

Utilization of Cr^{3+} -Modified Bentonite to Treat Specific Organic Waste water*

ZHENG Hong^{1,2}, WANG Yang¹, HU Bai-zhong³, LUAN Zhao-kun², ZHANG Qian¹

(1. School of Materials Science and Technology, China University of Geosciences, Beijing 100083;

2. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 10085;

3. Foreign Language Department, China University of Geosciences, Beijing 100083, China)

Abstract: In this paper, Cr^{3+} -modified bentonite was prepared and the adsorption of phenol, 1,4-dihydroxybenzene and aniline that can form hydrogen bonds with water molecules by the Cr-bentonite were studied. The optimal conditions, sample mass, stability and regeneration in the course of adsorption were investigated in detail. COD from garbage leachate as a comprehensive index of organic contaminants was used to examine the experimental effects, and a simple economic comparison with other conventional adsorbents was made. Possible mechanism was discussed.

Key words: Cr^{3+} ; bentonite; specific organic wastewater

CLC number: X703 **Document code:** A **Article ID:** 0529-6579 (2005) S2-0055-06

Montmorillonite is a potential and important material in adsorption/desorption reactions with the environmental pollutants because of its large surface area, large number of interlayer exchangeable inorganic cations and abundance in nature.

Commonly, the adsorption of organic pollutants by montmorillonite is poor because the mineral surfaces are hydrophilic^[1]. Up to date the study on montmorillonite at home and abroad has focused on its organic modification and pillar modification^[2]. The adsorption of specific organic contaminants by high valence metal cation-saturated montmorillonite, however, is found to be obviously improved^[3-7]. Al-saturated smectite adsorbs much greater amount of atrazine than Ca-saturated smectite does^[3]. The adsorption of the herbicide dimepiperate S- (, -dimethylbenzyl) -l-piperidinecarbothioate on homoionic Fe^{3+} -, Al^{3+} -, Ca^{2+} -, and Na^{+} - montmorillonite was studied, with the adsorption capacity decreasing in the order $\text{Fe}^{3+} > \text{Al}^{3+} > \text{Ca}^{2+} > \text{Na}^{+}$ clay^[4]. The stronger adsorption of organic pollutants by high valence metal cation-saturated montmorillonite is generally attributed to stronger H-bonding between more polarized H_2O associated with high valence metal cations than low valence cations. It appears that all these studies are limited to the agricultural chemicals.

The wastewater containing chromium extremely harms the environment and unfortunately is largely produced in economic activities, in which chromium mineral processing, electroplating, leather-making, printing and dyeing have been producing a great amount of wastewater containing chromium. Although chemical precipitation is a main effective way to treat the wastewater, the cost is high and secondary pollution is aptly resulted from treating sludge. Therefore, the utilization of the wastewater containing chromium to prepare the chromium modified bentonite to treat specific organic wastewater is expected not only to recover certain organic compounds, but also to solve the problem of sludge occurring in the course of treating the wastewater containing chromium.

In this paper, phenol, 1,4-dihydroxybenzene and aniline that can form hydrogen bonds with water molecules were studied. In the course of adsorption the optimal conditions, sample mass, stability and regeneration were investigated in detail. COD from garbage leachate as a comprehensive index of organic contaminants was used to examine the experimental effects, and a simple economic comparison with other conventional adsorbents was made.

1 Experimental Materials and Methods

Ca-bentonite used in this investigation, obtained

* 收稿日期: 2005-07-10

基金项目: 中国科学院生存环境研究中心环境水化学国家重点实验室开放基金资助项目 (2001010)

作者简介: 郑红 (1970 年生), 女, 副教授; E-mail: Luanzk@mail.rcees.ac.cn

from Xuanhua City, Hebei Province, is composed of 87.4 % of Montmorillonite, 3.6 % of quartz, 7.3 % of -cubic Quartz, 0.7 % of potassium, and 1.0 % of other materials. Garbage leachate was taken from Beijing Asuwei Garbage Disposal Plant. Phenol, 1, 4-dihydroxybenzene and aniline used in this investigation are analytical reagents.

Five g of Na-bentonite was added into 500 mL of 1 g/L $\text{Cr}(\text{NO}_3)_3$ solution (Generally, the concentration of the electroplating wastewater containing chromium is 1.2 g/L, and that of leather-making is 410 mg/L). The flask was oscillated for 12 hours in the constant temperature oscillator (at (25 ± 0.2) and at 150 r/min). Excessive $\text{Cr}(\text{NO}_3)_3$ was removed by distilled water washings until the supernatant was free of chromium ion, as tested by 1 mol/L NaOH solution. The Cr^{3+} -modified bentonite (i. e. Cr-bentonite) prepared was dried at 70 °C, grinded and sifted out with a 200-meshed sieve.

Adsorption of specific organic contaminants was carried out using batch-equilibration technique in HZS-H water bath and constant temperature oscillator. 0.1 g of bentonite sample was suspended in 20 mL of certain concentration organic solutions in a serial of 100 mL glass plug-contained conical flasks, respectively. The suspensions were oscillated at (25 ± 0.2) °C and 150 r/min until equilibrium was achieved. The equilibrium concentration of organic compounds was determined at the strongest absorption wave with a UV-160 spectrophotometer. The potassiumdichromate method was used to determine COD.

2 Results and Discussion

2.1 Characteristics of the Cr-montmorillonite

The results of X-ray diffraction show that d001 value of Cr-montmorillonite is evidently enlarged, compared with the original Ca-montmorillonite and Na-montmorillonite. The values of Na-, Ca- and Cr-montmorillonite are respectively 1.306 5, 1.501 9 and 1.659 8 nm. Larger interlayer distance can help organic molecules enter the interlayer of montmorillonite. The results of the chemical analysis, shown in Tab. 1, indicate that the contents of Cr_2O_3 in Na-, Ca- and Cr-montmorillonite are respectively 0, 0 and 2.83 %. The fact that the contents of Na_2O and CaO in Cr-montmorillonite are evidently lessened shows that Cr^{3+} has succeeded in exchanging ions with Na^+ and Ca^{2+} . Tab. 1 also indicates that the percent contents of water adsorbed are respectively 7.23 %, 7.80 % and 11.54 %. The higher water content in the Cr-montmorillonite can help integrate more specific organic molecules through hydrogen bonds.

Tab. 1 Contents of CaO , Na_2O , Cr_2O_3 and water adsorbed in different types of montmorillonites %

Montmorillonite types	Na-Mt	Ca-Mt	Cr-Mt
Na_2O	3.87	0.30	0.26
CaO	0.54	1.43	0.31
Cr_2O_3	0	0	2.83
H_2O	7.23	7.80	11.54

2.2 Equilibrium time of adsorption

Adsorption equilibrium of all types of organic compounds can be obtained after 2 hours. With the oscillating time lasting, the adsorption percentages change little.

2.3 Influences of pH values on adsorption

Influences of pH values on adsorption of several specific organic contaminants by the Cr-bentonite are shown in Fig. 1, which show that the adsorption percentages of aniline decreases as increasing pH values. In an acidity environment and a neutrality one, the adsorption percentages change little; but in an alkaline environment, especially in a strong alkaline one, the adsorption percentages of aniline evidently decrease. On the contrary, an alkaline environment helps the adsorption of 1, 4-dihydroxybenzene and phenol, and the adsorption effects are satisfactory at a pH of about 8 for all the organic compounds.

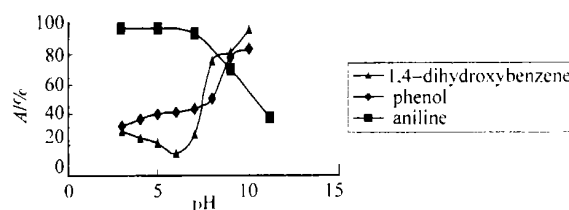


Fig. 1 Influence of pH values on adsorption of the specific organic compounds

2.4 Mass curves of the Cr-bentonite

Without adjusting the pH values (a weak acidity environment), the relationships between the equilibrium concentrations of aniline at different initial concentrations and the masses of the Cr-bentonite are shown in Fig. 2. At initial aniline concentrations of 10, 20 and 30 mg/L, the largest adsorption percentages of aniline are respectively 93.38 %, 88.47 % and 85.82 %. When the equilibrium concentrations of aniline meet the national third-level discharge standard of industrial wastewater for the second category contaminants (5 mg/L), the bentonite masses are respectively 0.10, 0.20 and 7.50 g/mL. With aniline at an initial concentration of 10 mg/L and at its equilibrium concentration meeting the national second-level discharge standard for the second category contaminants (2 mg/L), the bentonite mass is approximately 0.15 g/mL.

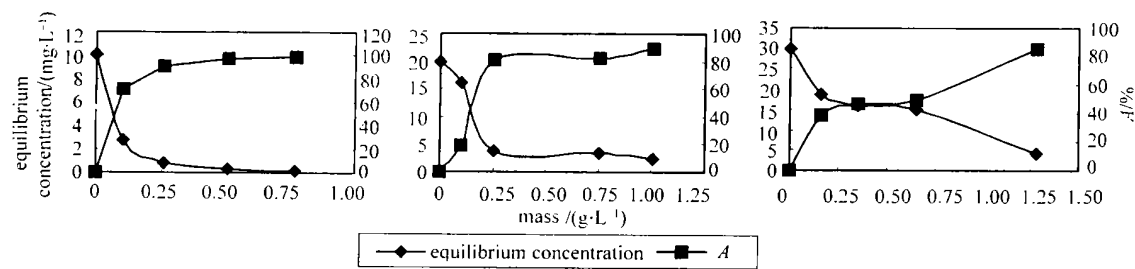


Fig. 2 Mass curves of Cr-bentonite at different aniline initial concentrations

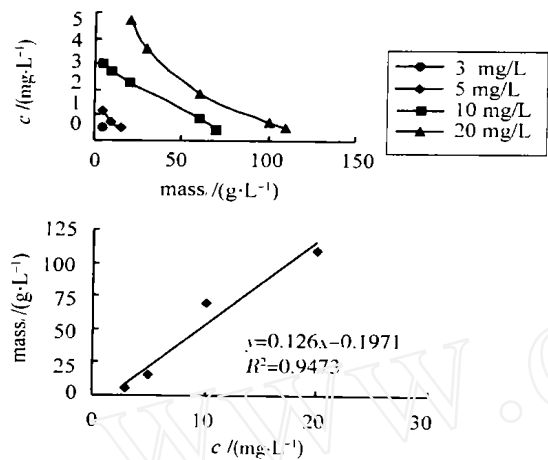


Fig. 3 Mass curves of Cr-bentonite at different initial concentrations of 1, 4-dihydroxybenzene

Under the optimal conditions the mass curves of the Cr-bentonite are shown in Fig.3 when 1, 4-dihydroxybenzene is at the initial concentrations of 3, 5, 10 and 20 mg/L. According to the national first-level discharge standard of industrial wastewater for the second category contaminants (0.5 mg/L for the volatilizing phenol), the masses of the Cr-bentonite are respectively 5.00, 1.50, 7.00 and 11.00 g/L, and the mass equation at different concentrations is $y = 126x - 0.1971$, $R = 0.9473$.

2.5 Comparison of adsorption effects by different 8 types of bentonites

At an optimal pH value, the adsorption effects of original Ca-bentonite, Na-bentonite and the Cr-bentonite were compared. As shown in Tab.2, the adsorption

percentages increase in the order of $\text{Na}^+ < \text{Ca}^{2+} < \text{Cr}^{3+}$ -bentonite.

The adsorption percentages of COD from garbage leachate by three types of montmorillonites were also found to increase in the same order of $\text{Na}^+ < \text{Ca}^{2+} < \text{Cr}^{3+}$ -montmorillonite, nevertheless the types of their interlayerions have less influences on COD, as shown in Tab.2.

2.6 Stability of the Cr-bentonite

The stability of the Cr-bentonite was determined by taking Cr-bentonite to adsorb 1, 4-dihydroxybenzene. 20 mL of 1, 4-dihydroxybenzene at initial concentrations of 10, 50 and 100 mg/L and 0.1 g of Cr-bentonite were added into three different conical flasks. pH values were adjusted at 8. The flasks were oscillated for 2 hours at (25 ± 0.2) and at 150 r/min. Another two samples of Cr-bentonite were soaked respectively in a 20 mL HCl solution where pH=2.0 and a 20 mL NaOH solution where pH=12.0 for 24 hours. A Analyst100 Atomic Adsorption Spectrophotometer was used to determine the Cr³⁺ concentrations of all the supernatant solutions. The results shown in Tab.3 show that the desorption percentages of Cr³⁺ at different 1, 4-dihydroxybenzene concentrations are less than 0.50 % and lessen with the 1, 4-dihydroxybenzene concentration increasing. The desorption percentages in a strong acidity environment are larger than those in a strong alkaline one, but all are less than 5.09 %, and the Cr³⁺ concentrations in the solutions are very low. Secondary pollution can not take place because of the stability of Cr-bentonite in the course of adsorption and fairly acid and base resistant property.

Tab.2 Comparisons of adsorption effects of different types of bentonites

Adsorption percentages	$c_0 / (\text{mg} \cdot \text{L}^{-1})$	Na-bentonite/ %	Ca-bentonite/ %	Cr-bentonite/ %
phenol	10	6.0	9.0	67.5
1, 4-dihydroxybenzene	10	26.2	36.4	80.1
aniline	20	13.8	23.7	88.5
COD from garbage leachate	160.8	34.1	48.0	60.3

Tab. 3 Stability of the Cr-bentonite

Conditions	pH		$c_0/(\text{mg L}^{-1})$		
	2.0	12.0	10	50	100
Desorption percentages/ %	5.09	1.40	0.50	0.44	0.35

2.7 Regeneration of the Cr-benonite

The regeneration effects of the Cr-benonites were studied through their adsorption of 10 mg/L 1, 4-dihydroxybenzene under optimal conditions , as shown in Tab. 4.

Tab. 4 Regeneration of the Cr-bentonite by Heating, acid and base

Effects/ %	105	150	200	acid	base
Original Cr-bentonite	79.2	79.2	79.2	79.2	79.2
First regeneration	62.3	66.5	68.7	63.2	92.7
Second regeneration	61.8	63.1	64.4	—	—
Third regeneration	60.1	61.9	65.3	—	—

The Cr-benonite can be regenerated well by baking for 4 hours at 105 , 150 and 200 . With regeneration times increasing , the adsorption effect goes down , but the adsorption percentages are not less than 60.1 % . The higher the temperature is , the better regeneration effects of the Cr-bentonite are .

The acid regeneration and base regeneration were finished by soaking the Cr-bentonite into an HCl solution where pH = 2.0 and an NaOH solution where pH = 12.0 for 24 hours , then baking for 4 hours at 105 . The results indicate that regeneration effects of the Cr-bentonite are better in an alkaline environment than in an acidity environment , mainly because the suspension solution of the regenerated Cr-benonite in an alkaline environment has a higher pH value , and high pH value helps adsorb 1, 4-dihydroxybenzene .

2.8 A simple economic comparison

The adsorption isotherm of 1, 4-dihydroxybenzene by the Cr-benonite shown in Fig. 4 indicates that its saturated adsorption capacity is 88 mg/g.

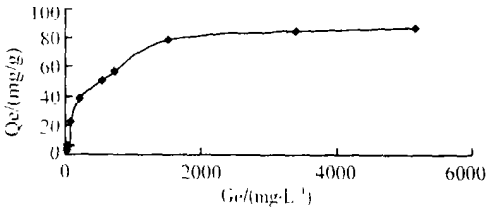


Fig. 4 Adsorption isotherms of 1, 4-dihydroxybenzene by the Cr-bentonite

A simple economic comparison among the active carbon , the organobentonite and the Cr-bentonite used to adsorb phenol compounds is shown in Tab. 5.

Tab. 5 A simple economic comparison about the Cr-benonite¹⁾

	Active carbon	Organobentonite	Cr-bentonite
Adsorption capacity (phenol compounds)	160mg/g	120.5mg/g	88mg/g
price (yuan/kg)	4.6	12.5	0.625
cost (yuan/adsorbing 1 kg of phenols)	28.80	193.00	7.00

1) The offer of the active carbon is ordered by Xinsen Chemical Engineering Co. Ltd. , Ningde City (powder , the phenol value is 160mg/g) ; of the benonite , (Ca-bentonite) by Yixian Bentonite Plant , Hebei Province ; of the organobentonite , by Hualian Organobentonite Plant , Tianjin. The Cr-bentonite can be prepared with the wastewater containing chromium , therefore , the price is close to that of Ca-bentonite .

Tab. 5 shows that the cost of the Cr-bentonite to dispose of 1kg phenol compounds is far less than that caused by the active carbon and the organoobentonite to do the same , meaning that Cr-bentonite has a practicable prospect .

2.9 Possible mechanism

Up to date many researchers think that the reason why montmorillonite with high valence metal cations in its interlayer has a much greater ability of adsorption of the organic molecules is mainly because of that a much greater ability of an interlayer coordination of the high valence cations can bond more water molecules around them , and that the correlation between the OH groups and the organic molecules through hydrogen bonds can adsorb much more organic molecules . The H-bonding mechanism has been strongly proved by the NMR study of montmorillonite to adsorb pyridine^[7] . The results of the experiment in this paper show that Na-montmorillonite and Ca-montmorillonite have a poor adsorption of some specific organic compounds , while the high valence Cr³⁺ can associate much more water molecules owing to its much stronger interlayer coordination ; the OH groups in the water molecules can correlate with phenol , 1, 4-dihydroxybenzene and aniline through the hydrogen bonds , and can thus adsorb much more organic molecules . The function of the hydrogen bonds between the water molecules in the interlayer of montmorillonite that coordinate with the metal cations and the specific organic molecules , according to H-bonding mechanism , is shown in Fig. 5 , taking phenol as an example . The adsorption effects of the chosen organic compounds have also proved this . That means the adsorption effects of aniline are the best , next , 1, 4-dihydroxybenzene and phenol . That is because the strongest electronegativity of N in the aniline molecules and two Os with stronger electronegativity in 1, 4-dihydroxybenzene can help them form hydrogen bonds with water molecules . An experiment of adsorption to dimethylbenzene is also cor-

ducted, finding a very poor result (only 5.5%), because the weaker electronegativity of C of two- CH_3 in the sub-chain of dimethylbenzene cannot form hydrogen bonds with the OH groups in water molecules to be adsorbed, while stronger hydrophilic montmorillonite cannot heavily adsorb hydrophobic dimethylbenzene. That is why all types of montmorillonites adsorb dimethylbenzene quite poorly. COD is a comprehensive index of the content of the organic matter. According to H-bonding mechanism, a very large portion of organic molecules in the garbage leachate that have the atoms with strong electronegativity and less radius can form hydrogen bonds with water molecules that can coordinate with and link the high valence metal ions. That is why the same adsorption of COD occurred compared with the adsorption of phenol, 1, 4-dihydroxybenzene and aniline. Nevertheless, the change of the types of interlayer ions of the montmorillonite has lesser influences on the adsorption of COD than that of phenol, 1, 4-dihydroxybenzene and aniline, because the organic molecules, as of dimethylbenzene, cannot form hydrogen bonds with the water molecules coordinated to be adsorbed.

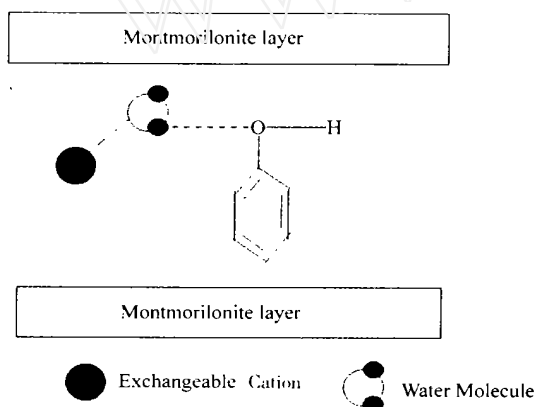


Fig. 5 H bonding between phenol molecule and water molecule coordinated with montmorillonite interlayer surface

3 Conclusions

(1) The adsorption of phenol, 1, 4-dihydroxybenzene and aniline by the Cr-bentonite is evidently better than by original Ca-bentonite and Na-bentonite. The adsorption process reaches equilibrium quickly; different organic compounds possess their own optimal pH values, and the adsorption effects are satisfactory at a pH of about 8 for all the compounds.

(2) Under the experimental conditions, When the equilibrium concentrations of aniline meet the national third-level discharge standard of industrial wastewater for the second category contaminants (5 mg/L) at initial aniline concentrations of 10, 20 and 30 mg/L, the bentonite

masses are respectively 0.10, 0.20 and 12.5 g/L. With aniline at an initial concentration of 10 mg/L and at its equilibrium concentration meeting the national second-level discharge standard for the second category contaminants (2 mg/L), the bentonite mass is approximately 0.15 g/mL.

When the initial concentrations of 1, 4-dihydroxybenzene are respectively 3, 5, 10, and 20 mg/L, and its equilibrium concentrations meet the national first-level discharge criterion of the second category contaminants of industrial wastewater (0.5 mg/L), its sample masses are respectively 5.00, 1.50, 70.00 and 11.00 g/L, with the mass equation as $y = 0.126x - 0.1971$, $R^2 = 0.9473$.

(3) The Cr-bentonite has fairly acid and base resistant property. The secondary pollution can not take place during the adsorption course.

(4) The Cr-bentonite can be regenerated by heating, acid or base. The effect of regeneration is better in an alkaline environment than in an acid environment.

(5) The cost for the Cr-bentonite to treat specific organic contaminants is far lower than that for active carbon and organobentonite to do the same.

(6) The adsorption effects of the chosen specific organic compounds can be explained by the H-bonding mechanism.

References:

- [1] WANG X R, WU S N, LI W S, et al. Progress on recovery of environmental pollution by organoclay [J]. Environmental Chemistry, 1997, 16 (1): 1 - 14.
- [2] WU P X, ZHANG H F, GUO J G, et al. Adsorption of phenol on organic - inorganic pillared montmorillonite [J]. Geochimica, 1999, 28 (1): 58 - 68.
- [3] SAWLINEY B L, SINGH S S. Sorption of atrazine by Al- and Ca-saturated smectite [J]. Clay and Clay Minerals, 1997, 45 (3): 333 - 338.
- [4] PUSINO A, LIU W, GESSA C. Dimefipate adsorption and hydrolysis on Al^{3+} , Fe^{3+} , Ca^{2+} , Na^+ - montmorillonite [J]. Clay and Clay Minerals, 1993, 41 (3): 335 - 340.
- [5] ALBA P, ILARIA B, GESSA C. Adsorption and degradation of triasulfuron on homoionic montmorillonite [J]. Clay and Clay Minerals, 2000, 48 (3): 19 - 25.
- [6] ALBA P, ILARIA B, GESSA C. Adsorption of two quinolinecarboxylic and herbicides on homoionic montmorillonite [J]. Clay and Clay Minerals, 2003, 51 (3): 143 - 149.
- [7] UKRAINYK I, SMITH K. Solid state ^{15}N NMR study of pyridine adsorption on clay minerals [J]. Environmental Sciences and Technology, 1996, 30: 3167 - 3176.

Cr^{3+} 改性膨润土用于处理特定有机废水的实验研究

郑 红^{1,2}, 王 扬¹, 胡百忠³, 栾兆坤², 张 金¹

(1. 中国地质大学材料科学与工程学院, 北京 100083;

2. 中国科学院生态环境研究中心, 北京 100085;

3. 中国地质大学外语系, 北京 100083)

摘 要: 制备了 Cr^{3+} 改性膨润土并用于吸附苯酚、对苯二酚和苯胺。研究了吸附过程的适宜条件、投样量、样品稳定性及再生情况。以 COD 为综合指标检测了处理垃圾渗滤液的实验效果, 并与常见的吸附剂进行了简单的经济技术对比。对可能的机理进行了探讨。

关键词: Cr^{3+} ; 膨润土; 特定有机废水

中图分类号: X703

www.cnki.net