Journal of Hazardous Materials B136 (2006) 365–370

Journal of Hazardous Materials

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Multifunctional microsized modified kaolin and its application in wastewater treatment

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Received 8 October 2005; received in revised form 14 December 2005; accepted 14 December 2005
Available online 23 January 2006

Abstract

The multifunctional microsized $ZnO–PO_4^{3-}$-modified kaolin of average diameter about 500 nm with the composition Na_2O:ZnO:Na_3PO_4:SiO_2:Al_2O_3 = 2.5–8.5:0.04–0.65:0.8–4.5:1.5–2.5:1 (molar ratio) were firstly synthesized from ZnO, Na_3PO_4, NaOH and kaolin and characterized by standard techniques, its application in oilfield produced wastewater purification was also studied. It was found that the physical properties of $ZnO–PO_4^{3-}$-modified kaolin such as specific surface area, porous volume and pore diameter increased independently compared to the starting kaolin. It was also found that the prepared kaolin has multifunctional properties to decrease COD and BOD value, remove scaling ion (Fe^{n+}, Ca^{2+} and Mg^{2+}), improve MF, decrease bacteria and inhibit corrosion and can be used effectively in oilfield wastewater purification.

Keywords: Kaolin; Synthesis; Multifunctional; Water purification; $ZnO–PO_4^{3-}$-modified

1. Introduction

The past few years have witnessed a remarkable reemergence of interest in the preparation of pillared layered materials from the pillaring agents of polymeric or oligomeric hydroxyl metal cation formed from the hydrolysis of metal salts of Zr^{4+}, Ga^{4+}, Al^{3+}, Cr^{3+}, Si^{4+}, Ti^{4+}, Fe^{3+}, La^{3+}, Ce^{3+} or mixture of them with kaolin [1–3]. These approaches have demonstrated that some pillared mineral compounds have remarkable properties, such as Al_{13}-pillared layered materials exhibit high catalytic, absorption, ion-exchange properties [4] and Ag^+-modified clay mineral compounds possess high anti-microbial and anti-fungal properties [5,6]. Theoretically, the correct choice of the intercalated compound and the pillaring procedure and activation is essential not only for properly "cementing" the layers and therefore providing high mechanical and thermal stability, but also for generating active sites for uses [7–9]. Therefore, the application of pillared or modified mineral compounds derived from kaolin aroused more interesting in the research area of new material synthesis. However, no $ZnO–PO_4^{3-}$-modified kaolin and its application in wastewater treatment have been reported so far. Here the multifunctional microsized $ZnO–PO_4^{3-}$-modified kaolin materials, aiming at get large specific surface area and pore volume possessing the multifunctional properties of good bactericide, corrosion inhibiting and scaling ion (Fe^{n+}, Ca^{2+} and Mg^{2+}) removal were synthesized and their application in oilfield produced wastewater purification was tested firstly.

2. Materials and methods

2.1. Materials

Kaolin used were analytical grade with the composition of $Al_4[Si_4O_{10}](OH)_8$ (surface area: 20 m^2/g and pore volume: 0.5 cm^3/g). ZnO, Na_3PO_4 and NaOH were analytical grade and used without further purification.

Produced wastewater was collected from Zhongyuan oilfield of China.

2.2. Synthesis of microsized $ZnO–PO_4^{3-}$-modified kaolin

Into 30% (m/m) NaOH solution ZnO was added and stirred till a clear solution formed at room temperature, then Na_3PO_4 solution was dropped in with the molar ratio of

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0304-3894/$ – see front matter
doi:10.1016/j.jhazmat.2005.12.024

Na_2O:ZnO:Na_3PO_4 = 5–50:0.05–1:0–5 and aged at room temperature for 48 h and filtered. Into the filtrate the kaolin was added and stirred about 1 h, then aged 2 h at room temperature to obtain the gel.

The gel prepared were sealed in stainless tube, heated at 100 °C for 2 h in an oven to prompt crystallization, then separated by filtering and washed with hot demineralized water until no free ion was detected. The solid were collected and analyzed.

2.3. Water purification process

Into the produced wastewater, the prepared ZnO–PO_4^{3-}-modified kaolin was added with stirring, 10 min later, water quality index: flocculate rate, chemical oxygen demand (COD), index of membrane filter (MF), bacteria, ion content, pH, suspend solid, corrosion rate were measured according to standard method [10–12].

2.4. Characterization techniques

The silicon, aluminum, zinc and phosphorus contents in the liquid phase were obtained by inductively coupled plasma atomic emission spectroscopy (AES) using ICP/6500 from Perkin-Elmer Inc. and the sodium content were determined by standard atomic absorption spectroscopy method. The elemental composition (silicon and aluminum) of the dry solid was obtained by AES after dissolving it in KOH (20%, m/m) solution. The crystallinity of the sample was determined by powder X-ray diffraction (XRD) using a scanning diffractometer of D/MAX-RA with Ni-filtered Cu Kα radiation (λ = 1.5418Å). A scan speed of 2°/min was used comparing with the intensity of the reflection pattern to that of pure kaolin. Solid morphology and average crystal size were determined by scanning electron microscopy (SEM, Hitachi H-700 instrument) and a gold film was sputtered onto the sample prior to observation (ISI DS-130). The surface area and pore size distribution of the samples were determined by N_2 adsorption–desorption at −197 °C on previously degassed samples at room temperature and 10^{-4} Torr pressure for BET surface area and meso-micropore analysis, macropore analysis was obtained by Hg intrusion, the pore size distribution of the samples was calculated in accordance with the BJH method [13–16].

The pH value of produced water was monitored using an Orion 290 pH meter. Na^+, Cl^-, K^+, Ca^{2+}, Mg^{2+}, $Fe^{2+/3+}$, S^{2-}, CO_3^{2-}/HCO_3^- and SO_4^{2-} were measured using Perkin-Elmer inductively coupled plasma-atomic emission spectroscopy (ICPAES) according to standard methods [10–12]. COD were carried out with a Hach-2000 spectrophotometer using dichromate solution as the oxidant in a strong acid media. BOD was performed by means of a Hg-free WTW 2000 Oxytop unit thermo-stated at 20 °C. Bacteria and corrosion rate were tested by standards methods [10,12].

3. Results and discussion

3.1. Chemical composition

The chemical analyses data of the gel and ZnO–PO_4^{3-}-modified kaolin product was summarized in Table 1. It can be found that the chemical treatment caused a significant change in the composition, i.e. the content in ZnO–PO_4^{3-}-modified product were not identical to that in the gel, especially Na_2O was more significant decreased while the content of Na in the product was several times higher than that in starting kaolin, maybe due to some of Al_2O_3 were dissolved and part of Si–O–Al bond were broken as molar ratio of SiO_2/Al_2O_3 increased from 1.5 to 2.5 when molar ratio of Na_2O/Al_2O_3 was up to 30 in the gel, indicating the modifying procedure was effective in product preparation.

3.2. XRD spectra

The XRD pattern of the kaolin and ZnO–PO_4^{3-}-modified product were shown in Fig. 1. It was found that the starting material consisted primarily of kaolin and a little amorphous component, but the crystallinity of ZnO–PO_4^{3-}-modified product was relatively high and some new lines observed that can be attributed to ZnO–PO_4^{3-}-modified structure formed respect to the original kaolin. When the molar ratio of Na_2O/Al_2O_3 increased from 5 to 50, a significant change that one band spilt into two or three peaks between 10 and 20° was observed and the band between 30 and 5° disappeared gradually, while some bands were preserved, indicating that with the increasing of ZnO–PO_4^{3-} and Na_2O, a kaolin–Zn^{2+}–PO_4^{3-}–Zn^{2+}–kaolin structure may has been formed, and with more ZnO–PO_4^{3-} introduced, more intercalated structure of modified material was constructed. In addition, Na content in the modified material was also a important factor to affect the structure (samples 3 and 5, Fig. 1), maybe due to part of Si–O–Al tetrahedron model broken and more O^- ion active site formed that was favorable to increase the specific surface area and pore volume.

Table 1
Chemical analyses data of the gel and ZnO–PO_4^{3-}-modified kaolin

Sample	Gel composition (M/M)					Product composition (M/M)				
	Na_2O	ZnO	Na_3PO_4	SiO_2	Al_2O_3	Na_2O	ZnO	Na_3PO_4	SiO_2	Al_2O_3
1	5	0.05	1	1.5	1	2.5	0.04	0.8	1.5	1
2	10	0.1	2	1.5	1	3.4	0.08	1.5	1.5	1
3	20	0.4	3	1.5	1	4.2	0.35	2.4	1.5	1
4	30	0.7	4	1.5	1	6.2	0.45	3.6	1.6	1
5	50	1.0	5	1.5	1	8.5	0.65	4.5	2.5	1

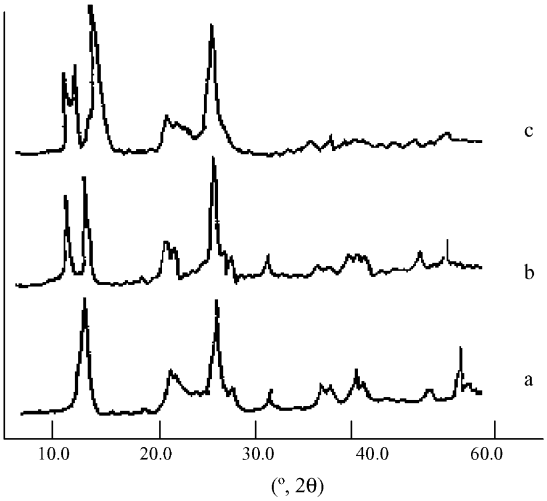

Fig. 1. XRD patterns of kaolin and $ZnO–PO_4^{3-}$-modified kaolin: (a) kaolin; (b) modified kaolin sample 3; (c) modified kaolin sample 5.

3.3. Morphology

The morphology of $ZnO–PO_4^{3-}$-modified sample examined by SEM and representative micrographs were shown in Fig. 2. Although the kaolin morphology was preserved, a more microsized and pored structure resulting from $ZnO–PO_4^{3-}$-modified were observed with the increasing of $ZnO–PO_4^{3-}$ and Na_2O contents. Apparently, the morphologies of $ZnO–PO_4^{3-}$-modified product were different from the starting material.

3.4. Surface area and pore size analysis

The result of surface area and pore size analysis were summarized in Table 2. From the data it can be concluded that the representative N_2 adsorption–desorption isotherms of the $ZnO–PO_4^{3-}$-modified kaolin were type IV according to the BDDT classification and exhibited a $H_1 + H_3$ type of hysteresis loop corresponding to slit-shaped porosity among particles with inner open cylindrical pores [13] and the kaolin treated with $ZnO–PO_4^{3-}$-modifying agent can lead to large variation in specific surface area and total pore volume for the samples. With the molar ratio of ZnO/Al_2O_3 and Na_3PO_4/Al_2O_3 increasing the specific surface area widened to about 30 times than that of the starting kaolin, and the volume ($V_{\mu P}$) of micropore broadened to about 10 times, the mesopore volume (V_{mP}) to about 30 times and the mesopore volume (V_{MP}) to about 30 times indicating that the modifying procedure is effective in increasing the pore volume.

Table 2
Physical properties of kaolin and $ZnO–PO_4^{3-}$-modified kaolin

Sample	S_{BET} (m^2/g)	V_{poro} (cm^3/g)			D (nm)
		$V_{\mu P}$	V_{mP}	V_{MP}	
1	185	1.56	3.42	2.53	25.6
2	390	3.50	4.21	2.84	23.2
3	650	4.62	4.55	3.10	23.0
4	610	4.56	4.35	2.96	24.3
5	420	4.00	3.95	2.57	23.5

3.5. Effect of the molar ratio of ZnO/Al_2O_3 and Na_3PO_4/Al_2O_3 on the particle size

It was found that the concentration of Na_3PO_4 and ZnO can affect the particle size remarkably and the influences of the molar ratio Na_3PO_4/Al_2O_3 and ZnO/Al_2O_3 on the particle size were shown in Figs. 3 and 4. When the molar ratio of Na_2O:ZnO:SiO_2 = 8.5:0.65:2.5, with the molar ratio of Na_3PO_4/Al_2O_3 increased from 0.1 to 4.5, the particle size reduced from 4500 to 350 nm. When the molar ratio of Na_2O:Na_3PO_4:SiO_2 = 8.5:0.8:1.5, the particle size of the $ZnO–PO_4^{3-}$-modified kaolin decreased from 3500 to 300 nm with the molar ratio of ZnO/Al_2O_3 increased from 0 to 0.65. The diameter distribution of the product with the composition of Na_2O:ZnO:Na_3PO_4:SiO_2:Al_2O_3 = 4.2:0.35:2.4:1.5:1 (molar ratio) was shown in Fig. 5. It was found that the average diameter of $ZnO–PO_4^{3-}$-modified kaolin product is about 500 nm and

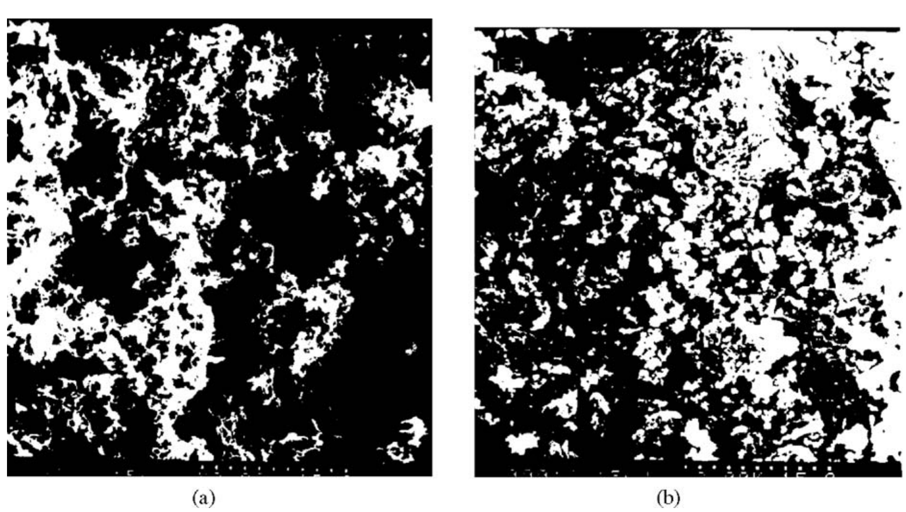

Fig. 2. Solid morphology by SEM of: (a) kaolin and (b) modified kaolin (sample 3).

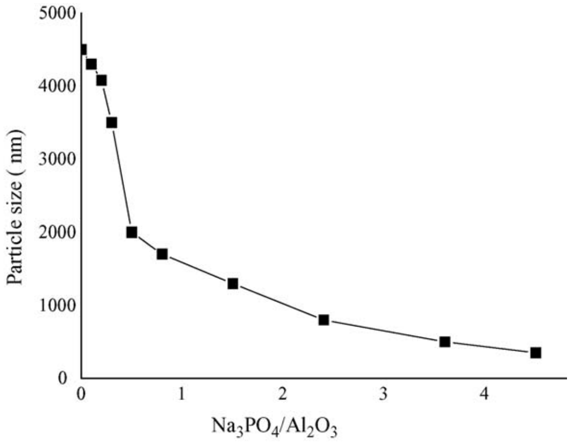

Fig. 3. Effect of Na_3PO_4/Al_2O_3 on the particle size.

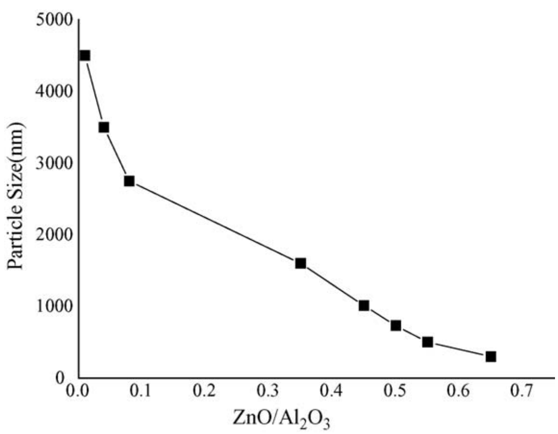

Fig. 4. Effect of ZnO/Al_2O_3 on the particle size.

the diameter distribution range was suitable for application in catalytic and absorption application.

3.6. Application in water purification

In application of produced wastewater treatment, it was found that with the concentration of $ZnO–PO_4^{3-}$-modified kaolin increased from 10 to 160 ppm, the COD decreased significantly and reduced from 5500 to 53 mg/L as shown in Fig. 6, which satisfied the demand of pourout or injection water.

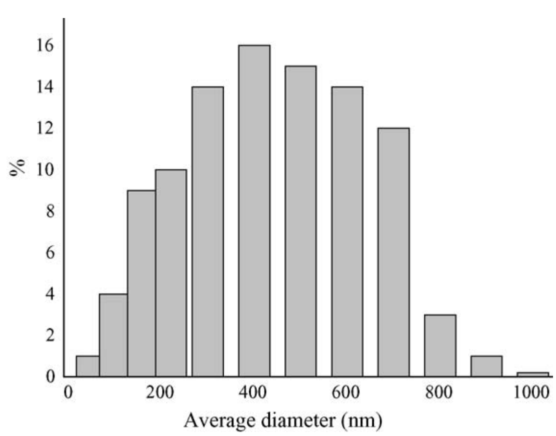

Fig. 5. Particle size distribution of the $ZnO–PO_4^{3-}$-modified kaolin.

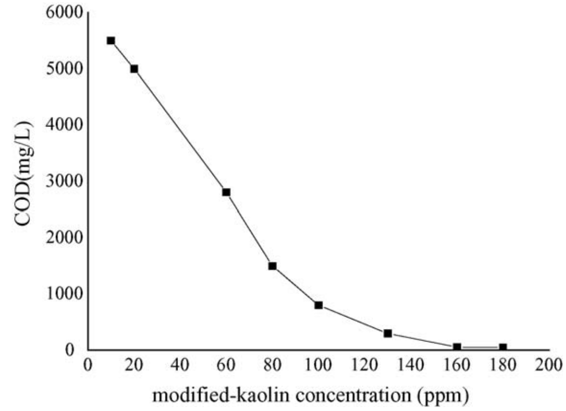

Fig. 6. Effect of $ZnO–PO_4^{3-}$-modified kaolin concentration on COD.

Table 3
Effect of ZnO/Al_2O_3 and Na_3PO_4/Al_2O_3 on flocculate time and COD value

ZnO/Al_2O_3 (M/M)	Na_3PO_4/Al_2O_3 (M/M)	Flocculate time (min)	COD (mg/L)
0	0	≥300	5500
0.1	0.5	12	102
0.2	0.5	8	80
0.2	1	7.8	68
0.3	2	3.2	55
0.3	3	3	53

The influences of ZnO/Al_2O_3 and Na_3PO_4/Al_2O_3 on flocculate time and COD value at 40 °C were shown in Table 3. It was found that with the molar ratio of ZnO/Al_2O_3 increased from 0.1 to 0.3 and Na_3PO_4/Al_2O_3 from 0.5 to 3, the flocculate time and COD reduced directly from 12 to 3 min and 102 to 53 mg/l, respectively. The results showed that $ZnO–PO_4^{3-}$-modified kaolin is effective in wastewater treatment and probably can replace wet-fixed-bed oxidation method at more than 200 °C or O_3 oxidation costly [17].

The effect of temperature on wastewater treatment was also a key factor, while using $ZnO–PO_4^{3-}$-modified kaolin the water

Table 4
Water quality index of treated and untreated water

Item	Required	Untreated	Treated
pH	6.5–8.5	6.5	7.2
MF	≥15	6	34
$\sum$Fe (mg/L)	≤0.5	47	0.27
Fe^{3+} (mg/L)		1.3	0.05
Corrosion rate (mm/a)	≤0.076	0.202	0.01
O_2 (mg/L)	≤0.05	0.04	0.04
SRB (no./mL)	≤10^2	10^2	0
TGB (no./mL)	≤10^3	10^3	10
Iron bacteria (no./mL)	≤10^3	10	0
S^{2-} (mg/L)	≤10	10	0
Oil content (mg/L)	≤10	120	1.2
Suspension (mg/L)	≤3.0	3.0	1.5
Scaling tendency	≤0.076	Serious	Little

Table 5
Ion content (mg/L) of treated and untreated water

	$Na^+ + K^+$	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	Total
Untreated	37600	2300	350	61800	300	560	200	102810
Treated	33480	450	30	56265	86	20	50	90386

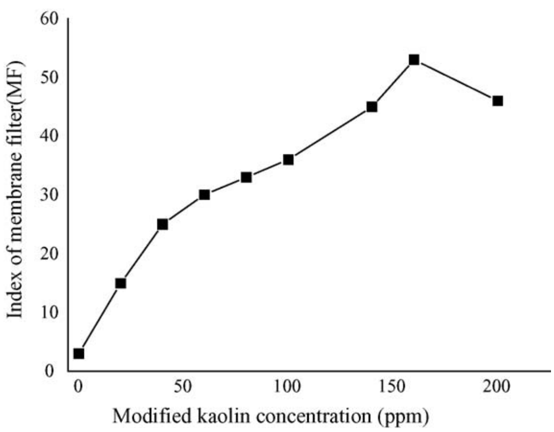

Fig. 7. Effect of $ZnO–PO_4^{3-}$-modified kaolin concentration on MF.

purification can be performed under 40 °C in short time and evidently the treatment procedure was simplified.

Index of membrane filter (MF) is another factor to evaluate the pour-into property of water and higher MF value show better pour-into property. For untreated water the MF was 6, with increasing of the concentration of $ZnO–PO_4^{3-}$-modified kaolin, MF value raised and when the concentration of $ZnO–PO_4^{3-}$-modified kaolin is 150 ppm, MF was up to 55 almost equal to that of running water (Fig. 7), indicating that the water treated by this method can satisfy the demand of pour-into water.

The other water index value treated with 100 ppm of $ZnO–PO_4^{3-}$-modified kaolin was shown in Tables 4 and 5. When 100 ppm of the product was used, a significant point that the concentration of the scaling ions: Fe^{n+}, Ca^{2+} and Mg^{2+} (that maybe deposited in contact with some of anions as OH^-, CO_3^{2-} and SO_4^{2-} in the groundwater) reduced from 47, 2300 and 350 mg/L to 0.27, 450 and 30 mg/L, respectively, SO_4^{2-} reduced from 300 to 86 mg/L and CO_3^{2-} from 200 to 50 mg/L was observed. It was also found that the total mineral content decreased about 10,000 mg/L and all water index of treated water were satisfied to the demand of pourout or injection water.

In addition, the other index of untreated and treated water such as bacteria, suspend solid, corrosion rate were also investigated. It was found that the modified kaolin prepared has good universal bactericide, suspend solid removal and corrosion inhibiting. The possible treated model can be summarized as Fig. 8.

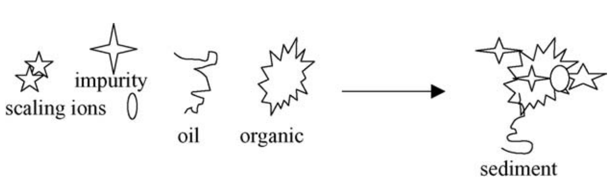

Fig. 8. Possible treated model.

4. Conclusion

On the basis of the above discussions, the multifunctional $ZnO–PO_4^{3-}$-modified kaolin material with large specific surface area and pore volume was synthesized, and their application in injection water purification was studied firstly. It was found that the prepared kaolin has the multifunctional properties of COD and BOD removal, scaling ion (Fe^{n+}, Ca^{2+} and Mg^{2+}) removal, MF improving, good bactericide and corrosion inhibitor and can be used effectively in oilfield wastewater treatment.

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