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Modified reductive expansion synthesis (M-RES) for the production of carbon porous material from deteriorated banknotes

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Abstract: A Modified reductive expansion synthesis (M-RES) has been proposed for the production of carbon based porous material from the residue of deteriorated banknotes using thermal activation. Thermal activation temperature and time were studied as synthesis variables along with the weight ratio urea/banknote loading. Shredded banknotes and synthesized samples were characterized by means of X-ray fluorescence, Scanning Electron Microscopy, Energy Dispersive Spectrometry and total surface area. The highest impact in the increment of total surface area is the activation thermal time of 40 min, with an average increment of 18.2 times the value of the shredded banknote total surface area, followed by the 0.5 urea loading (16.9 times) and the activation thermal temperature of 700 ^{o}C (16.4 times), the best combination of synthesis variables is obtained for the sample produced at 700 ^{o}C, for 40 min with 0.5 urea/banknote weight ratio loading, with total surface area 29.2 times higher. In the range value of the variables studied, the highest values of thermal activation temperature and time with high urea loading seems to be detrimental for the generation of higher surface area material.

Keywords— Modified reductive expansion synthesis, Porous materials, Thermal activation.

Introduction

Carbon based porous materials are extensively used in industrial processes as adsorbents for air purification, chemical volatile compound recovery, adsorption of SO_2 and NOx, treatment of water and wastewater, food processing and beverage, pharmaceutical industry, among others [1-4]. The most used material for contaminants adsorption is activated carbon (carbon based adsorbent with pore volume and surface area above 0.2 ml/g and 400 m^2/g, respectively), however activated carbon is not used in all industries due to its high cost, cumbersome regeneration and final disposal cost [2, 4-6].

In order to reduce fabrication costs, alternative production methods and cheap raw material have been explored. Thermal activation, the main method for the production of carbon based porous material, is an energy-intensive procedure based on the pyrolysis of the raw material in an inert or oxidizing atmosphere (air, water vapor and carbon dioxide etc.) at temperatures between 800 °C and 1000 °C for 2 to 3 hours. Decreasing thermal activation working temperature and time will reduce the process energy demand and costs.

Reductive expansion synthesis (RES) is a technique used to synthesis nano and submicron particles of iron, nickel and iron-nickel alloys [7]. The technique involves a procedure in which a mixture of metal nitrates and urea are subjected to rapid heating at high temperature and under an inert atmosphere to create nano and submicron zero valence particles of metals in a process that takes less than 5 minutes; the rapid generation of gases appears to “blow apart” the reacting mixture leaving an easily spread cloud of primary metal particles in the size range of 50 to 250 nm. Reduction state of particles formed is highly dependent of the surrounding atmosphere, iron oxide nano and submicron particles have synthesized just by replacing the inert atmosphere with air (M-RES, Modified Reduction Expansion Synthesis) [8].

Banknotes are usually made of a compounded special type of paper denominated "paper money"; paper money is composed approximately of 75% cotton and 25% linen fibers, which make it extremely mechanical resistant when compare with normal paper; however wear and tear render banknotes unusable after an average lifespan of 13.8 to 27.6 months, usually depending on bill denomination [9, 10]; after a banknote has been declared unusable as an standing legal note the standardized disposal process starts by shredding the material to a confetti size particles to avoid counterfeiting (sometimes this confetti material is agglomerated in the form of briquettes to facilitate handling). The confetti size material or briquetted are then disposed using various methodologies: landfill discarding, incineration and composting; albeit, this waste material does not contain hazardous levels of toxic materials still poses a significant environmental concern [9].

Among the properties a substance must have to be considered as a proper raw material for production of activated carbon are: abundance, hardness, inherent pore structure, high carbon content, low ash content and high yield in mass during the carbonization [11-13]. Several types of wood, coal, lignite, shells and bones of some fruits, such as coconuts and olives, among others are usually used as raw materials in the production of activated carbon. Preliminary studies related to the production of carbon based adsorbent materials from shredded banknotes using thermal activation reported the production of low surface area materials showing interesting results for the removal of organic matter from industrial effluent of the banknote printing process. This paper explore the use of MRES for the synthesis of carbon based adsorbent material from shredded banknotes, analyzing the effect of temperature and time of the thermal activation process, along with the amount of urea.

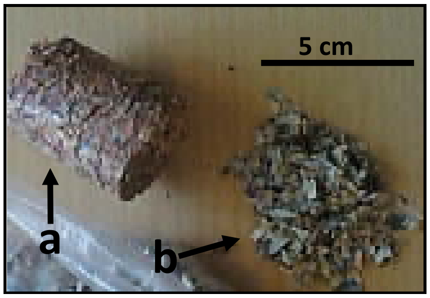

Figure 1. Shredded banknote photographs, a) briquetted, and b) confetti

Materials and Methods.

Materials characterization.

Volatile solids content was determinate following method 1684 (EPA, 2001) following the weight change between material on a dry basis and the material after heating at 550 °C and validate by means of a thermo gravimetric analysis (equipment, TA Instruments model 2050, ± 0.025mg), under oxidizing and non-oxidizing atmospheres (air 100 mL/min and N_2 100 mL/min, respectively). Moisture content and ash analyses were performed according to NTC 4467 (ICONTEC, 1998).

Bulk elemental chemical analysis characterization analysis was performed using a XRF Thermo Scientific Niton XL2 with geometrically optimized large area drift detector. Elemental chemical mapping and morphological characterization of selected synthesized materials was performed by scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS) using a Zeiss Neon 40 Field Emission Microscope operating at 20 kV. BET model was used to determine total surface area and pore sized distribution from N_2 adsorption isotherms obtained at −196◦C in a Quantachrome Coulter equipment.

Synthesis procedure

The standard synthesis procedure consisted in a batch of 1 g of confetti like shredded banknote impregnated in a 50 ml of an aqueous solutions of urea, the resulting mixture was left in an oven at 40 ^{o}C until complete water evaporation was achieved, there after the obtained solid was properly storage in sealed glass containers; several impregnation batches were performed in order to generated shredded urea impregnated banknote with different urea loadings (0.25, 0.5 and 1 weight ratio urea/banknote). For the thermal activation procedure, the impregnated shredded banknote sample was carefully transferred to an alumina boat (4x1x1cm). A Mini-Mite™ Thermo Scientific Lindberg/Blue Tube Furnace (alumina tube, 2.54 cm diameter, 70 cm length) was preheated to the selected thermal activation temperature (600, 700 or 800 ^{o}C); once the oven temperature was stable, the alumina boat containing the impregnated shredded banknote was introduce inside the oven and left inside for the intended thermal activation time (20, 40 or 60 min). After the activation time was completed, the alumina tube was carefully removed from the oven, natural cooling was allowed, and finally the synthesized sample was properly stored.

Results and Discussion

Moisture content and ash analyses reported an average values of 5.4 % humidity, 4.76 ashes content and 78.4 % volatile solids (weight %). Both nitrogen and oxidizing atmospheres TGA generates similar profiles up to temperatures neighboring 340 ^{o}C; with an initial 5 to 6 % weight lost in the temperature range from room temperature to 290 ^{o}C, losing weight at a rate of -0.06 % w/°C approx.; the amount of weight lost in this initial section coincides with the humidity determined. 40.9 % weight lost is observed from 290 °C to 340 °C (-0.91 % w /°C) as a result of the formation of volatile compounds from thermal degradation of cellulose and oily residues impregnated on the banknote during circulation. From 340 °C to 615 °C there is a 30.7 % loss in weight related to the degradation of volatile compounds trapped in pores. At 550 ° C, a dense smoke and yellow-brown viscous liquid related to the generation of bio-oil (bitumen) evolve from the sample. From this point under N_2 atmosphere there is a continues weight loss at a rate of -0.08 % w/°C, implying that the phenomena is essentially thermally driven (volatilization or decomposition); in the other hand, under oxidative atmosphere there is a sharp weight lost up to 450 ^{o}C, characterized by a variable lost rate which may be the combination of thermally and chemical driven phenomena in the form of volatilization, decomposition and chemical reactions (mainly oxidation); above 615 ^{o}C both profiles match again and essentially remain the same there after, with a residual weight of approximately 6%.

Morphological characterization of the shredded like banknote material performed in SEM is shown in Figure 2; it reveals bundled micron size fibers (average width from 20 to 50 µm), most of them decorated with it seems to be well dispersed, shiny particles. XRF bulk elemental chemical analysis (Table 1) and SEM-EDS elemental chemical mapping indicate the presence of chemical elements commonly found in inks and security features used in the production of banknotes. Average values of total surface area and volume pore for the confetti like banknotes are 2.8 m^2/g and 1.3 x 10^{-3} cc/g, respectively.

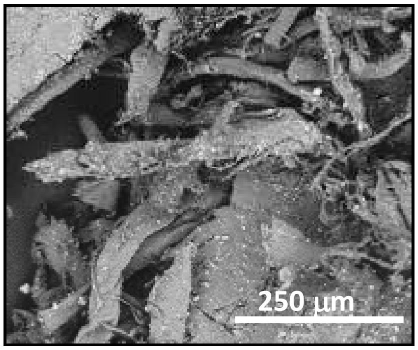

Figure 2. SEM photograph of the shredded banknotes.

Table 1 XRF bulk elemental chemical analysis of shredded banknotes (weight %).

Element*	Shredded Banknote	Element	Shredded Banknote
P	0.61	Zn	6.43
S	0.72	Ni	6.79
Si	1.04	Cu	7.47
Cr	1.68	Ca	9.99
K	2.38	Fe	26.2
Zr	5.01	Ti	31.6

* Composition of light atomic number elements (lighter than sodium) was not quantified.

Figures 3, 4 and 5 shown the 3D surface results of the total surface area for the carbonaceous synthesized material as a function of thermal activation temperature and time, for different urea/banknote weight ratio loadings.

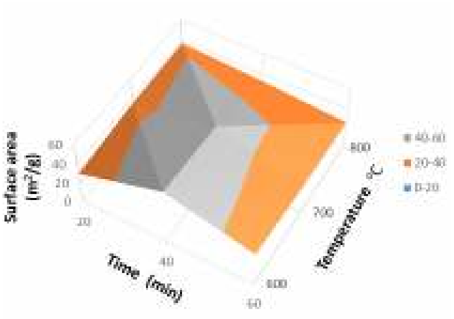

Figure 3. Total surface area of carbonaceous synthesized material as a function of thermal activation temperature and time, for 0.25 urea/banknote weight ratio loading.

In the case of the 0.25 urea/banknote weight ratio loading, the highest total surface area value obtained was for the sample synthesized at 700 °C and 40 min (49.5 m^2/g; these thermal activation temperature and time were also found to be the ones to produce the highest surfaces areas for the 0.5 and 1 urea/banknote weight ratio loadings (82.2 and 62 m^2/g, respectively). On the other hand the lowest total surface area values were obtained for samples synthesized at 800 °C and 60 min for the 0.25, 0.5 and 1 urea/banknote weight ratio loadings (26, 21 and 4 m^2/g, respectively).

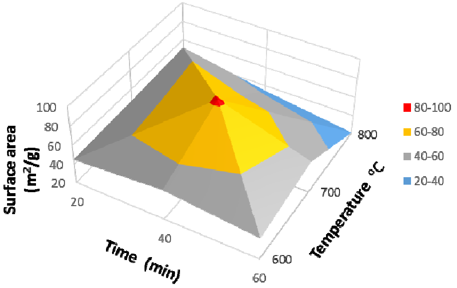

Figure 4. Total surface area of carbonaceous synthesized material as a function of thermal activation temperature and time, for 0.5 urea/banknote weight ratio loading.

When the highest total surface area values obtained for the urea loaded synthesized material are compared against the values of the shredded banknote (2.8 m^2/g) and the non-urea loaded sample (31.4 m^2/g, 11.2 times higher than the shredded banknote), is clear to conclude the positive impact the addition of urea to the thermal activation process has, generating synthesized samples with total surface areas 17.6, 29.2 and 22 times higher than confetti like banknote for the 0.25, 0.5 and 1 respectively.

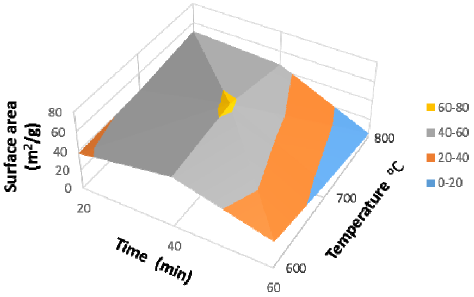

Figure 5. Total surface area of carbonaceous synthesized material as a function of thermal activation temperature and time, for 1 urea/banknote weight ratio loading.

An analysis of the average total surface area values for the each of the synthesis variables shows that the variable with the highest impact in the increment of total surface area is the activation thermal time of 40 min, with an average increment of 18.2 times the shredded banknote total surface area, followed by the 0.5 urea loading (16.9 times) and the activation thermal temperature of 700 °C (16.4 times); the best combination of synthesis variables is obtained for the sample produced at 700 °C, for 40 min with 0.5 urea/banknote weight ratio loading, with total surface area 29.2 times higher.

Figure 6 is a SEM representative picture of the synthesized samples, showing irregular shape and size particles, with average lengths ranging from 10 to 150 microns; particles surface seems to be uneven presenting some cracks and undulations.

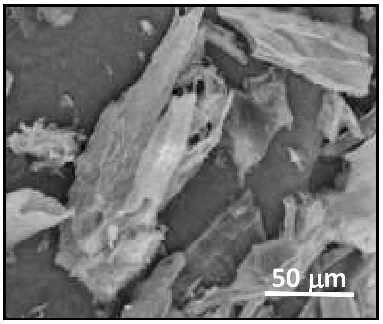

Figure 6. SEM representative picture of synthesized sample.

Figure 7 is a high magnification SEM representative picture of the synthesized samples, where the presence of both macro and meso pores can be observed, no clear evidence of the existence of micro porosity is obtained via SEM analysis.

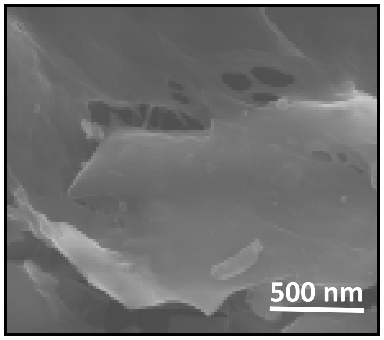

Figure 7. High magnification SEM representative picture of the synthesized samples

As reported en Table 1, shredded banknotes particles contain chemical elements related to in inks and security features, SEM-EDS capabilities were used to map the distribution of C, Ti and Fe on the surface of the synthesized sample, as shown in Figure 8.

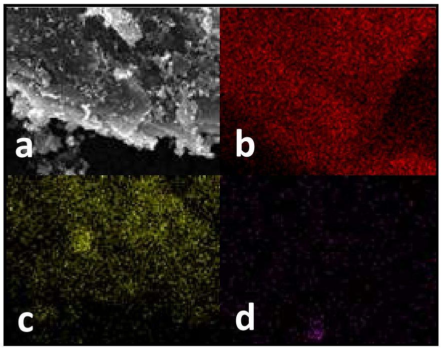

Figure 8. SEM-EDS mapping of synthesized samples, a) SEM picture, b) EDS mapping for C, c) EDS mapping for Ti and d) EDS mapping for Fe.

SEM-EDS mapping from Figure 8 reveal that the synthesized sample is a carbon base material, homogenously decorated with Ti and Fe particles (probably in the form of oxides, due to the synthesis conditions); this is a very interesting feature due to the fact that carbon supported catalyst containing Ti and Fe have been reported as highly effective in treatment of contaminated water. SEM-EDS mapping results are also supported by XRF elemental analysis performed on synthesized samples (Table 2); weight percentage of most of the reported chemical elements increases except for the cases of P, S and K which evolved during the thermal activation process as volatile compound.

Table 2 XRF bulk elemental chemical analysis synthesized material (weight %).

Element*	Material	Element	Material
P	nd	Zn	7.1
S	0.03	Ni	7.14
Si	1.11	Cu	8.01
Cr	2.06	Ca	10.1
K	nd	Fe	26.9
Zr	5.4	Ti	32.1

* Composition of light atomic number elements (lighter than sodium) was not quantified.

Conclusions

SEM morphological characterization of synthesized samples reveals that the M-RES synthesis process produces irregular shape, and size particles (average lengths ranging from 10 to 150 microns), with uneven surfaces where the presence of both macro and meso pores can be observed. The highest impact in the increment of total surface area is the activation thermal time of 40 min, with an average increment of 18.2 times higher than shredded banknote total surface area, followed by the 0.5 urea loading (16.9 times) and the activation thermal temperature of 700 ^{o}C (16.4 times), the best combination of synthesis variables is obtained for the sample produced at 700 ^{o}C, for 40 min with 0.5 urea/banknote weight ratio loading, with total surface area 29.2 times higher. In the range value of the variables studied, the highest values of thermal activation temperature and time, and urea loading seem to be detrimental for the generation of higher surface area material. Elemental chemical analysis obtained using XRF and SEM-EDS mapping reveal the presence of chemicals elements as Ti, Fe, Ca, Ni and Zn, among others, in the shredded banknote and in the synthesized material

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