

New Method for the Production of Barium Humate from Turkish Coal

Hacer Dogan¹, Murat Koral¹, Alican Vatansever¹, Tulay Inan², Mustafa Ziypak³, Zeki Olgun³, Ülker Beker¹

¹TUBITAK Marmara Research Center, Chemistry Institute, Kocaeli, Turkey ²Saudi Aramco, Dhahran, Kingdom of Saudi Arabia ³TKI (Turkish Coal Enterprises), Ankara, Turkey Email: hacer.dogan@tubitak.gov.tr

Received 30 April 2015; accepted 27 June 2015; published 30 June 2015

Copyright © 2015 by authors and Scientific Research Publishing Inc. This work is licensed under the Creative Commons Attribution International License (CC BY). http://creativecommons.org/licenses/by/4.0/ @_ 0

Abstract

Metal humates have been generally produced from water soluble alkaline humates with the related metal salts. In this study, a new method for the production of barium humate (Ba-HA) from Turkish coal was developed. Insoluble Ba-HA was produced from the result of the extraction of coal directly with barium hydroxide at 120°C. The effect of the amount of raw materials on the solubility and on the content of barium metal was investigated. The pilot plant trial was performed by using 100 kg of coal in one batch based on laboratory results. Ba-HA was characterized by means of FTIR and TGA. The calcination of Ba-HA at the different temperatures and in atmosphere of nitrogen and air was realized to provide the increase in the surface area and the decrease in the chromatographic groups giving yellow color. In terms of the surface area and UV-absorbance values, the calcination condition was selected as the temperature of 350°C and atmosphere of air. The calcinated Ba-HA was used in the adsorption of some heavy metals. The results show that Ba-HA may have potential to be used as a low cost, natural and eco-friendly adsorbent.

Keywords

Ba-Humate, Humic Acid, Leonardite

1. Introduction

Humic acids (HAs) are present in soils, natural waters, river, lake and sea sediments, peat, brown and brownblack coals and other natural materials as a product of chemical and biological transformations of animal and plant residues [1]. Coal humic substances are formed as intermediate product during coal formation.

How to cite this paper: Dogan, H., Koral, M., Vatansever, A., Inan, T., Ziypak, M., Olgun, Z. and Beker, Ü. (2015) New Method for the Production of Barium Humate from Turkish Coal. Advances in Chemical Engineering and Science, 5, 290-298. http://dx.doi.org/10.4236/aces.2015.53029

Humic acid is a chemically heterogeneous compound having different types of functional groups in different proportions and configurations. It contains carboxyl (-COOH), amine (-NH₂), hydroxyl(-OH) and phenol (Ar-OH) functional groups, and has a negative charge in weakly acidic to basic media because of deprotonation [2].

Alkali humates are produced as a result of the extraction with alkaline solution (sodium hydroxide, potassium hydroxide, or ammonium hydroxide) of coal sources such as lignite, Leonardite with high humic acid content [3]. Alkali metal humates (Na and K) are defined as the water soluble salts of humic acid. Commercial humates of sodium, potassium and ammonium were shown to improve plant growth and development, increase plant resistance to unfavorable environmental conditions when humic acids interact with two and multivalent metals, such as calcium, barium, iron, zinc, copper and others, they form new type of insoluble compounds [4]. Metal humates can be prepared in a relatively simple way by the precipitation of humic acid with suitable metal compounds.

Except for agricultural uses, humic acid and humates have been used in various industries such as in the ceramic industry as dispersants, in wastewater treatment as adsorbents, in drilling fluids as loss prevention additives, in the lead acid batteries as surfactant material, in black or dark colored inks as rheology improver, in medicine for treatment of various diseases.

Recent years, low cost and highly effective adsorbent materials have been developed for heavy metal adsorption. Humic acid based materials are also considered as one of the best examples for low cost sorbents. Water-insoluble coal derived metal humates have been used as a new low-cost sorbent for inorganic and organic pollutants. Many humic substances as oxihumolite, iron humate [5] and lignite [6] were chemically modified to new substances (humates) in order to improve the sorption and material properties of the original humic substances. Among the various functional groups of humic substances, carboxyl and phenolic OH groups, the acidic functional groups possess high complexation capacities with metal ions enabling humic acid to bind and remove heavy metals from soil and organic pollutants [7].

Seki and Suzuki [8] produced insolubilized humic acid by heating at 330°C for 1 h after the pretreatment of sodium humate with 2 M CaCl₂ solution. Insoluble humic acid was used as an adsorbent for cadmium and lead ions. Kříženecká *et al.* [7] prepared five metal humates (iron humate, aluminium humate, zinc humate, calcium humate, and magnesium humate) by the precipitation of potassium humate with the respective metal solutions and metal humates were tested as sorbents for the removal of inorganic or organic pollutants (metals, inorganic ions, dyes, and chlorophenols) from waste water. They found that partly soluble magnesium humate and calcium humate could not be used as sorbents. The literature results show that the calcination of metal humates (especially for Ca, Mg and Ba) make them insoluble in the alkaline and acidic solutions.

Leonardite based coal is soluble in the alkaline conditions because of the high content of humic acid. Humic acid is obtained from Leonardite by extraction with sodium or potassium hydroxide followed by coagulation, centrifugation and washing with water. Multivalent metal humates were produced from water soluble sodium or potassium humates and metal salts. The production of metal humates from coal by using water-soluble multivalent metal salts directly has not been observed in the literature.

In this study, barium humate (Ba-HA) was prepared directly from coal (Turkish Coal Enterprises-TKI) by using barium hydroxide. Ba-HA was separated from the solution with centrifuge. Ba ions were reacted with the acidic or phenolic groups present in humic acid fraction on Leonardite. The obtained Ba-HA included the insoluble organic and inorganic fraction in the coal. The use of the entire coal mass was provided with this new production method.

The derived Ba-HA was insoluble under the alkaline and acidic conditions. Pilot plant trial was performed in the reactor with the volume of 1 m³. Then, the modification of Ba-HA was carried out by the application of thermal treatment (calcination) to increase the surface area of Ba-HA. Temperature effect was examined by measuring surface area and UV-absorbance of Ba-HA aqueous solution. Adsorption experiments of Ba-HA have been performed for As, Cd, Co, Cr, Cu, Hg, Ni and Pb ion removal.

2. Materials and Methods

2.1. Materials

Leonardite coal (from Mugla Husamlar) sent by TKI was used. The ultimate and proximate analyses are shown in Table 1. The coal was first ground and then sieved. The particles under 200 μ m were used.

Barium hydroxide octahydrate (Ba(OH)₂·8H₂O) as barium source was supplied from Sigma Aldrich. Its solu-

Table 1. Ultimate and proximate analyses for Leonardite.				
	% on d.a.f. basis			
Ultimate analysis				
С	49.0			
Н	4.48			
Ν	1.58			
S	3.74			
0	41.20			
Proximate analysis				
Moisture	10.0			
Ash	33.0			
Volatile matter	68			

d.a.f.: Dried ash free.

bility in water at 20°C is 40 - 60 g/l. Humic acid content of Leonardite was determined according to ISO 5073 Brown coals and lignites—Determination of humic acids and it was found as 50%.

2.2. Ba-HA Preparation

2.2.1. Laboratory Trials

The experiments were performed using 1 L autoclave at 85° C and 120° C. In each run, 80 g of coal sample and different amount of water and barium hydroxide octahydrate (**Table 2**) were placed into the stainless steel autoclave. The autoclave then was heated to desired temperature with stirring. This temperature was maintained for 2 h. The autoclave was then allowed to cool to room temperature for 2 - 3 h. Ba-HA was separated by centrifugation and rinsed with distilled water and then dried under vacuum at 80° C overnight.

2.2.2. Pilot Plant Trial

Pilot plant trial was performed by using 1 m^3 jacketed reactor and decantation tank present in the pilot plant. 114 kg of coal, 26.7 kg Ba(OH)₂·8H₂O and 128 kg water were placed into the reactor. After the decantation, Ba-HA was dried under the ambient conditions. The reaction conditions are given in **Table 3**. Barium content in Ba-HA was found as 8%.

2.3. Calcination

Ba-HA produced in pilot plant was sieved under 200 μ m and then calcinated in the oven at the temperatures of 200°C, 250°C, 300°C and 350°C. The calcination temperatures were reached in directly or gradually under the atmosphere of nitrogenand air. Nitrogen gas was fed to the calcination oven to perform the calcination in the atmosphere of nitrogen. The applied conditions for each temperature are given below:

- Directly-air.
- Gradually-air.
- Directly-nitrogen.
- Gradually-nitrogen.

The calcination time was selected as 3 hours. The sample was hold in the oven at the desired temperature for 3 hours during direct calcinations. In the gradual calcinations, temperature has reached to 105°C for 1 hour and to the target temperature for 30 minutes. It was provided to remain at the target temperature for 1.5 hours as shown in **Figure 1**.



Figure 1. Time versus temperature increase in gradual calcinations.

Fable 2. Ba-HA	production	conditions	and results.
-----------------------	------------	------------	--------------

	1	2	3	4	5	6	7	8
Temperature, °C	120	120	120	85	85	85	85	120
Pressure, bar	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Stirring rate, RPM	400	400	400	400	400	400	400	400
Time, hour	2	2	2	2	2	2	2	2
Raw materials								
Ba(OH) ₂ %	4.0	6.5	9.0	4.0	6.5	9.0	6.5	6.5
Water, %	65.3	63.6	61.9	65.3	63.6	61.9	57.5	57.5
Leonardite, %	30.7	29.9	29.1	30.7	29.9	29.1	36.0	36.0
Results								
Ba amount in Ba-HA %	0.84	3.8	9.2	0.7	4.2	14.6	8.8	8.5
Solubility in alkaline, %	0.4	0.3	0.6	2.6	0.8	0.7	1.4	0.5
Ash, %	40	37	44.00	37	40	44	38	37

Table 3. Pilot plant trial conditions.

Temperature, °C	120
Pressure, Bar	3.6 - 4.0
Time, hour	3
Ba(OH) ₂ , %	6.5
Water, %	57.5
Leonardite %	36
Liquid/solid ratio	1.6

2.4. Characterization

The solubility was determined by stirring the sample in the aqueous conditions for 24 hours at pH = 11. Fourier-Transform Infrared (FTIR) spectra were recorded for the Ba-HA using Perkin Elmer Pyris 1 FTIR spectrophotometer. The samples were prepared by incorporation into KBr pellets. The thermal stability of Ba-HA sample was determined using a Perkin Elmer PYRIS 1 Thermal Gravimetric Analyses (TGA).

The BET specific surface area of the samples was measured with linear parts of BET plot of N_2 adsorption isotherms, using Quantachrome autosorb.

The calcinated samples under the different conditions are stirred in water for 24 hours and the supernatant was examined in UV spectrophotometer. It is required that Ba-HA during the adsorption process should not change the color of the liquid phase UV-spectra of the samples were recorded with UV-1650 PC (Schimadzu) spectrophotometer in a 1 cm quartz cuvette. Samples were mixed in water and the solution was measured in UV.

2.5. Batch Adsorption Experiments

Batch adsorption experiments were carried out by shaking 0.5 and 1 g of the calcined Ba-HA with 25 ml of solution of As, Cd, Co, Cr, Cu, Hg, Ni and Pb with 150 ppm concentration in PE bottles. The metal solution together with the adsorbent was agitated magnetically in the closed PE bottle for 2 and 24 hours. Then the solid phase was separated by centrifugation, the concentration of the metal in the solution was determined immediately by ICP-AES. The adsorption capacity was calculated using the following equations:

The adsorption degree, AD, as a function of time was also determined from the experimental data using the following relationship:

$$AD\% = 1 - C_t / C_i \times 100$$

where C_i and C_t are the concentrations of the metal ion in initial and final solutions respectively.

3. Results and Discussion

Figure 2 shows the spectra of Leonardite and Ba-HA. Absorption bands in the 3600 - 2800 cm⁻¹ spectral region for Leonardite and Ba-HA were very broad; absorbance in this region was determined by the presence of -OH, NH and C-H groups [9]. In Leonardite, the bands at 2900 cm⁻¹ and 2850 cm⁻¹ (aliphatic C-H stretching vibration) appear more intense and clear. Absorption within the range from 2000 to 1500 cm⁻¹ is characteristic for functional groups with double bonds for Leonardite. Usually these are C=O and C=C. Polysaccharide absorption bands can be observed, mostly around 1040 cm⁻¹. The spectrum presents intense bands around 1000 and 500 cm⁻¹ corresponding to mineral materials. The band at about 1470 cm⁻¹ (COO-) is more pronounced in Ba-HA.



Figure 2. FTIR spectra of Leonardite and Ba-HA.

Thermogravimetric degradation curves of Leonardite and Ba-Humat prepared from coal are shown in **Figure 3**. Ba-HA has greater ash content than Leonardite, since there are more inorganic parts.

The solubility of humic acid increased with increase in pH and decreased with increase in ionic strength. A pH of at least 8.0 was required to solubilize a "representative" fraction of a humic acid sample. The solubility of Leonardite in pH 10 was obtained as 15%. The solubility of Ba-HA samples under alkaline conditions was obtained about <1% as shown in Table 2. The values confirm the formation of Ba-HA from Leonardite.

The content of barium in the barium humate was determined by ICP-AES. The amount of Ba in the samples increased with increasing of barium hydroxide. The decrease in the liquid/solid ratio caused the increase in the amount of barium content in the solid phase. While liquid/solid ratio was 2.13, barium amount was obtained as 3.8% and the amount of barium increased to the value of 8.5% with the liquid/solid ratio of 1.6.

The acidic groups on HA are available for metal complexation. However, 20% of acidic groups on insoluble HA were found unavailable for metal complexation [8] and the metal complexation constants of insoluble HA agreed with the constants of HA.

As a result the acidic groups on HA are available for metal complexation. But 20% of acidic groups on insoluble HA were found unavailable for metal complexation [8] and the metal complexation constants of insoluble HA agreed with the constants of HA.

Of calcination process, it is clear that there is some loss in the weight of Ba-HA samples (Figure 4), which can be illustrated as follows:

- A higher rate of loss was obtained in directly calcinations when compared to gradually calcinations.
- Weight loss was high especially at 200°C during the directly calcination.
- There was no important difference between directly or gradually calcination under the ambient and nitrogen, except 200°C.
- Weight loss increased with the increase of temperature.

The BET surface areas of Ba-HA samples calcined at different temperatures are listed in **Table 4**. The results indicated that the surface area increased with increasing calcination temperature.

The surface area of the samples directly calcinated at different temperatures is higher than that of other conditions. Nitrogen atmosphere did not cause differences in the surface area. According to these results, it is possible to achieve the desired results by direct calcination at 350°C.

UV Measurements

Chromophoric organic matters released into aqueous medium from Ba-HA calcined at different temperatures were investigated in terms of absorbances with wavelength between 200 and 900 nm. Figure 5 depicted variations of UV absorbance spectra of samples after calcination at the different conditions. We attribute them to absorption of light by phenolics or quinones (a shoulder located around 280 - 290 nm).



Figure 3. Thermogravimetric analysis of Ba-HA sample and Leonardite.



Figure 5. UV absorbance spectra of samples after calcinations.

The effect of contact time and the adsorbent amount on the adsorption of As, Cd, Co, Cr, Cu, Hg, Ni and Pb ions on Ba-HA was investigated over time intervals from 2 up to 24 hours. Figure 6 shows the adsorption degree as a function of contact time for all metal ions. About 90% adsorption degree was achieved within 2 and 24 hours for all metal except As and Co during the use of 1 gr of Ba-HA.



Figure 6. Variation of adsorption percentage with contact time.

Table 4. Surface area of the samples calcinated at different conditions.

Calcination	Surface Area, m ² /g				
Temperature °C	Direct Calcination	Gradual Calcination	Direct Calcination under Nitrogen	Gradual Calcination under Nitrogen	
0			1.2		
150	2.13	2.46	1.14	1.52	
200	11.29	2.29	1.70	1.32	
250	10.50	5.49	11.01	7.58	
300	17.56	16.24	16.20	15.09	
350	20.60	17.78	21.50	21.63	

4. Conclusions

With the developed new method, it was shown that Ba-HA can be produced with the reaction of coal (Leonardite) and barium hydroxide at 120° C for 2 hours. Ba-HA in the desired properties was also obtained in the pilot plant trials under the same production conditions. While the solubility of Leonardite and Ba-HA in alkaline condition was obtained as 15% and <1, respectively.

Ba ions were reacted with the acidic or phenolic groups present in humic acid fraction on Leonardite. The obtained Ba-HA includes the insoluble organic and inorganic fraction in the coal. The use of the entire coal mass was provided with this new production method.

The calcination of Ba-HA at different temperatures showed the increase in the surface area and almost 20-time higher surface area was obtained at 350°C. Calcined Ba-HA sample was successfully used for selective metal ions and adsorption degree was obtained to be over 90% except As and Co in a period of 24 hours. This study shows that calcined Ba-HA can be used as a low cost and natural adsorbent.

References

- [1] Stevenson, F.J. (1994) Humus Chemistry. Genesis, Composition, Reactions. 2nd Edition, Wiley, New York.
- [2] Erdogan, S., Baysal, A., Akba, O. and Hamamci, C. (2007) Interaction of Metals with Humic Acid Isolated from Oxidized Coal. *Polish Journal of Environmental Studies*, **16**, 671-675.
- [3] Novák J., Kozler J., Jano P., Cezíková, J., Tokarová, V. and Madronová, L. (2001) Humic Acids from Coals of the North-Bohemian Coal Field: I. *Preparation and Characterisation Reactive and Functional Polymers*, 47, 101-109. <u>http://dx.doi.org/10.1016/S1381-5148(00)00076-6</u>

- [4] Tipping, E. (2002) Cation Binding by Humic Substances. Cambridge Environmental Chemistry Series-12. Cambridge University Press, Cambridge. <u>http://dx.doi.org/10.1017/CBO9780511535598</u>
- [5] Janoš, P., Herzogová, L., Rejnek, J. and Hodslavská, J. (2004) Assessment of Heavy Metals Leachability from Metallo-Organicsorbent—Iron Humate—With the Aid of Sequential Extraction Test. *Talanta*, 62, 497-501. http://dx.doi.org/10.1016/j.talanta.2003.08.032
- [6] Chassapis, K., Roulia, M. and Nika, G. (2010) Fe(III)-Humate Complexes from Megalopolis Peaty Lignite: A Novel Eco-Friendly Fertilizer. *Fuel*, 89, 1480-1484. <u>http://dx.doi.org/10.1016/j.fuel.2009.10.005</u>
- [7] Kříženecká, S., Hejda, S., Machovič, V. and Trögl, J. (2014) Preparation of Iron, Aluminium, Calcium, Magnesium, and zinc Humates for Environmental Applications. *Chemical Papers*, 68, 1443-1451. http://dx.doi.org/10.2478/s11696-014-0586-y
- Seki, H. and Suzuki, A. (1995) Adsorption of Heavy Metal Ions onto Insolubilized Humic Acid. Journal of Colloid and Interface Science, 171, 490-494. <u>http://dx.doi.org/10.1006/jcis.1995.1207</u>
- [9] Krumins, J., Klavins, M., Seglins, V. and Kaup, E. (2012) Comparative Study of Peat Composition by using FT-IR Spectroscopy. *Material Science and Applied Chemistry*, **26**, 106-114.