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EFFECT OF MODIFIED MONTMORILLONITE ON HEAVY METAL POLLUTION IN WATER

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ABSTRACT

With the rapid development of the global economy and society, the problem of heavy metal pollution in water body is increasing, which has seriously endangered the ecological environment and human health. In this paper, taking montmorillonite as one of new mineral materials as the research object, two methods of strong acid activation and organic activation were introduced. Research shows that the adsorption temperature is 30℃, the adsorption time is 8h, and in the 1% hydrochloric acid activated montmorillonite, the adsorption capacity is the best; The molecular weight of 50000 chitosan with montmorillonite in accordance with the quality ratio of 0.25:1 mixture preparation of adsorbent effect is best, and use the adsorbent adsorption Fe^{3+}, Cu^{2+} and Zn^{2+} three kinds of heavy metal ions adsorption balance basically the same, finally got the best adsorbent.

KEYWORDS

modified montmorillonite, heavy metal pollution in water.

1. INTRODUCTION

1.1 HEAVY METAL POLLUTION STATUS QUO

In recent years, the problem of heavy metal pollution in water is very outstanding, rivers and lakes library sediment pollution rate is as high as 80.1%[1]. According to the best of the Yangtze river basin water quality survey, its offshore waters have been varying degrees of pollution, elements including Pb, Cd, Cu, Hg pollution is serious, and Cd, Pb, Hg, the potential activity of big, are more likely to participate in the environment of various kinds of substance reacts[2]. Total mercury in the urban river surface water Ⅲ class standard of water has more than 35.11%, total cadmium over surface water Ⅲ class water standard of 18.46%, 25% of the total lead exceeded[3]. The pollution of heavy metal ions in water environment is also very serious in foreign countries, due to the discharge and mining of smelting waste, the surface water of Poland is not up to the three grade[4]. These pollutants has brought serious harm to aquatic animals, aquatic plants and human health, if not dealt with, the ultimate threat to human beings themselves. As all know the pollution of heavy metal ions in water environment has become a worldwide problem of environmental pollution.

1.2 THE SOURCE OF HEAVY METAL IN WATER

In general, the main sources of pollution for the mining, waste rock, concentrating mill, nonferrous metal smelting processing plants, electroplating plants, steel plants and electrolysis, pesticides, pharmaceuticals, paints and pigments and other industries. See Table 1 for details.

1.3 TREATMENT TECHNOLOGY OF HEAVY METALS IN WATER

After gradually understanding the dangers of heavy metal pollution, A lot of researches have been done on the harm of heavy metal pollution, many methods are proposed, including: chemical method, ion exchange method, sulfuration method, electrolysis method, activated carbon method and adsorption method[5]. Adsorption method is a promising method for the treatment of heavy metal ions containing waste water, the use of adsorbent materials, such as clay minerals, activated carbon, molecular sieves, it can't only reduce the concentration of heavy metal ions in water, but also be beneficial to the recovery of precious metals, especially suitable for treating low concentration waste water. Montmorillonite has been widely used because of its good adsorption effect.

TABLE 1: THE SOURCES OF HEAVY METALS AND ION TYPES IN WATER

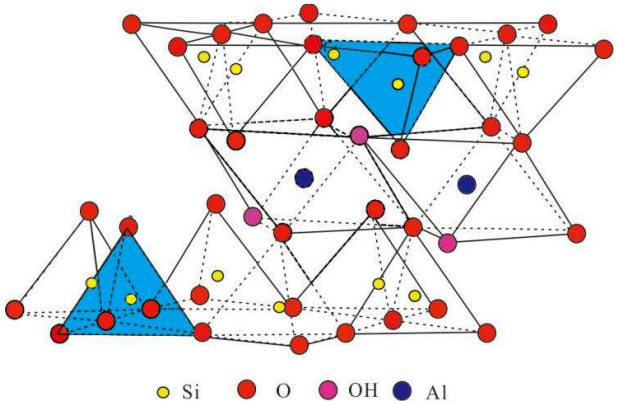
Toxic element	The main ion type in water	Source	
		Natural mineral	Anthropogenic sources
As	AsO_2^-, Arsenite AsO_4^{3-}, Arsenate	FeAsS, As_2S_3 AsO_2, $FeAs_2$ As_4S_4	Removing agent Chemical fertilizer Wash the prepreg
Cd	Cd^{2+}	$CdCO_3$, CdS, CdO	Electroplating,Paint,Photography
Cr	Cr^{3+} CrO_4^{2-}, Chromate $Cr_2O_7^{2-}$, Dichromic acid	$FeCr_2O_4$	Metal plating Industrial pigments Ink
Pb	Pb^{2+}	PbO, PbS, $PbCO_3$, $PbSO_4$	Cars, Ship sfuel, Ammunition
Hg	Hg_2^{2+}, Mercuric Aminochloride Hg^{2+}, mercury	Hg_2Cl_2, HgS, HgO	Production of chlorine, Electronic industry, Pesticides, fungicides
Se	SeO_3^{2-}, Selenite SeO_4^{2-}, Selenate	Trace elements in sulfide minerals	Copper smelting
Ag	Ag^+	Ag_2O, AgCl, AgS, AgF	Electroplating, Food, Beverage processing

2. THE SUMMARY OF MONTMORILLONITE

2.1 INTRODUCTION OF MONTMORILLONITE

Montmorillonite is a kind of clay mineral, which is composed of nanometer particles, also known as microcrystalline kaolinite. The crystal structure of montmorillonite is between two layers of silicon oxygen tetrahedron with a layer of alumina or eight aspect of -OH, between the silicon oxygen tetrahedron and alumina octahedral oxygen atoms connected by shared tetrahedral top and the eight sides relative[6]. The specific structure is shown in Figure 1. Because of this kind of clay mineral is abundant in nature and so, it has always been valued.

FIGURE 1: STRUCTURE DIAGRAM OF MONTMORILLONITE



The binding force between the layers of montmorillonite is small and it is easy to break into fine particles, water molecules or polar molecules can easily enter between the two crystal layers. Therefore montmorillonite has good expansibility, dispersibility and suspension property in the solvent[7]. In addition, montmorillonite has strong commutativity, water absorption and adsorption, which is an important structural characteristics of montmorillonite.

2.2 MODIFICATION OF MONTMORILLONITE

(1) ACID ACTIVATION MODIFICATION

The purpose of acid activation is to change the physical and chemical properties of montmorillonite and improve its performance. The activity, adsorption property and specific surface area of montmorillonite modified by acid are better than that of original montmorillonite. Acid activated montmorillonite are selected strong acid, such as hydrochloric acid, sulfuric acid, phosphoric acid or mixed acid. Weak acid such as acetic acid, carbonic acid and so on, because of its weak acidity, the number of ionization is less, the effect of montmorillonite treatment is not as good as strong acid, so the general acid activation of the selection of strong acid. But the concentration of acid should be controlled in a certain range, otherwise it will affect the effect of activation. The essence of acid activated montmorillonite is that after the acid treatment, many loose pores are produced. This is due to the strong acid dissolved in the montmorillonite layer between the oxide impurities, make it into soluble metal salt. However, the smaller radius of H^+ and the larger radius of Ca^{2+}, Mg^{2+}, K^+ and other cations exchange, resulting in the filling of the pores appear[8]. At the same time, the acid can dissolve the Al^{3+}, Fe^{3+} and Mg^{2+} ions in the oxygen octahedron, and the results also make channel increases, specific surface area increased. After the activation of the acid and the permeation of the ions, the montmorillonite structure is loosened and its specific surface area increases and the number of adsorption sites increases. As a result, the adsorption capacity of montmorillonite.

(2) ORGANIC MODIFICATION

There are many inorganic cations and silicon tetrahedron and aluminum oxide octahedral also exist in some metal cations in the montmorillonite layer and the surface, so that montmorillonite has a hydrophilic oleophobic nature, so in organic matter is not easy to disperse and easy to adsorb organic material[9]. In order to make montmorillonite can be very good with organic matter and organic adsorption of organic matter, the need for organic modification of montmorillonite. The organic modification of montmorillonite is mainly through the exchange of organic cations with inorganic cations in montmorillonite to alter the cationic form of montmorillonite surface and interlayer, to make it from hydrophilic to lipophilic, and organic matter can be very good solution. At the same time, due to the exchange of the long chain organic cations between inorganic cations in montmorillonite layer, the interlayer spacing of montmorillonite increases, the larger organic molecules can be allowed to enter into the interlayer to be exchanged for adsorption, so that it can absorb the type of material greatly increased[10]. Through the organic modification, the interface polarity of the montmorillonite surface and the chemical microenvironment of the surface and the interlayer are improved, and the affinity of the montmorillonite and the organic phase is increased, it can be used to interact with larger organic molecules and polar groups, which will not cause the destruction of the main structure of montmorillonite.

(3) INORGANIC MODIFICATION

The principle of inorganic modified montmorillonite is exchanged by the addition of one or more inorganic metal hydrated cations and interchangeable cations between montmorillonite layers, balancing its own negative charge. At the same time due to the role of the inter-layer solvent can be peeled off into thinner single crystal, through the dry roasting treatment, the formation of pillared association structure, opening montmorillonite layer to form a larger space. Thereby changing the dispersion state and performance of montmorillonite in water, improving the adsorption capacity and ion exchange capacity[11].

(4) INORGANIC-ORGANIC COMPOSITE MODIFICATION

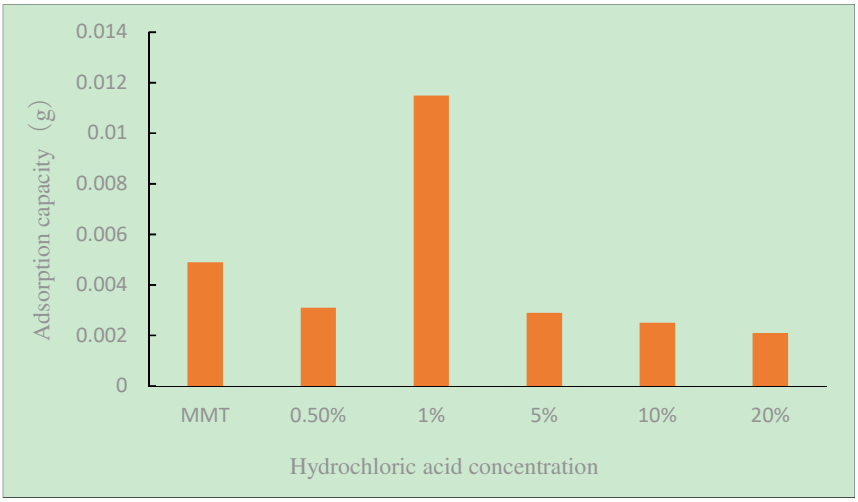
This method is the combination of two methods of inorganic modification and organic modification. This method is the first montmorillonite inorganic modification, and then inorganic modified montmorillonite for organic modification, this can reduce the amount of organic modifier, from the cost-saving point of view is a good way.

3. ADSORPTION OF HEAVY METALS BY MODIFIED MONTMORILLONITE

3.1 ACID ACTIVATION MODIFICATION

As the adsorption capacity of montmorillonite is weak, it is necessary to modify for improve its adsorption performance. A series of different acid activated montmorillonites were prepared by the addition of different concentrations of hydrochloric acid to montmorillonite as an adsorbent to adsorb Co^{2+} particles as an example. The adsorption capacity of Co^{2+} with different concentration of hydrochloric acid activated montmorillonite is shown in Figure 2.

FIGURE 2: ADSORPTION OF Co^{2+} BY DIFFERENT CONCENTRATIONS OF HYDROCHLORIC ACID ACTIVATED MONTMORILLONITE



It can be seen from the figure that the adsorption capacity of 1% hydrochloric acid activated montmorillonite is better than other concentrations of hydrochloric acid activated montmorillonite and acidified montmorillonite. The reason for this is that when 1% hydrochloric acid is immersed in montmorillonite, the soluble metal oxide and other acid-soluble impurities present in the montmorillonite are first dissolved, and the oxide is converted into a soluble ion. At the same time, H+ can interact with the montmorillonite layer to exchange exchangeable cations. Al^{3+}, Mg^{2+}, Fe^{2+} ions in the aluminum oxide octahedron and silicon tetrahedron can also be replaced by smaller H^+. So that the structure of montmorillonite become more lax, the channel increased, increased than the surface of trifoliate orange. At the same time, since H^+ replaces the polyvalent metal ions, the montmorillonite structural units are negatively charged, and the negatively charged ions can be adsorbed negatively charged negatively charged. Therefore, 1% hydrochloric acid activated montmorillonite has a strong adsorption capacity.

In addition, the adsorption temperature and adsorption time also have a certain impact on the adsorption capacity of the modified montmorillonite. The results showed that the adsorption capacity was the best when the adsorption temperature was 30 °C and the adsorption time was 8h, and the adsorption capacity of 1% hydrochloric acid was the highest. The adsorbent was used as raw material to adsorb Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+} respectively, and the maximum adsorption capacity was $Fe^{3+}>Ni^{2+}>Cu^{2+}>Zn^{2+}$[12].

3.2 ORGANIC MODIFICATION

Montmorillonite and molecular weight of 4 million, 2×10^5, 5×10^4 and 3000 of the four chitosan as raw materials, a series of chitosan-montmorillonite composite adsorbents were prepared by using chitosan sol and montmorillonite at a mass ratio of 0.25: 1. As a raw material to the trace of the solution and the constant heavy metal particles adsorption.

(1) TRACE ADSORPTION AND CONSTANT ADSORPTION

Trace adsorption refers to the initial concentration of heavy metal ions in the solution of the order of 10^{-6} (g / ml) or even lower concentration. Select heavy metal Co^{2+} as the object of adsorption.

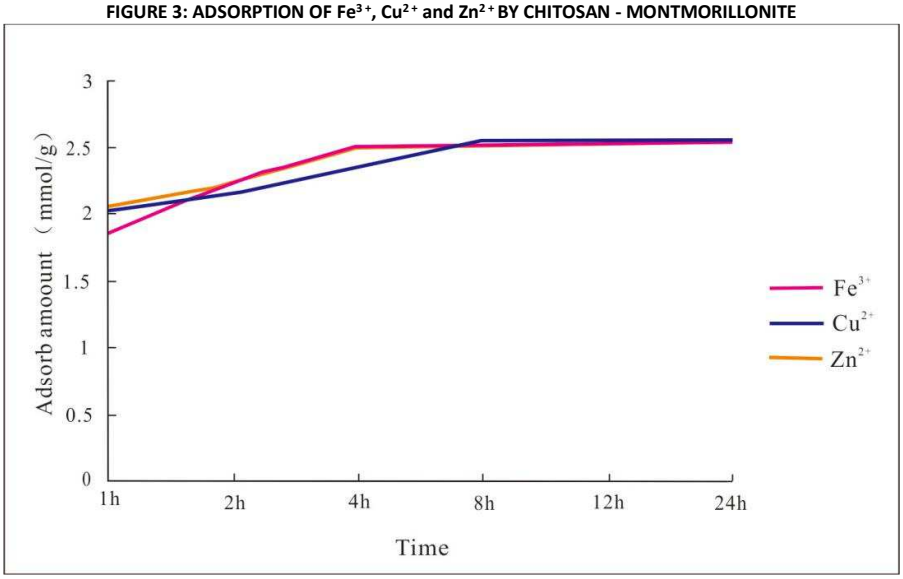
At 0.5 h and 1 h, the initial concentration of Co^{2+} was 8.25×10^{-6} g / ml, comparison of adsorption rates of chitosan, montmorillonite and chitosan montmorillonite composite. The adsorption capacity of four kinds of molecular weight chitosan on montmorillonite was larger than that of non loaded montmorillonite and chitosan. The maximum adsorption rates of chitosan - montmorillonite complex were 90.99% and 97.34% at 0.5h and 1h. The reason is that chitosan itself can be combined with heavy metal ions by chelation to remove heavy metal ions, when chitosan is supported on montmorillonite, a functional group on the chitosan molecule replaces an adsorption site on montmorillonite, and more than one chitosan molecule has a chelating effect with heavy metal ions, and there are multiple groups exist, coupled with the adsorption capacity of montmorillonite itself, the two superimposed, so that the adsorption rate greatly improved[13].

Constant adsorption refers to the initial concentration of heavy metal ions in the solution to a concentration of 10^{-4} (g / ml) or more, which is greater than the cation exchange capacity of the adsorbent

(2) ADSORPTION OF CHITOSAN - MONTMORILLONITE FOR DIFFERENT METAL PARTICLES

The composite prepared by chitosan with molecular weight of 50 thousand and and montmorillonite at a mass ratio of 0.25: 1 was used as the adsorbent. Respectively, adsorption of Fe^{3+}, Cu^{2+} and Zn^{2+} three kinds of heavy metal ions, and resulting adsorption curve is shown in Figure 3.

FIGURE 3: ADSORPTION OF Fe^{3+}, Cu^{2+} and Zn^{2+} BY CHITOSAN - MONTMORILLONITE



Through the comparison of the adsorption curve, it can be seen that the adsorption curves of the three ions are almost coincident, so the equilibrium adsorption capacity is basically the same, indicating that the maximum adsorption capacity of chitosan montmorillonite composite to different heavy metal ions was the same. And the adsorption curves of Fe^{3+} and Zn^{2+} are basically coincident between 2-24h, indicating that the adsorption behavior of the two adsorbents is basically the same. Therefore, the adsorption capacity of Fe^{3+}, Cu^{2+} and Zn^{2+} adsorbents adsorbed by chitosan with molecular weight of 50 thousand and and montmorillonite at a mass ratio of 0.25: 1 was basically the same, and the adsorption effect was the best.

4. CONCLUSION

Montmorillonite has a layered structure, a large specific surface area, exchangeable inter-layer cation and other properties to eliminate heavy metal ions in the pollution has a significant advantage. But due to the presence of impurities such as oxides, resulting in reduced adsorption capacity. In order to improve the adsorption properties of montmorillonite, it needs to be modified. In this paper, two methods of strong acid activation and organic activation were used to modify montmorillonite, main research contents and conclusions:(1) The adsorption capacity was the best when the adsorption temperature was 30 °C and the adsorption time was 8h, and the adsorption capacity of 1% hydrochloric acid was the highest. The adsorbent was used as raw material to adsorb Fe^{3+}, Ni^{2+}, Cu^{2+} and Zn^{2+} respectively, and the maximum adsorption capacity was Fe^{3+}>Ni^{2+}>Cu^{2+}>Zn^{2+}. (2) The molecular weight of 50000 chitosan with montmorillonite in accordance with the quality ratio of 0.25:1 mixture preparation of adsorbent effect is best, and use the adsorbent adsorption Fe^{3+}, Cu^{2+} and Zn^{2+} three kinds of heavy metal ions adsorption balance basically the same, finally got the best adsorbent.

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