectively.

(4) The 0.2g manganese dioxide powders and 25ml CdCl_2 solutions of Cd^{2+} mass concentration of 78.675mg/L were mixed, and then 25ml KCl, NaCl, CaCl_2 and NH_4HCO_3 solutions of 0.1mol/L were added, respectively. The 0.2g manganese dioxide powders and 50ml CdCl_2 solutions of Cd^{2+} mass concentration of 78.675mg/L were mixed, and used to match with the non-added-inorganic salt solutions.

Then, all mixtures were oscillated at 25°C room temperature. The mixtures made in the 1.1 were oscillated for 1h, 2h, 3h, 4h, 6h, 12h, 48h and 72h, respectively, and taken according to the sampling time; the other ones were oscillated for 6h, and taken samples. The taken samples were placed silently for 24h, and centrifuged. The supernates of the samples were taken. The concentrations of Cd^{2+} in the supernates were measured by ICP, the adsorption capacity and rate of Cd^{2+} on manganese dioxides were calculated.

3. The result and analysis

3.1 The influence analysis of the time on the adsorption

It was observed from Figure 1 and 2 that the adsorption capacity and rate of Cd^{2+} on the manganese dioxide increased gradually at the beginning of the reaction in the experiment, the increasing range of the adsorption capacity and rate started to decrease after 3 hours and reached maximum in sixth hour, and then remained stable on the whole with time, which indicated the whole adsorbing process in 72 hours was smooth and steady. The results of previous studies showed that the time of reaching maximum was different in the adsorption experiments of different heavy metal ions on MnO_2 . It was observed from the studies of Chen Hong and Fan Yaoting that the time of reaching maximum was 30 minutes in the adsorption experiments of As^{3+} in the waste water and uranium ions on MnO_2 , respectively [3, 4]; the time of reaching maximum was 60 minutes in the adsorption experiments of Mn^{2+} and other cation ions on MnO_2 in the studies of Morgan, Stumm and Posselt [5, 6], the time was 1—2 days in the adsorption experiments of Zn and Co ions in the study of Loganathan [7]; which perhaps resulted from the different adsorption mechanisms in the different experiments.

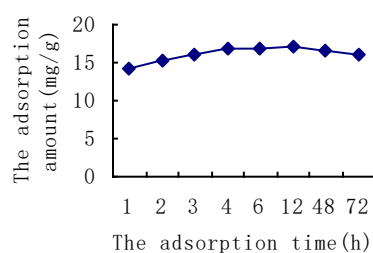


Fig. 1. The relationship of the adsorption capacity and the adsorption time.

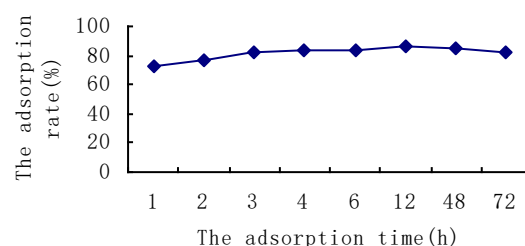


Fig. 2. The relationship of the adsorption rate and the adsorption time.

3.2 The influence analysis of the initial concentration of Cd^{2+} on adsorption

It was observed from Figure 3 and 4 that with the increasing of the initial mass concentration of Cd^{2+} , the adsorption capacity and rate of Cd^{2+} on the manganese dioxide increased gradually, and reached maximum when the mass concentration of Cd^{2+} was 62.94mg/L and 31.47mg/L, respectively, and then both decreased gradually. Because the adsorption rate is a specific value of the adsorption capacity and the mass concentration of Cd^{2+} , it increased at the beginning of the experiment when the increasing of the adsorption capacity was more than the one of the mass concentration of Cd^{2+} , however, when the mass concentration of Cd^{2+} was 31.47mg/L, the increasing of the adsorption capacity was less than the one of the mass concentration of Cd^{2+} , the adsorption rate reached maximum, 96.5%, and then started to decrease.

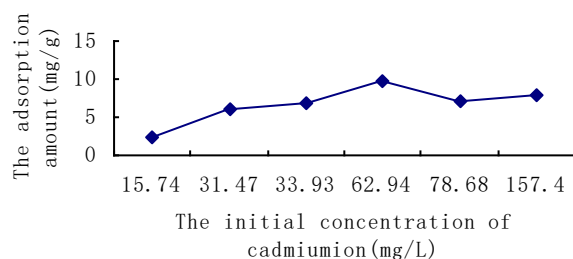


Fig. 3. The relationship of the initial concentration of Cd^{2+} and the adsorption capacity.

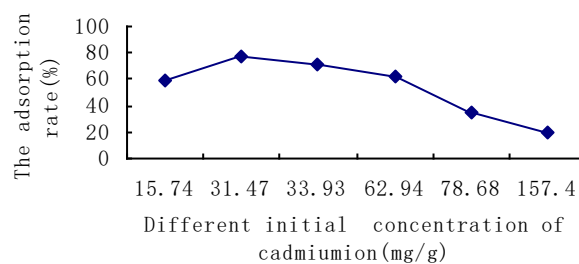


Fig. 4. The relationship of the initial concentration of Cd^{2+} and the adsorption rate.

It could be observed from the isothermal adsorption curve that the solution concentrations increased at the time of the adsorption equilibrium with the increasing of initial concentration of the solutions, and the adsorption capacity increased as well.

In order to explore further the relationship between the solution concentration and the adsorption capacity at the time of the adsorption equilibrium, the isothermal adsorption curve was fitted by the Langmuir isothermal adsorption curve and the Freundlich adsorption curve.

It could be observed from the fitted equations and the correlation coefficients that the adsorption curve of Cd^{2+} on the manganese dioxide in the experiment was more suitable for the Langmuir isothermal adsorption curve, compared with the Freundlich adsorption curve ($R^2=0.3298$); the correlation of both curves was better ($R^2=0.9784$) (Fig. 6.).

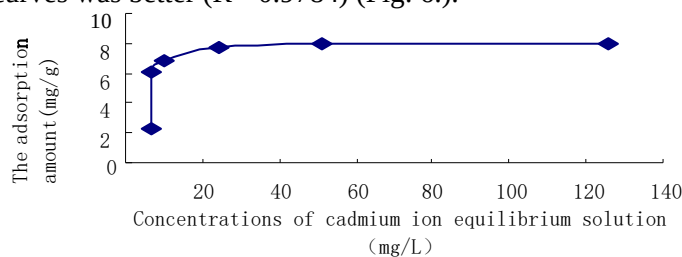


Fig. 5. The isothermal-adsorption curve

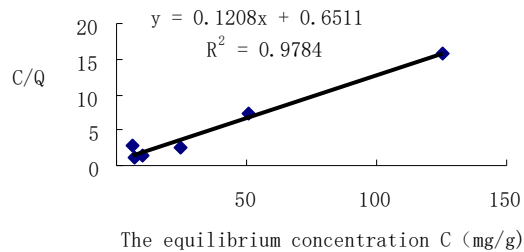


Fig. 6. The relationship of C/Q and C in the adsorption equilibrium of the manganese dioxide

3.3 The influence analysis of different pH values on adsorption

From 3.5 to 5 of pH value, the adsorption capacity of Cd^{2+} on the manganese dioxide decreased, and reached minimum, 14.097 mg/g, when pH value was 5; the adsorption capacity and rate both increased gradually when pH value was more than 5 (Fig. 7 and 8). The adsorption capacity and rate both increased rapidly when pH value was about 7; and then they increased slowly when pH value was more than 7, i.e. alkaline condition; they both reached maximum when pH value was 11. In addition, when pH value was about 8.2, a white floccule, i.e. cadmium hydroxide, was generated in the solutions of cadmium chloride. Hence, at the moment of $\text{pH} \geq 8.2$, the adsorption capacity included the cadmium sediments combined by hydroxyl ions. Under normal circumstances, when pH value was 7–8, the white floccules, i.e. cadmium hydroxide, were not generated in the cadmium chloride solutions.

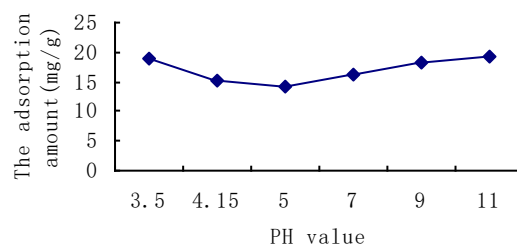


Fig. 7. The relationship of the adsorbing capacity and the pH value

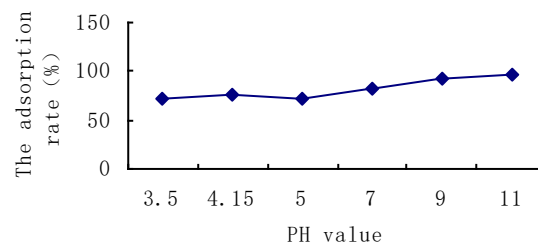


Fig. 8. The relationship of the adsorption rate and the pH value

Two reasons could be used to account for the growing of the adsorption capacity and rate of cadmium ions with the increasing of the pH value. On the one hand, when pH value increased, cadmium ions were hydrolyzed more easily and formed the oxyhydrogen complex, $\text{Cd}(\text{OH})^+$, which were adsorbed more easily by iron and manganese oxides; on the other hand, the increasing of pH value lowered the positive potential on the surface of manganese dioxides, and increased the concentration of the hydroxyl anions, which increased negative charges on the surface of the adsorbents, leading to the increasing of the adsorption.

3.4 The influence analysis of different inorganic salt mediums on adsorption

The adsorption capacity and rate of Cd^{2+} on manganese dioxide both decreased when 25ml KCl, NaCl and CaCl_2 solutions of 0.1mol/L were respectively added into the solutions in the experimental procedure 2.4; but when NH_4HCO_3 solutions were added into the solutions, the adsorption capacity and rate of Cd^{2+} increased slightly, compared with the check sample not added by inorganic salt mediums. The sequence, from large to small, of the adsorption capacity was NH_4HCO_3 , none, KCl, NaCl and CaCl_2 , according to the inorganic salt mediums added; the sequence, from large to small, of the adsorption rate was NH_4HCO_3 (99.90%), none (99.26%), NaCl (92.61%), KCl (91.92%) and CaCl_2 (91.77), according to the inorganic salt mediums added (Fig. 9 and 10).

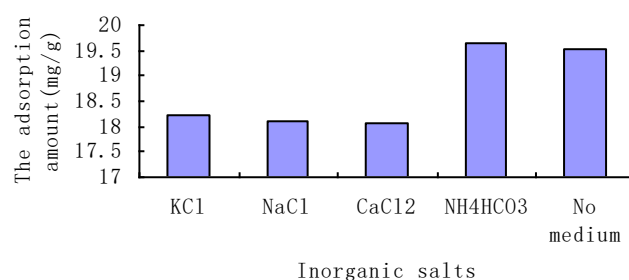


Fig. 9. The relationship of the adsorption capacity and the inorganic salts

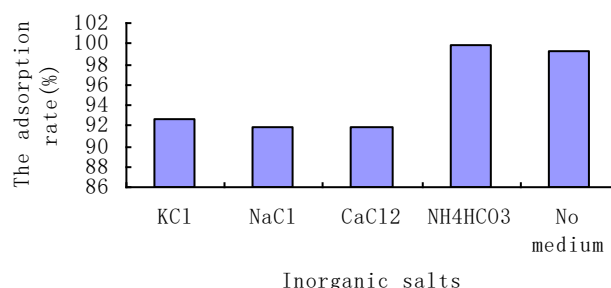


Fig. 10. The relationship of the adsorption rate and the inorganic salts

Generally speaking, positive ions and the Cd^{2+} established patterns of competitive adsorption, leading to fight for the adsorption sites of the mineral surfaces; moreover, different electrolytes changed pH values in the solutions, and some inorganic ligands in the solutions and Cd^{2+} could combine into CdCl^+ , CdOH^+ , $\text{Cd}(\text{OH})_2$, $\text{Cd}(\text{OH})_3^-$, CdOHCl , and CdCO_3 , which accounted for the influences of different electrolytes on the adsorption capacity and rate of the manganese dioxides. When the solutions of KCl, NaCl and CaCl_2 were added into the samples, the positive ions of inorganic salts and the Cd^{2+} could establish patterns of competitive adsorption, and fight for the adsorption sites of the mineral surfaces, leading to the decreasing of the adsorption capacity and rate of Cd^{2+} on manganese dioxides.

There reasons could accounted for the phenomenon that the NH_4HCO_3 added into the samples could promote the adsorption behaviors of Cd^{2+} on manganese dioxides. Firstly, the NH_4HCO_3 happened the double hydrolysis, leading to the growing of pH value in the solutions. The sediments of cadmium hydroxides were formed when pH values in the solutions were more than 7, which resulted in occurring the sediment adsorption, i.e. $\text{NH}_4^+ + \text{HCO}_3^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O} + \text{CO}_2$, $\text{Cd}^{2+} + \text{OH}^- = \text{Cd}(\text{OH})_2 \downarrow$. Secondly, some sediment adsorptions also were formed in the response equation, $\text{Cd}^{2+} + \text{CO}_2 + \text{H}_2\text{O} = \text{CdCO}_3 \downarrow + 2\text{H}^+$. Thirdly, NH_4^+ and Cd^{2+} happened the complexation, leading to form the complexing adsorption. However, the specific reasons could be required to study further.

4. Conclusions

In the experiment, the influence factors of adsorption behaviors of Cd^{2+} on manganese dioxides were analyzed, the influence mechanisms were ascertained mainly, and the optimum conditions of adsorptions of Cd^{2+} on manganese dioxides were obtained. The major conclusions were showed below.

(1) The adsorption equilibriums of Cd^{2+} on manganese dioxides were achieved in 6 hours, in which the adsorption capacity was 16.946 mg/g.

(2) The absorption rate could reach maximum, 96.5%, when the mass concentration of Cd^{2+} was 31.47mg/L. The adsorption isotherm accorded preferably with the Langmuir isothermy equation.

(3) From 3.5 to 5 of pH value, the adsorption capacity of Cd^{2+} on the manganese dioxide decreased, and reached minimum, 14.097 mg/g, when pH value was 5; the adsorption capacity and rate both increased gradually when pH value was more than 5. The adsorption capacity and rate both increased rapidly when pH value was about 7; and then they increased slowly when pH value was more than 7, i.e. alkaline condition; the adsorbing capacity and adsorption rate both reached maximum when pH value was 11.

(4) The addition of NH_4HCO_3 solutions of 0.1mol/L into the samples could promote the adsorption behaviors of Cd^{2+} on manganese dioxides; but the adsorption behaviors of Cd^{2+} on manganese dioxide were restrained when KCl, NaCl and CaCl_2 solutions of 0.1mol/L were respectively added, the restraining sequence, from large to small, for the adsorption capacity of manganese dioxides was CaCl_2 , NaCl, and KCl, according to the inorganic salt mediums added. With the growing of inorganic salt concentration, the restraining effects for the adsorption behaviors of Cd^{2+} on manganese dioxides were further increased in the same order.

Acknowledgements

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