Use of Chitosan-modified Bentonite for Removal of Cu^{2+}, Cl^- and 2,4-Dichlorophenoxyacetic Acid (2,4-D) from Aqueous Solution

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Batch experiments were performed to investigate the removal of Cu^{2+}, Cl^-, and 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solution using chitosan-modified bentonite. When the chitosan was loaded on the bentonite, the inter-layer space of the montmorillonite increased and the adsorption efficiency enhanced, as chitosan contains large numbers of $-NH_2$ and $-OH$ functional groups that could serve as coordination sites to bind heavy metals. In this study, the bentonite that was prepared through three procedures: Na_2CO_3 treatment, thermal treatment and compound treatment, was modified by chitosan. Experimental results demonstrated that the average removal rates of Cu^{2+}, Cl^-, and 2,4-D effectively were 94.87 %, 86.19 % and 91.06 %, respectively.

Key words: *Bentonite, chitosan, compound modification, adsorption efficiency*

Introduction

Water pollution and its treatment to avail safe drinking water is a major concern of the 21st century.[1] Various treatment methods have been developed for decontamination purposes, such as adsorption, coagulation, precipitation, filtration, electrodialysis, membrane separation.[2] Adsorption is recognized as one of the most effective processes for the removal of Cu^{2+}, Cl^-, and 2,4-dichlorophenoxyacetic acid (2,4-D) from aqueous solutions in the above mentioned techniques.[3]

Bentonite has attracted a lot of interest over the last century for its versatile application and abundance on most continents of the world.[3–4] It is the most common mineral within the family of 2:1 clays, whose structure is built from two tetrahedral silicate (SiO_4) layers and an octahedral layer of AlO_6, the latter being sandwiched between two tetrahedral layers.[3] The chemical nature and pore structure of bentonite determine its large surface area and therefore good cation exchange capacity (CEC) and adsorption properties. According to the montmorillonite inter-layer exchangeable cation, bentonite can be classified into sodium base bentonite, calcium base bentonite, etc.[4,11–15,23]

Chitosan is the product of the partial N-deacetylation of chitin, which contains large numbers of $-NH_2$ and $-OH$ functional groups that can serve as coordination sites to bind heavy metals.[15] Its chemical name is (1,4)-2-amino-2-deoxy-β-D-glucan. Therefore, the chitosan does not dissolve in water or organic solvents, which limits its wide application.[16] After the chitosan had been loaded onto the bentonite, the amino could combine with the montmorillonite, intercalating part of the chitosan into the montmorillonite layers. As a result, the inter-layer space of the montmorillonite is increased and the adsorption efficiency is enhanced.[17–19]

After raw bentonite (Ca-Bent) was modified by Na_2CO_3 (BNa^+), the rate of water adsorption and the expansion ratio increased. In addition, the BNa^+ has a high CEC and good dispersion in water. Hence, Na_2CO_3 is often used to modify Ca-Bent.

Thermal treatment could increase the specific surface area of the bentonite, which leads to the removal of water from the surface or between the layers.

Modified by a surface active agent and organic chelating agent simultaneously, the bentonite could realize synchronization of organic pollutants and heavy metal ions adsorption, rendering the bentonite more application value.

Overall, each method could enhance the ability of adsorption of modified bentonite separately, however, compound modification could make its water purification effect stronger and more comprehensive.

There are many different kinds of pollutants in wastewater, however, with the development of industry and agriculture, the Cu^{2+}, Cl^-, 2,4-D and residual chlorine are increasingly the main pollutants, so the present study chose Cu^{2+}, Cl^-, and 2,4-D as representatives.

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As far as we know, numerous studies on the modification of bentonite to remove only one pollutant have been carried out, but few have related to the simultaneous removal of several pollutants. This study was therefore designed to test the feasibility of bentonite to simultaneously remove Cu^{2+}, Cl^-, and 2,4-D in aqueous solution after compound modification.

Experimental

Materials

All the chemicals used in this study were of analytical reagent grade. The Ca-bentonite was obtained from Henan region of China. The chemical composition of the bentonite is given in Table 1. Bentonite was characterized with respect to CEC, which was 575.0 mmol kg^{-1}. Low-molecular weight chitosan (degree of deacetylation was 85 %, 90 %, 95 %, respectively) was purchased from Jinan Haidebei Marine Bioengineering Co., Ltd.

Material preparation

Preparation of Na_2CO_3 modified bentonite (BNa^+)

500 g of the raw bentonite was added into the aqueous solution of ethanol (ψ = 1 : 1) to prepare the bentonite slurry. Na_2CO_3 in an amount equivalent to 4 % of the raw bentonite was added into the slurry. The pH of the slurry was adjusted to 9.0. The slurry was then shaken for 2 h in a thermostat shaker (Memmert) at 80 °C with frequency 110 min^{-1}. The slurry was centrifuged in a centrifuge (Fulgor) at rotational frequency 3000 min^{-1} for 10 minutes. The solid was then washed several times with ultrapure water until the absence of CO_3^{2-} was confirmed with $Ca(OH)_2$ test. The sample was subsequently dried at 105 °C for 4 h.[20]

Thermal treatment of sodium bentonite

The BNa^+ was heated in the oven at 450 °C for 2 h and then cooled down to room temperature.[21]

Compound modification of bentonite

100 g of the thermal-treated BNa^+ was added into 1000 ml of solution containing 20 g of cetrimonium bromide (CTMAB). The amount of the surfactants equalled 1.5 times CEC of the bentonite. The suspension was shaken at 30 °C for 2 h and mixed with 200 ml of metal chelating agent solution containing 20 g metal chelating agent (Am). The suspension was shaken at 30 °C for 12 h. After sitting for a moment, the sample was filtered and washed several times with ultrapure water until the absence of bromide ions was confirmed with $AgNO_3$ test. The solid was then dried, crushed, ground, and sieved through a 100-mesh and placed in a desiccator.[22] Then the adsorption experiments were conducted to select the bentonite which had the optimal adsorption efficiency (B-Am).

Chitosan modifications

The selection of degree of deacetylation (Dd)

0.5 g of chitosan (degree of deacetylation was 85 %, 90 %, 95 %, respectively) was dissolved with 50 ml of oxalic acid solution (φ = 2 %). 25 g of B-Am was added into the solution and reacted at 50 °C in a water bath for 2 h with constant stirring. Then the mixture was dried, crushed, ground, and sieved through a 100-mesh and placed in a desiccator.[17] Thereupon the adsorption experiments were conducted to select the bentonite which had the optimal adsorption efficiency (B-Am-Dd).

The selection of mass ratio (bentonite to chitosan)

0.5 g B-Am-Dd was dissolved with ultrapure water with strong stirring for 2 h. Then 1.0 % chitosan solution was added step by step under certain temperature. Mass ratio was 1 : 0.005, 1 : 0.01, 1 : 0.02, 1 : 0.04, and 1 : 0.05, respectively. The solution was shaken for 2 h at 50 °C and cooled down to room temperature. Then the sample was filtered under reduced pressure, dried, crushed, ground, and sieved through a 100-mesh and placed in a desiccator.[17]

Adsorption experiments

The modified bentonite was added into 50 ml of $CuCl_2$ solution with the concentration of Cu^{2+} being 15 mg l^{-1}, 50 ml of 15 mg l^{-1} 2,4-D solution, 50 ml of tap water, respectively. The suspension was shaken at 25 °C with frequency 110 min^{-1} for 12 h and centrifuged at frequency 4000 min^{-1}. Then the residual quantity of Cu^{2+}, Cl^-, and 2,4-D was detected, the adsorption efficiency was compared.[17,22] All adsorption experiments in this study were performed in triplicate and the results are given as average. Adsorption efficiency was calculated from equation:

$$R = (\gamma_0 - \gamma_t)/\gamma_0.$$

Results and discussion

Characterization

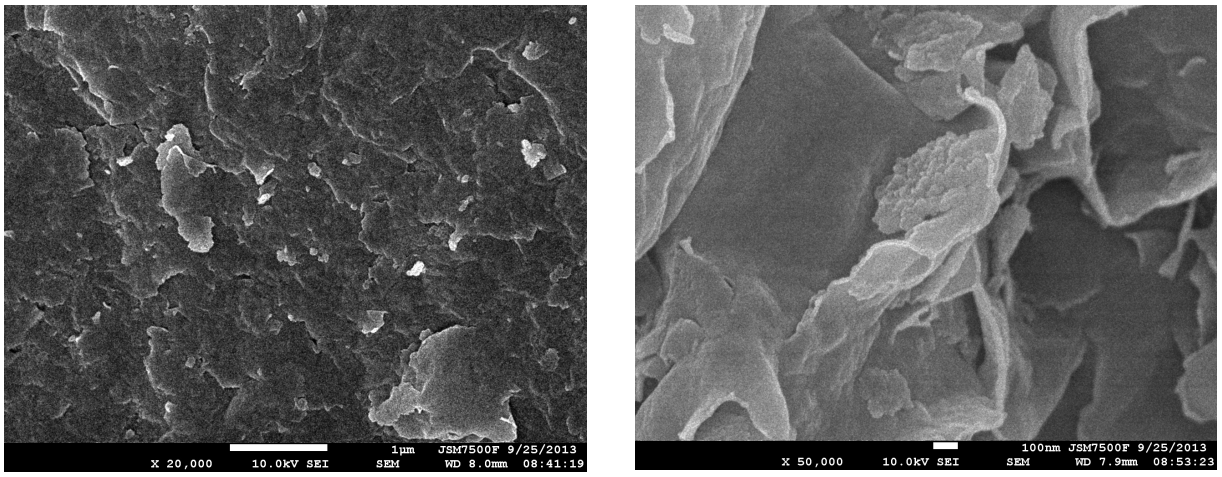
Fig. 1 shows the SEM images of raw and modified bentonite by chitosan. Its distinct appearance after modification may be seen from Fig. 1. The structure of the raw bentonite is inseparable, with only a few holes on the surface, while the surface of the bentonite modified by chitosan is obviously loose and uniform. In addition, we can see the chitosan is indeed loaded on the bentonite.

The effect on the adsorption efficiency of bentonite

The bentonite, prepared by Na_2CO_3 and thermal treatment, was modified by CTMAB and metal chelating agent nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), citric acid (CA), respectively. Cu^{2+}, Cl^-, 2,4-D and residual chlorine were removed by five different adsorbents: bentonite (B), bentonite modified by CTMAB (BC), benton-

Table 1 – *Chemical composition of Ca-bentonite*
Tablica 1 – *Kemijski sastav kalcijeva bentonita*

$w(SiO_2)$/%	$w(Al_2O_3)$/%	$w(Fe_2O_3)$/%	w(CaO)/%	w(MgO)/%	$w(Na_2O)$/%	$w(K_2O)$/%
54.90	27.71	2.82	0.08	1.85	3.14	0.08



(a) **(b)**

Fig. 1 – *SEM of raw (a) and modified (b) bentonite*
Slika 1 – *SEM-prikaz neprerađenog (a) i modificiranog (b) bentonita*

ite modified by CTMAB and NTA (BCN), bentonite modified by CTMAB and EDTA (BCE), bentonite modified by CTMAB and CA (BCC). Then the adsorption efficiency was compared.

Table 2 shows that after the bentonite was treated by CTMAB, the change of the adsorption efficiency on Cu^{2+} and residual chlorine was not obvious, while the adsorption efficiency on 2,4-D increased significantly from 37.51 % to 73.77 %.

Table 2 – *Adsorption performance of differently modified bentonites*
Tablica 2 – *Adsorpcijska učinkovitost različitih modificiranih bentonita*

Adsorbents Adsorbensi	*R*/%		
	Cu^{2+}	Cl^-	2,4-D
B	34.53	28.04	37.51
BC	51.46	47.05	73.77
BCN	78.13	67.01	74.05
BCE	67.20	59.49	68.99
BCC	63.80	60.76	61.42

Interlayer cations of silicon structure hydrolysis, producing a layer of water film between the raw bentonite layers, so the raw bentonite cannot adsorb 2,4-D effectively. However, along with the surfactant cations deposit on the layers of bentonite, the alkyls of the surfactant are embedded into the interlayer space, forming a layer of organic phase and increasing the interlayer space simultaneously. Both results help improve the adsorption efficiency of 2,4-D. For Cu^{2+} and Cl^-, the formation of organic layer has a disadvantage on the adsorption, while the increase in interlayer space improves the adsorption ability. So the adsorption efficiency for the two ions was the synthetic result of the two competing influences.

Table 2 also shows that the adsorption efficiency of Cu^{2+} obviously increased after the treatment by Am. When Am was NTA, the adsorption efficiency can be obtained from 34.53 % to 51.64 % to 78.13 %, was the highest. The results indicated that the effect of NTA was better than EDTA and CA, so the BCN was chosen for the further experiment.

Metal chelating agent Am can firmly chelate with Cu^{2+}. The stability of the Am-Cu is NTA > EDTA > CA. The effect of organic chelating agent on the adsorption of Cu^{2+} increases as the stability of the chelate compounds.[20] NTA is small and could provide four coordinate bonds for metal ions, thus showing strong ability of chelation with a variety of metal ions. Therefore, the adsorption efficiency of NTA-pretreated bentonite for Cu^{2+} is the best.[27–34]

Effect of the deacetylation degree of chitosan on bentonite modification

The BCN was modified by the chitosan (0.5 g) of 85 %, 90 % and 95 % deacetylation degree respectively. Then the adsorption efficiency was compared.

Table 3 – *Effect of the deacetylation degree of chitosan on adsorption of modified BCN bentonite. Mass ratio of bentonite to chitosan was 1 : 0.01.*
Tablica 3 – *Utjecaj stupnja deacetiliranja kitozana na adsorpciju modificiranog bentonita BCN. Maseni omjer bentonita i kitozana iznosi 1 : 0.01.*

Degree of deacetylation Stupanj deacetiliranja	*R*/%		
	Cu^{2+}	Cl^-	2,4-D
85 %	90.33	79.64	89.41
90 %	94.87	86.19	91.06
95 %	94.03	84.98	91.01

Table 3 shows that when the degree of deacetylation of chitosan was 90 %, the best efficiencies could be obtained and they are 94.87 %, 86.19 % and 91.06 % for Cu^{2+}, Cl^-, and 2,4-D, respectively.

Compared with the BCN, the adsorption efficiency of bentonite improved obviously after being modified by chitosan. With the chitosan loading on the bentonite (Fig. 1), the positively charged ammonium can combine with the negatively charged montmorillonite, making part of chitosan intercalate into the interlayers of the montmorillonite. As a result, the montmorillonite interlayer spacing was increased and its adsorption efficiency was improved.[15–17]

According to the theoretical, the amount of free amino groups and the positive chitosan ions were observed to increase along with the increase of degree of deacetylation of chitosan. Hence, the loaded capacity of the chitosan on the bentonite and the adsorption efficiency were bound to increase. When the bentonite combines with the chitosan, its property will change and the adsorption ability will be enhanced. The degree of deacetylation was higher, the particle size of the chitosan was smaller and the dissolution of chitosan was more easily. However, the chitosan was difficult to crush. Therefore, the degree of deacetylation of chitosan using in this study was 90 %.[10,37]

The effect of mass ratio on bentonite modification

The bentonite was modified by the chitosan (the degree of deacetylation was 90 %) and the mass ratio of bentonite to chitosan are 1:0. 005, 1: 0.01, 1:0.02, 1:0.04 and 1:0.05, respectively.

Then the adsorption efficiency was compared.

Table 4 – *Effect of mass ratio of BCN bentonite to 90 % deacetylated chitosan on adsorption efficiency of modified bentonite*

Tablica 4 – *Utjecaj masenog omjera bentonita BCN i kitozana deacetiliranog 90 % na adsorpciju modificiranog bentonita*

ζ(bentonite:chitosan) ζ(bentonit:kitozan)	*R*/%		
	Cu^{2+}	Cl^-	2,4-D
1 : 0.005	87.27	73.30	83.26
1 : 0.01	94.87	86.19	91.06
1 : 0.02	92.07	78.93	89.29
1 : 0.04	89.27	71.02	82.32
1 : 0.05	83.47	74.61	81.35

Table 4 shows that after the bentonite was modified by chitosan, the adsorption efficiency for Cu^{2+} and Cl^- increased significantly. When the mass ratio ζ was 1 : 0.01, the best adsorption efficiencies can be obtained and they were 92.06 %, 76.13 %, and 86.43 % for Cu^{2+}, Cl^-, and 2,4-D, respectively.

The adsorption ability of chitosan-bentonite was influenced by the amount of chitosan that got into the interlayer of the bentonite. When the amount increased with the concentration increasing and the amount did not exceed the CEC, the chitosan could introduce $-NH_4$ and $-OH$ to increase the interlayer spacing of montmorillonite. However, when the amount was excessive, the chitosan would result in decreasing the adsorption efficiency by blocking the channel of bentonite.[15–19]

Conclusions

In this study, bentonite modified by chitosan was prepared and applied to the removal of pollutants Cu^{2+}, Cl^-, and 2,4-D from aqueous solution. The preparation of the bentonite, the degree of chitosan deacetylation, and the mass ratio of bentonite to chitosan also was investigated.

The adsorption efficiency of Cu^{2+}, Cl^-, and 2,4-D onto the raw bentonite is very low. It significantly enhanced its adsorption efficiency after modification using chitosan.

2. Optimal preparation was conducted using Na_2CO_3, thermal treatment, and composite compound by CTMAB and NTA. Then the bentonite was modified by chitosan whose degree of deacetylation was 90 %, and the mass ratio of bentonite to chitosan was 1:0.01. This condition was conducted to obtain the best adsorption efficiencies and they were 90.13 %, 75.66 %, and 87.80 % for Cu^{2+}, Cl^-, 2,4-D, respectively.

3. The removal of pollutants Cu^{2+}, Cl^-, 2,4-D from the wastewater was also conducted to evaluate the feasibility of chitosan-bentonite to be used as alternative adsorbent in industrial practice for environmental remediation.

Resume

1. Good physicochemical properties, rich resources and low price are advantages of bentonite. However, raw bentonite is mainly composed of calcium base bentonite (Ca-bent). Because Ca-bent has a low content of montmorillonite, it cannot be used on a large scale.

2. Ca-bentonite could realize comprehensive utilization and yield composite products that have high additional value through composite modification of bentonite, which can improve economic efficiency of the bentonite and avoid the waste of resources, in order to realize the mixture of urban life wastewater and all kinds of industrial wastewater treatment.

3. Bentonite and its modified products will be the ideal choice, instead of the traditional adsorbents, to remediate wastewater.

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List of symbols and abbreviations
Popis simbola i kratica

R	– adsorption efficiency, % – adsorpcijska učinkovitost, %
w	– mass fraction, % – maseni udjel, %
γ_0	– initial mass concentration, mg l^{-1} – početna masena koncentracija, mg l^{-1}

γ_t – final mass concentration, mg l^{-1}
– konačna masena koncentracija, mg l^{-1}

ζ – mass ratio
– maseni omjer

φ – volume fraction, %
– obujamski udjel, %

ψ – volume ratio
– obujamski omjer

2,4-D – dichlorophenoxyacetic acid
– diklorofenoksioctena kiselina

Am – metal chelating agent
– kelatni agens

B – bentonite
– bentonit

B-Am – chelating agent modified bentonite
– bentonit obrađen kelatnim agensom

B-Am-Dd – bentonite modified by chelating agent and deacetylated chitosan
– bentonit modificiran kelatnim agensom i deacetiliranim kitozanom

BC – bentonite modified by CTMAB
– bentonit obrađen CTMAB-om

BCC – bentonite modified by CTMAB and CA
– bentonit obrađen CTMAB-om i CA-om

BCE – bentonite modified by CTMAB and EDTA
– bentonit obrađen CTMAB-om i EDTA-om

BCN – bentonite modified by CTMAB and NTA
– bentonit obrađen CTMAB-om i NTA-om

BNa^+ – bentonite with Na^+ cations
– bentonit s ugrađenim ionima Na^+

CA – citric acid
– limunska kiselina

Ca-Bent – raw bentonite
– neprerađeni bentonit

CEC – cation exchange capacity
– kapacitet izmjene kationa

CTMAB – cetrimonium bromide (hexadecyltrimethylammonium bromide)
– cetrimonijev bromid (heksadeciltrimetilamonijev bromid)

Dd – degree of deacetylation
– stupanj deacetiliranja

EDTA – ethylenediaminetetraacetic acid
– etilendiamintetraoctena kiselina

NTA – nitrilotriacetic acid
– nitrilotrioctena kiselina

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SAŽETAK

Uklanjanje Cu^{2+}, Cl^- i 2,4-diklorfenoksioctene kiseline iz vodene otopine bentonitom modificiranim kitozanom

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Ispitivano je uklanjanje Cu^{2+}, Cl^- i 2,4-diklorfenoksioctene kiseline (2,4-D) iz vodene otopine bentonitom modificiranim kitozanom. U takvu je bentonitu povećana udaljenost među slojevima montmorilonita i time poboljšana adsorpcijska moć. Kitozan sadrži mnogo skupina $-NH_2$ i −OH koje također mogu koordinirati ione teških metala. Prije modificiranja kitozanom bentonit je tretiran vodenom otopinom Na_2CO_3, toplinski je obrađen te obrađen kelirajućim agensom. Modificiranim bentonitom prosječno je iz vodene otopine uklonjeno 94,87 % Cu^{2+}, 86,19 % Cl^- i 91,06 % 2,4-D.

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