Cation Xanthated Exchangers from Colombian Sub-Bituminous Coals Effectively Removed Cadmium and Lead from Aqueous Solutions

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Abstract

In Colombia, low rank coals are almost totally used for power and metallurgical aims, which are activities that produce contamination. In this investigation, as an alternative to the traditional use of low rank coals, we prepared cationic xanthated exchangers from a subbituminous coal (67.6% C, 4.6% H, 22.4% O, 0.6% S, 3.2% ashes and 46.2% volatile matter) of Montelíbano-Córdoba; this exchanger showed better exchange capacities for cadmium and lead (1.8 meq/g) than traditional sulphonated exchangers (0.56 and 1.11 meq/g for cadmium and lead respectively). Xanthation was verified at 30 °C and at 5-10 °C with NaOH and CS_2. The best performance of xanthation, determined by Infrared spectrometry and ion exchange experiments, occurred at low temperatures maybe due to CS_2 volatility. By diminishing the particle size of coal the exchange capacity increased. The exchange capacity was evaluated by flame atomic absorption spectrometry.

Keywords: subbituminous coal, cation exchange, exchangers xanthates

1. Introduction

Over 6185 million tonnes (Mt) of hard coal and 1042 Mt of brown coal/lignite are currently produced worldwide; Colombia produces 74 Mt of the world´s hard coal [1]. Most of this coal is used for the generation of electricity. An area of scientific and environmental interest is the development of clean technologies that take advantage of the physical and chemical characteristics of coal and use it like raw material for non-power applications. One of these applications is obtaining carbonaceous exchangers to remove metallic cations. For a long time, the ionic exchange properties of low rank coals, natural or modified through processes like sulphonation, have been recognized [2-5]. The effectiveness of lignite for the removal of Pb(II) ions from aqueous solution was evaluated by Rao *et al.*; the maximum adsorption of Pb(II) ions onto lignite was 98% [2]. In 1998, Rivera *et al.* obtained carbonaceous exchangers by sulphonation of subbituminous coals from Montelíbano, Córdoba [6].

Xanthates can display several types of bonds between metals and the group CS_2. Xanthations have been used since long ago. Starch was xanthated by continuous process to produce an additive for pulp and paper products [7]. In 1990, Marañón and Sastre prepared cation exchangers from xanthation of magalla, the residual biomass of cider process. Due to its polymeric properties and to the nature of its components magalla has natural properties of ionic exchange [8]. In 1992, these authors studied the behaviour of magalla in the sorption of trace metals in packed beds [9].

The adsorption of metals into low rank coals continues attracting scientific interest. Anwar *et al.* investigated the adsorption of Cr(III) by two coal varieties from Lakhra and Thar coalfields (Pakistan); they studied the effect of adsorbent dose, pH, contact time and agitation speed on the adsorption of Cr(III); Cr(III) removal was 2.61 mg of Cr(III) per gram of Lakhra coal [10]. In other study, the removal of Cr(VI) from aqueous solutions using low-rank Turkish brown coals was studied as a function of contact time, solution pH, temperature, concentration of metal solutions and amount of adsorbent; adsorption capacities of 12.4 mM of Cr(VI)/g were observed [11].

The objectives of this work were to prepare xanthated cationic exchangers from subbituminous coals to remove cadmium and lead in aqueous solutions. The cationic exchangers were compared to traditional sulphonated coals for the removal of these metal. This research is important because in Colombia the low rank coal is almost totally used with power and metallurgical aims, which are highly contaminant activities.

2. Methods

2.1. Materials and instruments.

NaOH and CS_2, and $CdCl_2$ and $Pb(NO_3)_2$ (to prepare the 7000±5 ppm solutions of lead and cadmium) were analytical reagents (Merck). A Perkin Elmer AAnalyst 300 instrument was used for the flame atomic absorption measurements. The infrared spectra were taken in a FT-IR Nicolet 5DXC instrument.

2.2. Sample.

A subbituminous coal was taken directly from the mine in Montelíbano (Córdoba, Colombia) and preserved in water. The coal was washed, dried, grounded and sieved and three coal groups with particle sizes of 0.1-0.5 (T1), 0.5-1.0 (T2), and 1.0-2.4 mm (T3) were obtained. Samples were extracted and swollen with tetrahydrofuran during three days, and then were washed and dried.

2.3. Xanthation and sulphonation.

These experiments were carried out by triplicate for every particle size and reaction temperature. A 6 M NaOH solution was added to the coal (a 3:1 molar relation between NaOH and the quantity of OH in the coal -calculated from elemental analysis making coal oxygen content = coal OH content-) and, after 5 minutes, CS_2 (a 1:1 molar relation between NaOH and CS_2). Then, the mixture was stirred during 40 hours either at 5-10 °C or 30 °C. For sulphonation of coals, H_2SO_4 (98%) was used at 150 °C during 75 minutes (a 1:4 relation acid:coal) for a T1 particle size coal.

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This was the smallest particle size and it was used with sulphonated coals to compare with T1 xanthated coals. Then, the coals were washed up to a filtrate pH lower than 8 and dried.

2.4. Ion Exchange experiments.

For every combination of particle size and reaction temperature, 50.00 mL of 7000 ppm solutions of the metals (by triplicate) were mixed with 0.5000 g of xanthated or sulphonated coal. After stirring for 24 hours, the filtrate was evaluated by flame atomic absorption spectrometry (three averaged measurements every three seconds for a total of 9 measurements).

3. Results

We used a type B subbituminous coal with 67.6% of carbon, 4.6% of hydrogen, 22.4% of oxygen, 0.6% of sulphur, 3.2% of ashes and 46.2% of volatile matter on dry base was used; its calorific capacity was 9925 BTU/Lb; calorific capacity and elemental analysis were carried out by SGS de Colombia S.A. in Barranquilla according to ASTM norms for coal analysis. (http://www.co.sgs.com/es_co/minerals_co?lobId=19556)

The calibration curves showed an average correlation coefficient of 0.998 for filtrates of xanthated or sulphonated exchangers experiments. The relative standard deviation (RSD) of the method was 3.8% for lead and 7.8% for cadmium exchange tests. The precision of the instrument for 30 measurements of a 0.68 ppm solution of Cd or Pb was less than 1%. Recovery experiments were 103% (±1%) for cadmium and 97% (±4%) for lead. These values were not statistically different from 100% according to the student t-test at a 95% confidence level. The limit of detection of the atomic absorption instrument (concentration of the blank plus three times its standard deviation in concentration units) was 0.1 ppm.

The infrared spectra showed greater C=S stretching bands near 1400 cm^{-1} and lower OH phenolic stretching to 3184 cm^{-1}, for the coal xanthated at lower temperature (Figure 1).
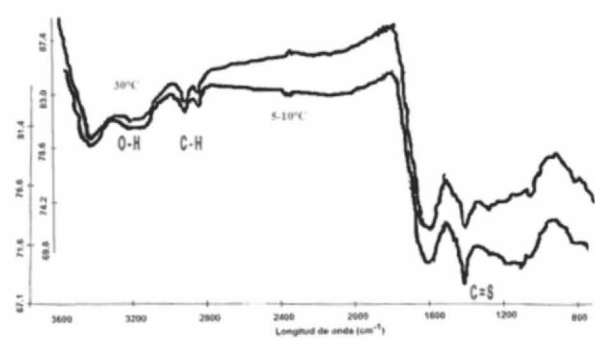

Figure 1. Infrared spectra of the xanthated coals. When the coal was xanthated at 5-10°C greater C=S stretching bands and lower OH phenolic stretching were observed indicating a higher yield of xanthation.

Table 1 shows the exchange capacity for xanthated exchangers. For the sulphonated exchanger, the exchange capacity (meq/g) was 0.56 ± 0.04 (RSD 7%) and 1.11 ± 0.02 (RSD 1.9%) for cadmium and lead respectively. For the xanthated exchanger, the exchange capacity (meq/g) was 1.8

± 0.2 (RSD 10%) and 1.80 ± 0.07 (RSD 1.9%) for cadmium and lead respectively, for the same T1 particle size. In order to determine if a significant difference existed in the results for xanthated exchangers, a student t-test was used. For all comparisons, we considered results to be significant at $p < 0.05$. Between the exchangers with different particle sizes, there was a significant difference for cadmium exchange for T1-T2 and T1-T3 sizes at a reaction temperature of 5-10 °C and for T1-T2 and T1-T3 sizes at 30 °C. For lead exchange, there was a significant difference between all the particle sizes at any temperature excepting T2-T3 sizes at low temperature. Finally, there was a large significant difference between the exchange capacities of xanthated and sulphonated exchangers for both cations.

Table 1. Exchange capacity of the xanthated exchanger.

Xanthation temperature and sample size		Pb EC (meq/g) ± SD; RSD	Cd EC (meq/g) ± SD; RSD
5 – 10 °C	T1	1.80 ± 0.07; 4%	1.8 ± 0.2; 10%
	T2	1.18 ± 0.05; 4%	1.4 ± 0.1; 7%
	T3	1.08 ± 0.07; 7%	1.4 ±0.1; 6%
30 °C	T1	1.54 ± 0.02; 1%	1.6 ± 0.1; 6 %
	T2	1.32 ± 0.04; 3%	1.3 ± 0.1; 10%
	T3	1.08 ± 0.04; 4 %	1.28 ± 0.07; 5%

EC. = Exchange capacity; SD = Standard deviation, RSD = Relative standard deviation. T1, T2, T3 = Coals with particle sizes between 0.1-0.5 mm, 0.5-1.0 mm and 1.0 – 2.5 mm, respectively.

4. Discussion

The exchange capacity of the exchanger xanthated at 5-10 °C was higher than the ones showed by the exchanger prepared at room temperature (30 °C); this can be attributed to a greater reaction yield at low temperature, because carbon disulphide is very volatile at this temperature and more disulphide remains in the reaction flask; this explanation was supported by the infrared spectra: greater C=S stretching bands and lower OH phenolic stretching were observed indicating a higher yield of xanthation at low temperature more CS_2 groups were bonded to the coal and less OH groups did not react.

The differences in ion exchange capacities between coals of different particle size was possibly due to their differences in superficial area; coals with small particle size must have a large superficial area and, therefore, they showed a larger ion exchange than large particle size coals. The lack of significant differences between coals with different particle size can be due to the magnetic stirring that could have degraded the particle size. The larger exchange capacities of xanthated exchangers demonstrate that they have a greater amount of exchangeable sites than sulphonated exchangers. These adsorption sites are probably carboxylic acid and phenolic hydroxyl functional groups, mainly, present on the coals surface [12-14]. The mechanism of adsorption of metals is most likely ionic exchange; Murakami et al. studied the interaction between surface functional groups of brown coal and metal cations by cation exchange experiments; for all cations, the extent of cation exchange (ECE) of the raw coal increased with pH, which suggested that the ECE for raw coal was controlled mainly by the acid dissociation equilibrium of carboxyl groups [5].

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5. Conclusions

We prepared xanthated exchangers from subbituminous coals. Xanthated exchangers showed better exchange capacities than traditional sulphonated exchangers. By diminishing the particle size the exchange capacity of the xanthated exchanger increased. The best yield of xanthation occurred at low temperatures. Magnetic stirring was not a good stirring method for ion exchange experiments with coal because partial degradation of the particle size occurred.

6. Acknowledgements

7. References

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