

PREPARATION AND EVALUATION OF ADSORPTION PROPERTIES OF THE MAGNETIC BAGASSE

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ABSTRACT

The presence of toxic elements in the aquatic environment has been of great concern because their toxicity at lower concentrations and also they are cumulative and carcinogenic. Toxic elements are absorbed and stored in animal and vegetable tissues, for instance, uranium radionuclides. Radioactive uranium waste is generated at hospitals and universities. Furthermore uranium is used as fuel for nuclear power plants. There are some methods available for the removal of metal ions from aqueous solutions. These are ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption. The last one, adsorption, has directed the research of new materials with good removal capacity. The purpose of this paper was to study the preparation of magnetic bagasse, which consisted of sugarcane bagasse as polymeric matrix with magnetite nanoparticles core. These particles have presented superparamagnetic properties. Some studies were carried out such as time required for the uranium-bagasse equilibrium in the interval from 5 to 90min, the effects of biomass piece size ($\Phi < 0.64$, $0.64 \leq \Phi \leq 9.61$ and $\Phi > 9.61$)mm², pH in the intervals from 2 to 5 and 10, stirring speed from 240 to 500r.p.m. and adsorbent dose from 2 to 25g.L⁻¹. The efficiency of magnetic bagasse for the removal of U(VI) was 94%.

1. INTRODUCTION

The increase in industrial activities has intensified environmental pollution through accumulation of pollutants such as organic compounds and toxic elements.

The presence of toxic elements in the aquatic environment has been of great concern because their toxicity at lower concentrations, and also they are cumulative and carcinogenic. Toxic elements are absorbed and stored in animal and vegetable tissues, for instance, uranium radionuclides.

Uranium has the highest atomic weight among the natural elements. It is a radioactive element and contributes to natural background radiation in the environment.

It is very used as nuclear power plants fuel. U-235 is the main isotope used in the production of fuel element, as it is fissionable. The fuel cycle includes uranium mining/beneficiation and production of fuel element to the generation of nuclear energy. The fuel cycle generates considerable amounts of nuclear waste with different radioactivity levels. Hospitals and universities also generate uranium radioactive waste.

There are some methods available for the removal of metal ions from aqueous solutions. These are ion exchange, solvent extraction, reverse osmosis, precipitation and adsorption.

The last one, adsorption, has directed the research of new materials with good removal capacity.

In this sense, the biomass has demonstrated to be an atoxic and low cost alternative material, besides being abundant and biodegradable [1,3,6,7]. The sugarcane bagasse is a waste generated in large amounts in sugar and alcohol industries. It was studied [2] to uranium removal by adsorption. The adsorption occurs when molecules and ions of a concentrated fluid are sorbed onto an adsorbent solid surface.

The purpose of this paper was to study the preparation of magnetic bagasse, which consisted of sugarcane bagasse as polymeric matrix and magnetic nanoparticles core (Fe_3O_4). In the last years, synthesis of nanometer scale particles has been concerned of applied research in many areas, such as biology, medicine and environment.

Magnetic particles of size below a critical diameter ($<26\text{nm}$) exhibit superparamagnetism [5], that is, they do not become permanently magnetized, because there is no residual magnetization after removing the magnetic field (null remanence and coercivity).

When magnetic nanoparticles are in suspension, in water for instance, they are able to answer to action of the magnetic field, making possible the magnetic separation. In this way, particles can be recovered from the waste stream using a magnet and without magnetic field they remain in suspension on the water. Therefore, the particles may be reused.

Therefore, this innovative study makes possible the use of two separation techniques for metal removal: 1) adsorption separation, 2) magnetic separation.

2. EXPERIMENTAL

2.1. Reagents

Standard solution of uranyl nitrate was obtained by dissolution of U_3O_8 nuclear pure; Fe(II) chloride tetrahydrate; Fe (III) chloride hexahydrate; solution of arsenazo III 0.06%, nitric acid and sodium hydroxide.

2.2. Preparation of Magnetic Bagasse

Raw sugarcane bagasse was washed with water to eliminate the ferment's smell. It was sundried ($27\pm 2^\circ\text{C}$), cut in small sizes, after that, it was separated using sieves of various opening sizes. It was thermically treated in muffle at 300°C during 30min. Magnetite nanoparticles were prepared by addition the bagasse to 150ml of solution being 0.21g of Fe(II) chloride tetrahydrate and 0.31g of Fe(III) chloride hexahydrate (molar ratio 1:2). This system was stirred during 1h. After that, it was added a 5mol/L NaOH solution until to reach the pH 11 at room temperature (with the purpose of precipitating the magnetite). The bagasse covered with magnetite was washed with deionized water until it reaches pH ~ 7 . After that, the precipitation process was carried out on this bagasse. Finally, the particles were dried in a hot-plate and used for adsorption experiments. These particles were called magnetic bagasse.

2.3. Adsorption Studies

Batch adsorption experiments were carried out by stirring 2mL of a solution of uranyl nitrate with a known amount of magnetic bagasse. After stirring at specified speed and time, the liquid phase (supernatant) was separated to determinate the U concentration. A spectrophotometer UV-Vis, mod. B582 Micronal, was used to determinate the U concentration by arsenazo III method [4]. The %removal was determined by the equation 1.

$$\% \text{removal} = (C_0 - C) \times 100 / C_0 \quad (1)$$

where: C_0 = concentration of U ions (mg.L^{-1}), before equilibrium;
 C = concentration of U ions (mg.L^{-1}), in the equilibrium.

The uranium mass adsorbed per gramme of magnetic bagasse was calculated by difference between the U concentration of the solution before equilibrium and in the equilibrium, multiplied by the uranium volume used in batch experiment and divided by magnetic bagasse mass. The adsorption capacity was determined by the equation 2:

$$\text{Capacity of adsorption } (\text{mg.g}^{-1}) = (C_0 - C) \times V / M \quad (2)$$

where: V = volume of uranyl ions solution (L) in contact with the magnetic bagasse.
 M = mass (g) of the adsorbent.

The studies were realized in triplicate. All results represent measurements with an estimated standard deviation of about 3%.

3. RESULTS

3.1. Study of Equilibrium Time

For the study of the equilibrium time the batch method was used according to the methodology described, varying the agitation time in the interval from 5 to 90min. Other variables were fixed as pH3.5, adsorbent dose 12.5g.L^{-1} , speed of 400r.p.m. and uranium concentration at 0.1g.L^{-1} . The results can be verified in Fig. 1.

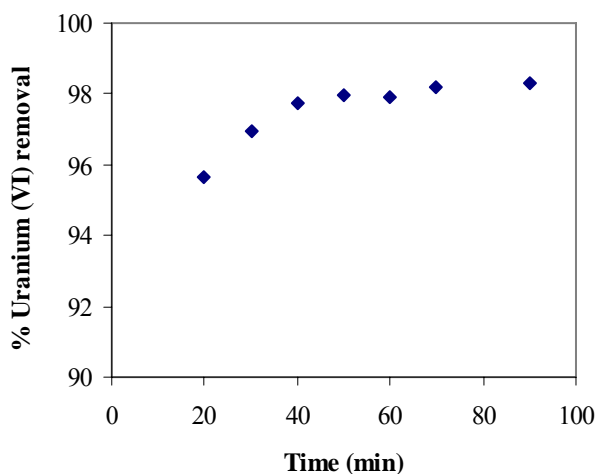


Figure 1. Influence of time for U removal by magnetic bagasse.

3.2. Effect of Piece Size of Magnetic Bagasse

The batch adsorption experiments were carried out using three different piece sizes of magnetic bagasse for uranium at pH5, with adsorbent dose 12.5g.L^{-1} and agitation time of 50min at 400r.p.m. The results were showed in Fig. 2

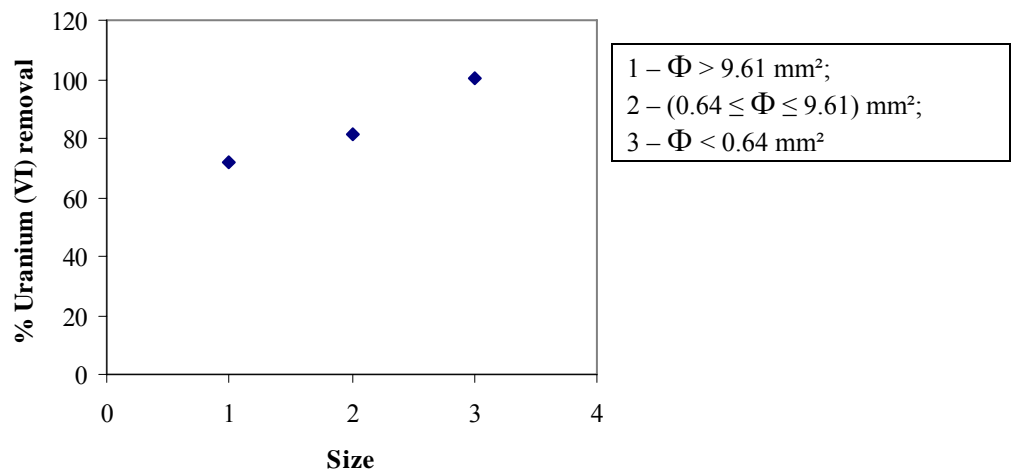


Figure 2: Effect of piece size of magnetic bagasse in the uranium removal.

3.3. Study of pH

The adsorption of uranium was studied in the pH range from 2 to 5 and pH10. The results are illustrated in Fig. 3.

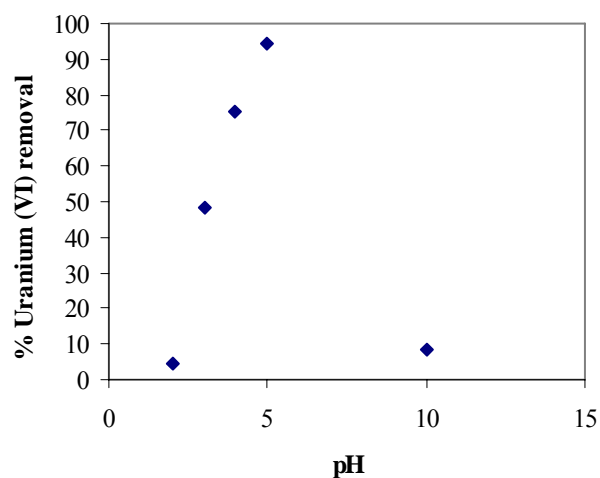


Figure 3: Effect of pH in the uranium removal.

3.4. Effect of Stirring Speed

The stirring speed was studied in the range from 240 to 500r.p.m., where the agitation time at 50min, adsorbent dose at 12.5g.L^{-1} and uranium concentration at 0.1g.L^{-1} , were fixed. The results are illustrated in Fig. 4.

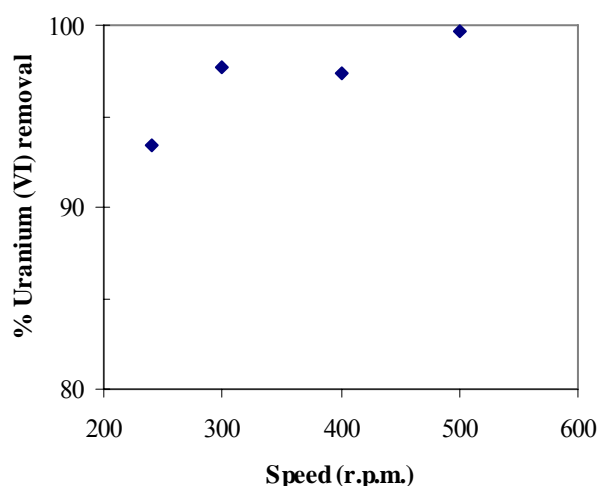


Figure 4: Influence of the speed in the uranium removal.

3.5. Effect of Adsorbent Dose

In this study the adsorbent dose was defined as the amount of magnetic bagasse in contact with a determined volume of uranium solution. The amount of bagasse varied from 4mg to 50mg in 2mL of the uranium solution 0.1g.L^{-1} , pH5. The agitation time was fixed at 50min and the speed at 400r.p.m. The results of %removal and the adsorption capacity are in Fig. 5 and Fig. 6, respectively.

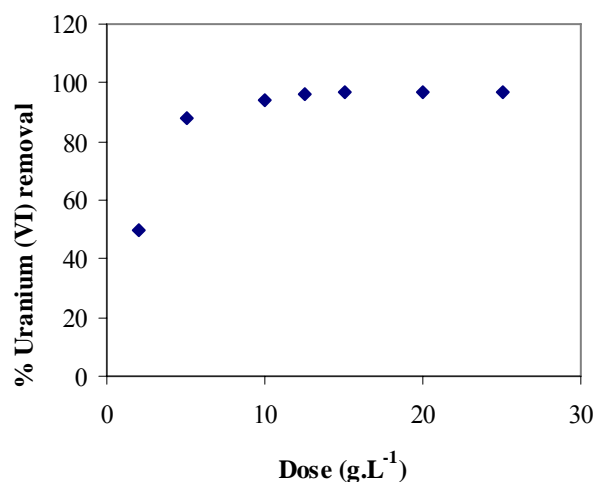


Figure 5: %removal of U in relation to dose of magnetic bagasse.

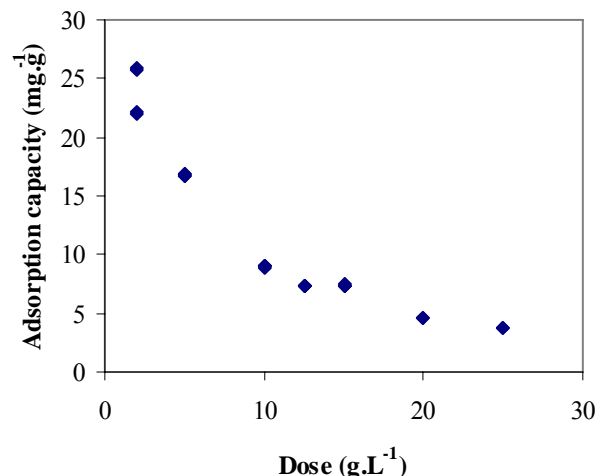


Figure 6: Variation the adsorption capacity of U by magnetic bagasse dose.

4. DISCUSSION AND CONCLUSIONS

This study presented a new material development using sugarcane bagasse, a natural residue, added with magnetite nanoparticles. It was denominated magnetic bagasse. As result, the new material allowed application of the two separation techniques: 1) adsorption, by active sites of the bagasse and magnetite and 2) magnetic, by superparamagnetic property of the magnetite nanoparticles.

The magnetic bagasse has been used for adsorption of U(VI) from aqueous solutions in contact time range from 5 to 90min, Φ particle size ($\Phi < 0.64$, $0.64 \leq \Phi \leq 9.61$, $\Phi > 9.61$)mm², pH from 2 to 5 and pH10, stirring speed from 240 to 500r.p.m., dose from 2 to 25g.L⁻¹.

The adsorption study showed better results in the following conditions:

- The results of varying time are plotted in Fig. 1. The maximum removal occurred starting from 40min, that is, the equilibrium time was achieved in 40min.
- The better adsorption result was obtained with magnetic bagasse pieces of smaller sizes ($\Phi < 0.64$)mm² due to larger contact surface, that is, specific area surface, as observed in Fig. 2. However, in the following studies, the intermediary sizes, $0.64 \leq \Phi \leq 9.61$ mm², were adopted, due to facility of preparation of pieces.
- The uranium adsorption is maximum by magnetic bagasse at pH5, according to Fig. 3. The %removal increased from 4% at pH2 to 94% at pH5. Above this pH occurred the hydrolysis, visually observed by coloring change and precipitates formation. The solution pH10 showed intense yellow, unclouded color and no precipitates.
- In Fig. 4, it was verified that the adsorption process is favorable at increasing stirring speed. The adsorption achieved the equilibrium at 300r.p.m.
- Fig. 5 showed that to larger doses increased the %removal, until achieving the equilibrium. In the dose > 10 g.L⁻¹ the increase of removal was not significative due to equilibrium of adsorbent adsorption capacity. In dose 10g.L⁻¹, the maximum removal was 9mg.g⁻¹.

This study showed that the magnetic bagasse is an efficient adsorbent for removing uranyl ions from aqueous medium, and it presented large perspectives of application on the treatment of radioactive waste. The magnetic bagasse removed until 94% of uranium from the nitric acid solution and it was easily separated from liquid medium using a magnet.

Future studies will be carried out with the magnetic bagasse, such as: characterization, adsorption of others metals and tests with real radioactive waste.

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