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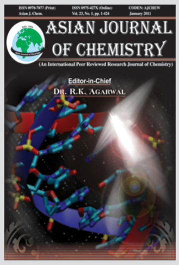

Preparation and Characterization of Bentonite Gel

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This method involves the preparation of bentonite gel from the samples of Wenshan Ca-bentonite of Yunnan. The reaction conditions are as follows: 4 % sodium oxalate; density of pulp is 15 %; the phosphate agent is sodium hexametaphosphate, its dosage is 0.5 %, the gelling agent is magnesium oxide; the result:the cation-exchange capacity is 104 mmol/100 g soil, the content of montmorillonite is 98 %, the colloid index is 100 mL/g soil, the expansion rate is 93 mL/g soil.

Key Words: Bentonite gel, Sodium, Phosphate, Gelling, Characterization.

INTRODUCTION

Bentonite is composed of hydrous aluminosilicate minerals, the staple of which is montmorillonite. Bentonite gel is kind of deep processing and development products with bentonite as main starting material, which is a kind of thixotropic gel and belongs to the non-newtonian liquid. Having the specific property of resisting well the dilute acid and alkali and good water proof, stability and heat resistance as high as 150-175 ºC, it has been widely used in building materials, environmental protection, daily chemical, pharmaceutical, ceramic, glass, paper making, casting, cleaning, batteries, *etc.*[1].

The authors synthesized the organic bentonite gel using the high quality bentonite from Wenshan Prefecture in Yunnan Province as matrix, by modifying it with $Na_2C_2O_4$ as the sodium agent, sodium hexametaphosphate [$Na(PO_4)_6$] as the phosphate agent and magnesium oxide as the gelling agent. Through XRD, IR, BET, SEM, the measurements of cation exchange capacity (CEC), the amount of methylene blue absorption, the content of montmorillonite , the colloid index, the expansion rate, the quality of the bentonite gel is determined and evaluated. The results show that the synthesized bentonite gel has good performance and can be used to the toothpaste carrier, cosmetic gel, chemical catalyst carrier and adsorbents, *etc*.[2].

EXPERIMENTAL

Raw materials: Bentonite was obtained form Wenshan Prefecture, Yunnan Province, P.R. China and dried and sieved through a 200-mesh and stored for further use. The elemental composition of raw bentonite are given in Table-1. The major chemical compositions of raw bentonite are listed in Table-2 .

TABLE-1
ELEMENTAL COMPOSITION OF RAW BENTONITE/wt %

Element	Content (%)	Element	Content (%)	Element	Content (%)
O	52.9	Na	0.04	Rb	0.0066
Si	29.3	P	0.0366	Pb	0.0045
Al	8.36	Sr	0.0154	Th	0.0027
Mg	2.53	Ba	0.0121	Ni	0.0026
Fe	0.978	Mn	0.0123	Ga	0.0022
Ca	0.967	S	0.0122	U	0.0012
K	0.395	Zn	0.0114	Nb	0.0010
Ti	0.135	Cl	0.0107	–	–
F	0.0667	Zr	0.0104	–	–

TABLE-2
MAJOR CHEMICAL COMPOSITIONS OF
RUN-OF-MINE ORE/wt %

Element	Content (%)	Element	Content (%)
SiO_2	61.3	CaO	1.31
Al_2O_3	15.6	K_2O	0.462
MgO	4.14	TiO_2	0.219
Fe_2O_3	1.36	–	–

It can be seen from Table-1 that the raw bentonite contains 25 elements, including seven kinds of major elements: O, Si, Al, Mg, Fe, Ca, C. According to the results of element test and SQX calculation show that the raw bentonite was Ca-bentonite.

Process of preparation of bentonite gel

Sodium modification: The experiment studied the influencing factors of different sodium agents and dosage, different pulp concentration to the measurements of cation exchange capacity (CEC), the amount of methylene blue absorption, the content of montmorillonite, the colloid index, the expansion rate of Na-bentonite[3,4] (**Scheme-I**).

Phosphate modification: The experiment studied the influencing factors of different phosphate agents and its dosage to the measurements of cation exchange capacity, the amount of methylene blue absorption, the content of montmorillonite, the colloid index, the expansion rate of bentonite gel.

Gelling modification: The experiment studied the influencing factors of different gelling agents and its amount to the measurements of cation exchange capacity (CEC), the amount of methylene blue absorption, the content of montmorillonite, the colloid index, the expansion rate of bentonite gel.

XRD analysis: The raw bentonite, the Na-bentonite and the bentonite gel were analyzed by a D/MAX III X-ray diffraction (Japan).

IR analysis: The raw bentonite, the Na-bentonite, P-bentonite and the bentonite gel were analyzed by a WFH-30/6 infrared spectrophotometer (Tianjin, China).

BET analysis: The raw bentonite, the Na-bentonite and the bentonite gel were analyzed by a NOVA 2000e surface area and pore analyzer (Quantachrome Instruments).

SEM analysis: The raw bentonite and the bentonite gel were analyzed by a XL30-scanning electron microscope (Philips).

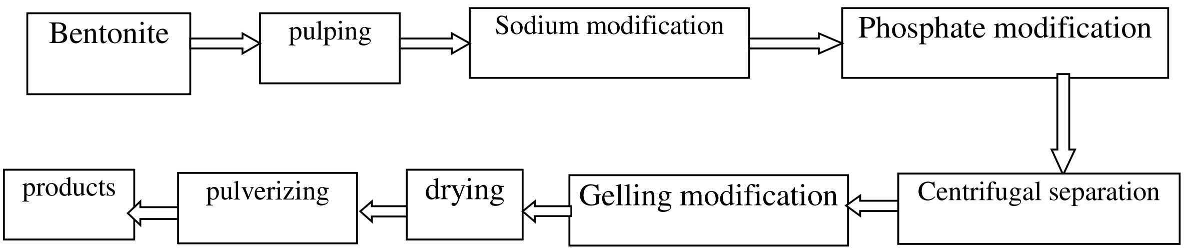
RESULTS AND DISCUSSION

Choice of sodium agent: It can be seen from Table-3 that the Na-bentonite has higher value in every physical and chemical index, compared with the raw bentonite. And different sodium agents has different influence to the physical and chemical index of Na-bentonite, in which sodium chloride and sodium carbonate get higher CEC value. But its increase rate of the colloid index and the expansion rate is not obvious. Taking into account reducing costs and increasing its added value,we choosed sodium oxalate as sodium agent.

Choice of different pulp concentration: Table-4 shows pulp concentration has little influence on the expansion rate and colloid index, but the influence of pulp concentration mainly focused on CEC value. Considering the water conservation and cost-effective, the 15 % pulp concentration was selected[5].

Choice of dosage: Table-5 shows that ,as the dosage increased, the increase of CEC value was not obvious, but expansion rate and colloid index continuously were improved. When the dosage is 5 %, the physicochemical property is better on the whole. Continued increase in dosage of sodium, the increase of expansion rate was not obvious,and more sodium will lead to the decline of colloid index[6]. So the dosage of 4 % was selected.

Choice of phosphate agent: It can be seen from Table-6 that phosphating process has little effect on the colloid index, but has much greater effect on CEC, amount of methylene blue absorption and expansion rate.we can see from Table-6



Scheme-I

TABLE-3
INFLUENCE OF DIFFERENT SODIUM AGENTS TO THE PHYSICOCHEMICAL PROPERTY OF Na-BENTONITE

Sodium agent	CEC (mmol/100 g)	Amount of methylene blue absorption (g/100 g)	Content of montmorillonite (%)	Colloid index (mL/g)	Expansion rate (mL/g)	Moisture content (%)
Without sodium	52.7	29.60	66.90	52.5/15g	18.0	7.80
Sodium chloride	90.67	31.20	70.59	13	20.0	7.80
Sodium carbonate	100	34.00	76.92	27	58.0	6.80
Sodium fluoride	101.33	32.10	82.50	> 100	93.0	8.20
Sodium oxalate	77.56	36.26	82.04	> 100	92.3	6.27
Sodium pyrophosphate	70	39.06	88.37	≈ 100	90.6	4.20

TABLE-4
INFLUENCE OF DIFFERENT PULP CONCENTRATION TO THE PHYSICOCHEMICAL PROPERTY OF BENTONITE GEL

Pulp density (%)	CEC (mmol/100 g)	Amount of methylene blue absorption (g/100 g)	Content of montmorillonite (%)	Colloid index (mL/g)	Expansion rate (mL/g)
5	58.53	35.69	80.75	> 100	88.0
10	77.35	35.06	79.32	> 100	89.9
15	75.62	35.56	80.45	> 100	89.9
20	66.73	35.76	80.90	> 100	91.0
25	68.98	35.83	81.06	> 100	92.8

TABLE-5
INFLUENCE OF SODIUM OXALATE TO THE PHYSICOCHEMICAL PROPERTY OF BENTONITE GEL

Dosage (%)	CEC (mmol/100 g)	Amount of methylene blue absorption (g/100 g)	Content of montmorillonite (%)	Colloid index (mL/g)	Expansion rate (mL/g)
2	79.98	34.88	78.91	43	42.3
3	73.83	33.47	75.72	97	68.1
4	79.01	33.33	75.41	98	88.7
5	78.83	33.53	75.86	99	93.4
6	83.01	32.88	74.39	97	93.8

TABLE-6
INFLUENCE OF DIFFERENT PHOSPHATE AGENTS TO THE PHYSICOCHEMICAL PROPERTY OF BENTONITE GELL

Phosphate agent	CEC (mmol/100 g)	Amount of methylene blue absorption (g/100 g)	Content of montmorillonite (%)	Colloid index (mL/g)	Expansion rate (mL/g)
Sodium	82.97	37.16	84.07	100	87.98
Hexametaphosphate	88.61	40.46	91.54	100	94.91
Hexametaphosphate	96.05	43.72	98.91	100	100.00
Sodium pyrophosphate	87.95	42.30	95.70	100	95.90
Sodium hypophosphite	80.81	40.81	92.33	100	96.00

TABLE-7
INFLUENCE OF DIFFERENT CONCENTRATION OF SODIUM HEXAMETAPHOSPHATE TO THE PHYSICOCHEMICAL PROPERTY OF BENTONITE GEL

Ddosage (%)	CEC (mmol/100 g)	Amount of methylene blue absorption (g/100 g)	Content of montmorillonite (%)	Colloid index (mL/g)	Expansion rate (mL/g)
0.2	94.69	42.24	95.57	100	87.9
0.3	97.21	43.83	99.16	100	90.2
0.4	97.99	43.30	97.96	100	92.0
0.5	104.75	43.39	98.17	100	93.5
0.6	97.29	43.36	98.10	100	90.0

that compared with other phosphate agent, the sodium hexametaphosphate is the best agent, the content of montmorillonite is close to 99 %, CEC is 96 mmol/100 g, colloid index and expansion rate are 100 mL/g. So we choose sodium hexametaphosphate as phosphate agent.

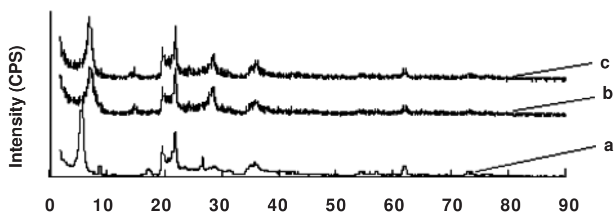
Choice of different concentration of phosphate agent: It can be seen from the Table-7 that the dosage of sodium hexametaphosphate has little effect on content of montmorillonite and colloid index, but has significant impact on CEC and expansion rate. With the increase of the dosage of sodium hexametaphosphate, the CEC and expansion rate increased, but they will be decreased if the dosage of sodium hexametaphosphate exceeds 0.5 %. So the dosage of phosphate agent is 0.5 %.

Choice of gelling agent: Table-8 shows that the viscosity of all the bentonite gel are stronger using magnesium oxide, calcium chlorideare as gel agent, but calcium will be re-introducted into gel system if using the calcium chlorideare as gel agent. Magnesium oxide does not have an influence to health, so it's better to use magnesium oxide as gel agent.

TABLE-8
INFLUENCE OF DIFFERENT GELLING AGENT TO THE PHYSICOCHEMICAL PROPERTY OF BENTONITE GEL

Ggelling agent	Non pectization	$MgCl_2$	$AlCl_3$	$AlCl_3$	$CaCl_2$
Viscosity (mPa s)	7.5	7.0	8.0	7.0	8.0

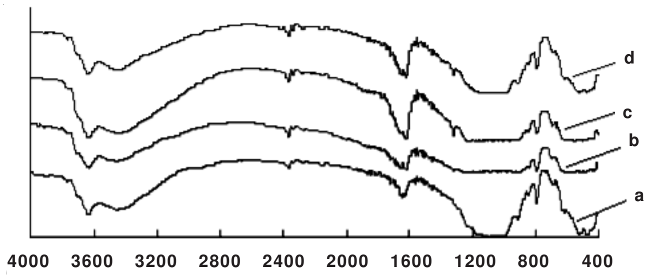
XRD analysis: Fig. 1 shows the X-ray diffraction patterns of the raw bentonite, the Na-bentonite and the bentonite gel, respectively. We can see from Fig. 1 that the peak of the Na-bentonite and the bentonite gel had obvious displacement, compared with the peak of the bentonite; after the sodium purification, the impurity in the bentonite sample has obviously decreased; the d(001) value of Na-bentonite has dropped to 1.23 nm from 1.56 nm compared with raw bentonite and the d(001) value of bentonite gel has increased to 1.25 nm from 1.23 nm compared with Na-bentonite. The apparent reduction of the lamellar spacing indicates that the exchangeable Mg^{2+} and Ca^{2+} among the montmorillonite interlayer has been replaced by the low charge Na^+ with a smaller ionic diameter, thus we guessed the synthesis of bentonite gel modification have achieved.



(a) Raw bentonite; (b) Na-bentonite; (c) Bentonite gel

Fig. 1. XRD spectra

IR analysis: Fig. 2 shows that IR spectra of the bentonite, the Na-bentonite, the bentonite modified by phosphate and the bentonite gel, respectively. Having the same skeleton structure in four IR spectra of bentonite, it means that they are typical montmorillonite mineral. The absorption bands of bentonite at 3620 cm^{-1} (attributed to Al-O-H stretching vibration), 3400



(a) Raw bentonite; (b) Na-bentonite; (c) P-bentonite; (d) Bentonite gel

Fig. 2. IR spectra

cm^{-1} (assigned to H-O-H stretching vibration), 1640 cm^{-1} (attributed to H-O-H bending vibration), 1040 cm^{-1} (assigned to Si-O-Si asymmetrical stretching vibration), 525 cm^{-1}, 470 cm^{-1} (attributed to Si-O-R). Unlike the other bentonite, the raw bentonite has a strong infrared absorption peak at 796 cm^{-1}. The main reason may be the contents of Ca^{2+}, Mg^{2+}, Al^{3+} are very high, the hydration ability of which is strong and the Na^+ is lower, the hydration ability of which is weak. So the raw bentonite is kind of minerals mainly containning montmorillonite and we guess the Na^+ had replaced some ions of the Ca^{2+}, Mg^{2+}, Al^{3+}. Furthermore the bentonite gel, as distinct from the Na-bentonite and bentonite modified by phosphate, has a strong and broadened peak at1034 cm^{-1}. This is because the esistence of the Ca^{2+}, Mg^{2+} and Al^{3+} leads to the absorption band of Si-O bond weakened and faded away finally.

BET analysis: Table-9 shows the surface area, pore volume and pore diameters data of the bentonite, the Na-bentonite and the bentonite gel, respectively. Table-9 shows that surface area-pore volume and pore diameters of the raw bentonite is lowest, respectively, 19.37 m^2/g, 0.030 mL/g and 3.55603 nm. The surface of Na-bentonite is lower, but increased range of pore volume and pore diameters are very obvious and the pore volume and pore diameters of bentonite gel are reduce,compared with Na-bentonite,but the surface area of bentonite gel increased obviously. It indicated that the bentonite gel has been purified.

TABLE-9
DATA OF SURFACE AREA,PORE VOLUME, PORE DIAMETERS

Saple	Surface area (m^2/g)	Pore volume (mL/g)	Pore diameters (nm)
Raw bentonite	19.37	0.030	3.55603
Na-bentonite	21.96	0.055	5.98459
Bentonite gel	29.22	0.046	3.56045

SEM analysis: Fig. 3 shows a SEM image of the raw bentonite and Fig. 4 shows a SEM image of the bentonite gel. It can be seen from the images that the structure of raw bentonite is irregular, erose and curling phenomenon. The surface of Na-bentonite with crystals characteristic is flat and stretch, muddy background, unsharp outline and regular surface structure. The crystallinity of bentonite after modified was deteriorated clearly and it indicates the activity and colloid performance get improved.

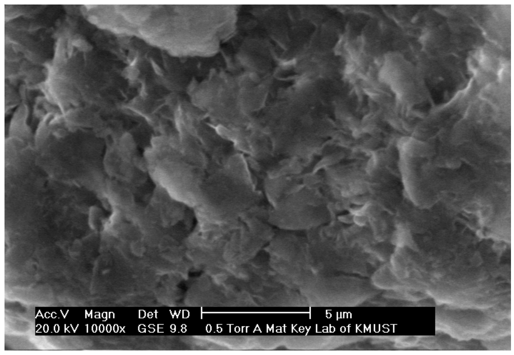


Fig. 3. SEM of raw bentonite (10000X)

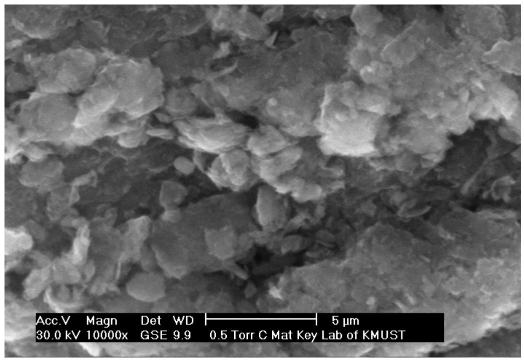


Fig. 4. SEM of bentonite gel (10000X)

Conclusion

The bentonite gel have been synthesized using the high quality bentonite from Wenshan Prefecture in Yunnan Province as matrix, by modifying it with $Na_2C_2O_4$ as the sodium agent, sodium hexametaphosphate [$Na(PO_4)_6$] as the phosphate agent and magnesium oxide as the gelling agent. Through XRD, IR, BET, SEM, the measurements of cation-exchange capacity (CEC), the amount of methylene blue absorption, the content of montmorillonite, the colloid index, the expansion rate, the quality of the bentonite gel is determined and evaluated. The best reaction conditions are as following: the sodium agent is sodium oxalate; its dosage is 4 %; density of pulp is 15 %; the phosphate agent is sodium hexame taphospha, its dosage is 0.5 %, the gelling agent is magnesium oxide. The result:the cation-exchange capacity is 104 mmol/100 g soil, the content of montmorillonite is 98 %, the colloid index is 100 mL/g soil, the expansion rate is 93 mL/g soil. The results show that the synthesized bentonite gel has good performance and it can be used to the toothpaste carrier, cosmetic gel, chemical catalyst carrier and adsorbents, *etc*. and will have the good environment benefit, the economic efficiency and the social efficiency[7].

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REFERENCES

1. S. Abend and G. Lanaly, *Appl. Clay Sci.*, **16**, 201 (2000).
2. G.-H. Yao, *Northwesrern Geol.*, **18**, 43 (1997).
3. D.F. Luo, X. Liu and W.L. Lian, *Non-Metallic Mine*, **27**, 6 (2004).
4. Test Methods of Bentonite (JC/T 593-1995).
5. M.G. Cao and Y.H. Yu, *Mining Metallurg. Eng.*, **21**, 24 (2001).
6. X.Y. Zhang, *Non-Metallic Mine*, **28**, 34 (2005).
7. A.F. Geng, W. Wang and J.H. Yan, *J. Changchun Inst. Opties Fine Mechanies*, **24**, 44 (2001).