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EVALUATION OF SHREDDER BANKNOTES AS FEEDSTOCK IN THE PRODUCTION OF ADSORBENT MATERIAL APPLIED IN WASTEWATERS TREATMENT OF PAPER MONEY PRINTING PROCESS

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ABSTRACT

The preparation of adsorbent material from the residue of deteriorated banknotes by thermal activation was studied, as well as its application in the treatment of effluents originated in the process of paper money printing. Based on the result obtained in thermogravimetric analysis and literature review, oxidative atmosphere, temperatures of 700 and 800^{o}C and pyrolysis times and 1 and 1.5 hrs were selected. Specific surface area was characterized, by means of nitrogen gas adsorption; the ability to remove organic matter was evaluated, in terms of the change in the chemical oxygen demand of an industrial effluent from the banknote printing process. The highest surface area obtained was 31.4 m^2/g under pyrolysis conditions of 700^{o}C and 1.5 hr. A 33.3% reduction in the chemical oxygen demand of an industrial effluent from the banknotes printing process using samples of adsorbent material synthesized from shredder banknotes, suggesting that banknotes residue can be reused within the same industrial process that produces it.

Key words: Shredder banknotes, Adsorbent material, Wastewater treatment.

INTRODUCTION

Solid adsorbent materials are extensively used in the treatment of contaminated industrial effluents due to their high surface area; high adsorption capacity and the possibility of tailor-made their adsorbent properties for specific functions. The most used material for contaminants adsorption is activated carbon; however, activated carbon is not used in all industries due to its high cost, cumbersome regeneration and final disposal cost[1,2], making attractive the development of alternative production methods from cheap raw material and inexpensive processes. In order to reduce production costs, several raw materials have been studied, many of them being wastes and by-products from agriculture

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and forestry processes, as wood-sawdust, olives stones, coconut shells among others[3-8]. Thermal activation (carbonization) is based on the pyrolysis of the material in an inert or oxidizing atmosphere (air, water vapour, carbon dioxide etc.). At temperatures between 800°C and 1000°C, carbonization reduces non-carbon species using thermal decomposition, increasing carbon content and generating some porosity on the material, usually with some contribution to available surface area; carbonization is generally an inexpensive and simple process to implement[9]. Chemical activation is performed by mixing the raw material or the material obtained after carbonization with a dehydrating agent such as acids and bases, followed by a pyrolysis usually at temperatures below the ones used in thermal activation.

Banknotes made of cotton fibber are produced worldwide by central banks and specialized companies, with a lifespan that ranges from 13.8 to more than 27.6 months[10]. Disposal methods varies from landfill discarding, incineration and composting[11]. Security inks and other products used in the printing of banknotes, produces contaminated effluents characterized by the presence of colour, high chemical oxygen demand and high concentration of dissolved solids[12]. Treating this wastewater traditionally involves filtering, coagulation, flocculation and adsorption processes. Activated carbon was the main adsorbent material used. This paper studies the preparation of adsorbent material from shredder banknotes by oxidative thermal activation under different conditions of temperature and time for the use in the treatment of effluents from the process of banknotes printing.

EXPERIMENTAL

Shredder banknotes characterization

Regardless of the type of disposal selected, any old, damaged or unfitted banknotes must be first shredder in order to avoid the possibility of reconstitution or counterfeiting; frequently to facilitate handling the shredder banknote is agglomerated in the form of a briquette.

Fig. 1: Photograph of shredder banknote and briquetted

Moisture content and ash analyses were performed according to NTC 4467 (ICONTEC, 1998). Volatile solids content was determined following method 1684 (EPA, 2001), which is based on weight change between material on a dry basis and the material after heating at 550^{o}C. The obtained results show that the shredder banknote has an average humidity of 5.4%, ashes content of 4.76 and volatile solids 78.4%; all percentages expressed in weight. A thermogravimetric analysis (TGA) equipment, TA Instruments model 2050 (± 0.025 mg), was used to determine the shredder banknotes weight change, when heated from room temperature to 850^{o}C at a heating rate of 5^{o}C/min and under oxidant and non-oxidant atmospheres (air 100 mL/min and N_2 100 mL/min, respectively), Fig. 2 shows the TGA profile of the shredder banknote samples.

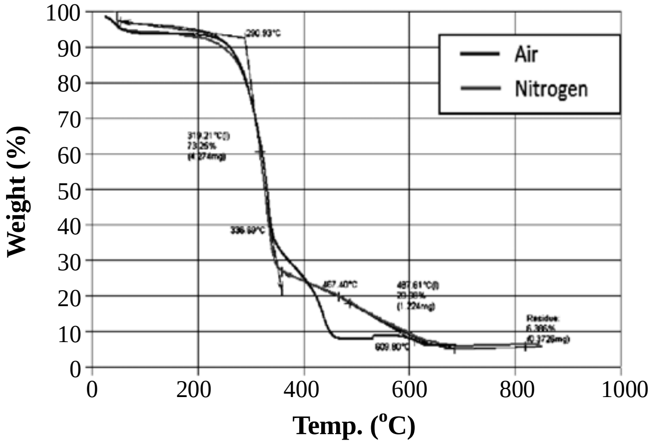

Fig. 2: TGA profiles of the shredder banknote samples

Both type of atmospheres treatment in TGA present similar behaviour up to temperatures around 340^{o}C, characterized by an initial 5 to 6% weight loss in the temperature range form room temperature up to 290^{o}C; the rate of weight loss in this initial interval is -0.06% w/°C, approximately; the amount of weight loss in this initial section coincides with the humidity previously determined. From 290^{o}C to 340^{o}C, a 40.9% weight loss is observed, the sample rapidly lose weight at a rate of -0.91% w/°C in the form of volatile compounds from thermal degradation of cellulose and the characteristics oily compounds impregnated on the banknote during circulation. From approximately 340^{o}C to 615^{o}C, there is a 30.7% loss in weight usually related to the degradation of volatile compounds trapped in the pores of the material. About 550^{o}C, it is observed that the sample gives off a thick smoke and yellow-brown viscous liquid, which can be related to the generation of bio-oil (bitumen) from the degradation of the remaining volatiles. Although in both atmospheres, TGA in this temperature ranges have the same weight loss, their profile behaviours diverged considerably; under N_2 atmosphere, there is a continuous weight loss at a rate of -0.08% w/^oC, implying that the phenomena is essentially thermally driven (volatilization or decomposition); On the other hand, under oxidative atmosphere (air), there is a sharp weight loss up to 450^{o}C, characterized by a variable loss rate, which may be the combination of thermally and chemical driven phenomena in the form of volatilization, decomposition and chemical reactions (mainly oxidation); beyond 615^{o}C both profiles match again and essentially remain the same there after, with a residual weight of approximately 6% of the original sample weight.

Adsorbent material synthesis and characterization

Based on the result obtained in the thermogravimetric analysis and literature review oxidative atmosphere, temperatures and pyrolysis times of 700 and 800^{o}C and 1 and 1.5 hrs respectively[13-16], were chosen for the synthesis of adsorbent material from shredder banknotes; the pyrolysis experiments were performed in and tubular oven (Mini-mite™ Thermo Scientific Lindberg/Blue M oven model TF55035A) under oxidant atmosphere (air). Adsorption isotherms of nitrogen (N_2) at 77 K were determined on a Quantachrome Autosorb-1 surface analyzer™. The BET and BJH models were used to estimate the specific surface areas (m^2/g) and pore volume distribution of the adsorbent material samples (Gomez -Serrano et al, 2001). Morphological analyses of the shredder banknotes and adsorbent material samples were carried out in a scanning electron microscope (SEM) model Pro Phenom G2 desktop. Additionally, elemental chemical composition was determined using an X-Ray fluorescence (Magi XPro, Philips) and an Energy-dispersive X-ray spectroscopy (Zeiss Neon 40). Organic matter removal capacity was determined following the American Water Works Association (AWWA) standard method 5220D; chemical oxygen demand (COD) of 1600 mg O_2/L and pH of 6.75 were determined from a sample of contaminated industrial effluent collected from the printing process of banknotes. To determine the organic matter removal capacity of the adsorbent material, experiments were performed adding 0.05 g ± 0.1 mg of adsorbent material (Sartorius BP 2215 balance) into a 200 mL capacity amber glass containers, where 100 mL of contaminated effluent was poured. These containers were kept for 24 hrs under constant stirring to ensure uniform mixing and then the COD of each sample was measured; distilled water was used as blank experiment. For comparison purpose, a commercial available adsorbent material, Carbochem LQ1000, was also tested (1058 m^2/g).

RESULTS AND DISCUSSION

Fig. 3a shows a SEM picture of shredder banknote corresponding to a fragmented briquette. It can be observed, how the briquette is formed by clusters of shredder banknotes in which the fibers of cotton are visible; Fig. 3b is a magnification of the one of the cotton fiber observed in Fig. 3a.

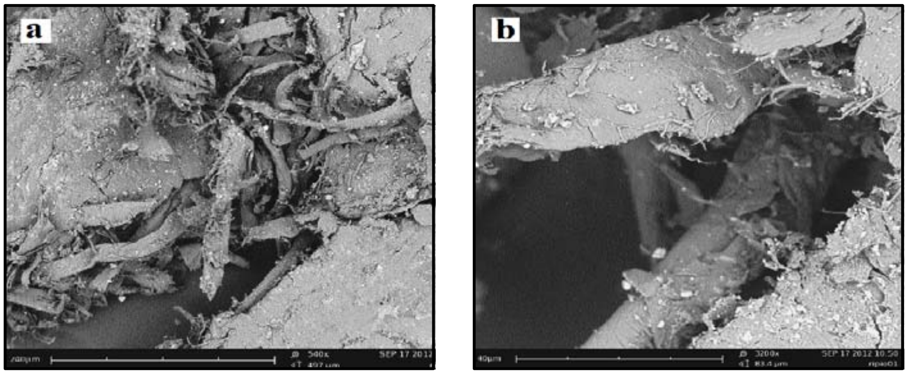

Fig. 3: SEM photograph of shredder banknotes as fragmented briquette

Width of individual cotton fibers can be estimated from Fig. 3. Overall, they seem to be in the order of 20 to 50 μm wide; most of the fibers look decorated by tiny, shiny, well dispersed particles, residual form the inks and security features usually found in banknotes. Fig. 4a and b shows a SEM representative picture at different magnifications of the adsorbent material obtained after the pyrolysis of shredder bank note of approximately 30 μm wide, with a very irregular surface having what seem to be cracks and undulations.

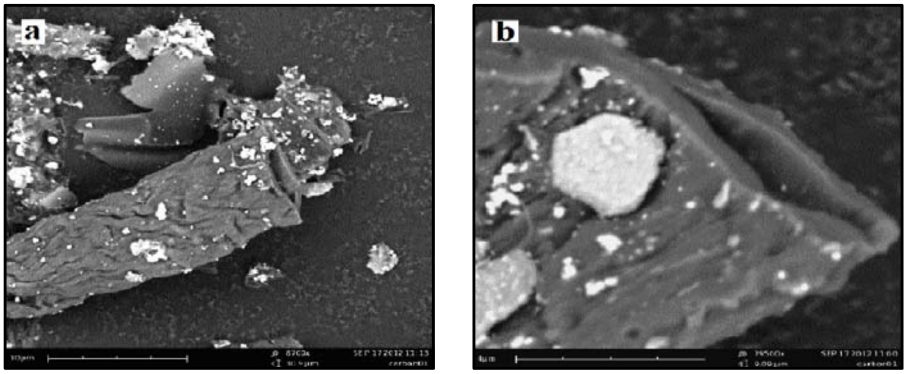

Fig. 4: SEM photograph of an individual particle of adsorbent material

The presence of tiny and shiny particles is also evident in the adsorbent material. X-ray fluorescence and EDS analyses of both, shredder banknotes and adsorbent material, indicate the presence of chemical elements commonly found in inks and elements used in banknotes, Significant percentages of titanium and iron were determined (Table 1).

Elemental composition of light atomic number elements (lighter than sodium) was not quantified.

Table 1: Elemental chemical analysis of shredder banknotes and adsorbent material

Element	Shredder banknote	Adsorbent material	Element	Shredder banknote	Adsorbent material
P	0.61	nd	Zn	6.43	7.1
S	0.72	0.03	Ni	6.79	7.14
Si	1.04	1.11	Cu	7.47	8.01
Cr	1.68	2.06	Ca	9.99	10.1
K	2.38	nd	Fe	26.2	26.9
Zr	5.01	5.4	Ti	31.6	32.1

Average values of surface area and pore volume are summarized in Table 2. An average surface area of 19.75 m^2/g is reported for all the adsorbent material samples. A highest area value of 31.6 m^2/g for the sample synthesized at 700^oC and 1.5 hr and a lowest area value of 12.23 m^2/g for the sample synthesized at 800^oC and 1 hr, were determined. The areas reported for the adsorbent material synthesized are 4.5-12 times higher than the surface area obtained for the shredder banknotes.

Table 2: Surface area and pore volume of shredder banknotes and adsorbent material

Temp. (Celsius)	Pyrolysis time (hr)	Surface area (m^2/g)	Pore volume (cc/g)
Shredder banknote		2.8	1.3×10^{-3}
700	1	19.56	1.2×10^{-2}
800	1	12.23	7.6×10^{-3}
700	1.5	31.4	1.9×10^{-2}
800	1.5	15.79	1.0×10^{-2}

Adsorption isotherms of the shredder banknote and the adsorbent material with the larger surface area correspond to type IV, characteristics curves of mesoporous solids, whereby at low pressures ($P/Po > 0.35$) there is an increase in the adsorption of nitrogen relative to untreated shredder banknote's micropore filling characteristic. As pressure increases the material ($0.35 < P/Po < 0.85$), smaller pores are filled presenting a stabilization in volume adsorbed and then the capillary condensation in the micropores occurs followed by the mesopores filling process. It is evident that the pyrolysis treatment increased N_2 adsorption capacity of the base material, improving the surface area and pore volume due to the thermal degradation of volatile compounds. Pore volume distribution profiles (Fig. 5) indicated mainly presence of macroporosity in the raw shredder banknote material and the formation of mesoporous after treatment; none of the treated samples present formation of microporosity, differences in surface area among samples rise from the differences of the accumulative distribution of mesoporous versus macroporosity, samples with higher surface area show more accumulative mesoporosity at smaller size diameter.

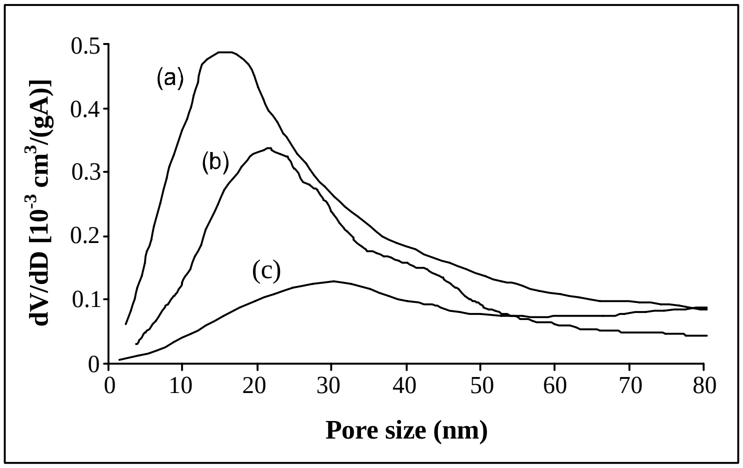

Fig. 5: Pore size distribution plot (a) adsorbent material 700°C, 1.5 hr, (b) adsorbent material 800°C, 1 hr and (c) shredder banknotes

The organic matter removal capacity obtained for the adsorbent material varied from 13.33 to 33.33% of the original COD value in the contaminated industrial effluent (1600 mg O_2/L). Among the tested samples, the adsorbent material that shows the highest removal was synthesized at 700°C for 1 h. To compare the ability of removal of the synthesized adsorbent material with commercially available adsorbent material, 3 aliquots of the same industrial effluent were tested with Carbochem LQ1000 (surface area of 1058 m^2/g). Carbochem LQ1000 showed an average removal of 94% (Table 3), almost 3 times the removal capacity than that obtained with the most removal effective synthesized adsorbent material; however, it should be noted that the Carbochem LQ1000 sample has more than 50 times the surface area of the synthesized adsorbent material and therefore, the adsorption capacity of organic matter not only depends on the surface area and pore volume, but is also influenced by the surface chemistry of the material, as reported in various papers.

Table 3: Chemical oxygen demand of the contaminated industrial effluent treated with adsorbent material

Temp. (Celsius)	Pyrolysis time (h)	Surface area (m^2/g)	COD (mg O_2/L)	Removal
700	1	19.56	1067	33.33
800	1	12.23	1387	13.33
800	1.5	15.79	1387	13.33
Carbochem LQ1000		1058	96	94.1

CONCLUSION

Shredder banknotes and adsorbent material were characterized by means of TGA, XRF, SEM and surface area. Adsorbent material was prepared from shredder banknotes by thermal activation under oxidizing atmosphere, temperatures and pyrolysis times of 700 & 800°C and 1 & 1.5 hrs, respectively. The ability to remove organic matter was evaluated, in terms of the change in the chemical oxygen demand of an industrial effluent from the banknote printing process. Increments in the order of 4.5 to 12 times of the original values of the shredder banknote surface area was obtained in the synthesized adsorbent materials; however, being low, when compared to commercial activated carbon surface area (Carbochem LQ1000). The biggest surface are obtained for the adsorbent material was 31.6 m^2/g for the sample synthesized at 700°C and 1.5 hr and a smallest area was 12.23 m^2/g for the sample synthesized at 800°C and 1 hr.

The highest reduction of the chemical oxygen demand of an industrial effluent from the banknotes printing process using samples of adsorbent material synthesized from shredder banknotes was 33.3%, almost one third of the obtained for the Carbochem LQ1000 (94% reduction); however, it should be noted that the Carbochem LQ1000 sample has more than 50 times the surface area of the synthesized adsorbent material; therefore, the adsorption capacity of organic matter not only depends on the surface area and pore volume, but is also influenced by the surface chemistry of the material. It was demonstrated that shredder banknotes could be a potential feedstock for the production of adsorbent material and that resultant materials have the capacity to reduce the chemical oxygen demand of an industrial effluent from the banknotes printing process.

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