Removal of cadmium in wastewater by sorption on ceramics

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Abstract. The removal of cadmium by ceramics surfaces was investigated to evaluate sorption effectiveness of these materials in residual waters. The effects of solution pH, contact time, metal concentration and dose of sorbent material were studied in batch experiments. Ceramic material was compositionally and morphologically characterized before and after the removal of cadmium by scanning electron microscopy to establish the metal sorption. Sorbent material was also tested in residual water with high cadmium content, achieving a 98% removal efficiency.

1. Introduction
In Colombia there is an evident increase in the pollution rate of water sources, of which there are no current figures that provide real information on the composition and amount of waste that ends up in lagoons, lakes, marshes and rivers. Hazardous waste causes major effects on people's health, studies have shown that the accumulation of cadmium in the arteries is a risk factor for developing coronary heart disease, because it produces oxidative stress, high blood pressure and atherosclerosis [1]. Cadmium (Cd) is a metal that is not considered an essential element, neither for animals nor for plants, since it does not fulfill any biological role or function in the organism, and on the contrary it is considered highly toxic for both plants and animals [2].

Following the problems addressed by effluents from industries and service providers, and their threat to ecosystems and human health, a wide variety of methods have been used to eliminate these pollutants, which include biological treatment, coagulation, flotation, oxidation, hyperfiltration and adsorption, such as the use of biomass and materials from the use of waste for adsorption of heavy metals [3-9]. Due to this, the industry promotes the use of materials with properties such, high porosity, ion exchange, low permeability, chemical and physical stability and high surface area. However, the sorption processes also depend on the factors such as the ionic strength, the pH and the anions present in the solution, the concentrations of the adsorbent and the adsorbate [10].

That is why in this work we propose the removal of cadmium present in wastewater, using a ceramic material, synthesized in the “Laboratorio de Química Orgánica y Biomolecular (LQOBio)” [11]. This ceramic material was tested as a sorbent in aqueous waste generated in the laboratories of the chemistry school of the “Universidad Industrial de Santander (UIS)”, Colombia, which according to figures of the waste management program 80% correspond to aqueous solutions with heavy metals [12]. All these wastes at this time do not receive any kind of treatment, they are only labeled, packaged and delivered to a management company, for final disposal.
2. Materials and methods

For this work, a ceramic system previously synthesized in the LQOBio [11] was used, which relation to Si/Al is 2:1, this was ground and sieving, until obtaining a particulate material of 2 microns in size, which was implemented in the sorption tests.

For the sorption test, a 5-point calibration curve was prepared from a standard cadmium solution, the standard was subsequently contacted with the ceramic material to determine the optimal removal parameters (contact time, metal concentration and amount of sorbent material), once these parameters were obtained, carry out sorption tests on toxic waste from industry, for the determination of the residual concentration of the solution, the atomic absorption (AA) technique was used in the Thermo Electron model Solar S2 equipment.

- Contact time. To determine the best contact time a 25 ml of Cd solution (2 mg/L) with a pH of 4.5 a 0.05 g of ceramic was added, then determining the percentage of removal every 2 hours for 28 hours.
- Metal concentration. Having defined the contact time between solute and sorbent, the influence of the concentration of the solution was evaluated, for this purpose 5 solutions of 0.5 mg Cd/L, 1.0 mg Cd/L, 1.5 mg Cd/L, 2.0 mg Cd/L, 2.5 mg Cd/L were prepared, leaving as fixed parameters the amount of sorbent material 0.05 g, contact time 16 h, solution volume 25 mL and pH 4.5.
- Amount of sorbent material. Finally, the amount of sorbent material was evaluated, having 6 tests in which the amount of ceramic was 0.01 g, 0.02 g, 0.03 g, 0.05 g, 0.10 g and 0.20 g, these were placed in contact with 25 mL of 2 mg Cd/L solution, at pH of 4.5, for 16 h.
- Sorption test with liquid waste (toxic waste). Once the optimal parameters were evaluated, they were implemented in the removal of Cd in liquid waste (toxic waste), which were supplied by the “Laboratorio Química de Consultas Industriales, Escuela de Química, UIS, Bucaramanga, Colombia”.

Ceramic systems were characterized in terms of their composition and morphology, by scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDS). These analyzes were performed, before and after removal test.

3. Results and discussion

3.1. Cadmium removal test

Once the ceramic material was obtained, the parameters of contact time, metal concentration and grams of sorbent were evaluated. Determination of the concentration of the metal in the final solution was made by linear regression starting from a calibration curve; followed by this, the removal percentage was determined.

3.1.1. Contact time. Figure 1 shows the percentage of cadmium removal as time increases, it is evident that the material has a high removal capacity since the values range between 78% and 98%, with a time of 16 h with which the best removal was obtained.

3.1.2. Metal concentration. As shown in Figure 2, when the concentration of the solution is 0.5 ppm, the elimination was 83%, indicating that the metal ions available in the solution are lodged in the sorbent, however the sorbent is not found. In its saturation state, when the concentration increases to 1 ppm, it is observed that the removal percentage decreases and begins to increase as the concentration of the solution increases, because there are more metal ions available to be lodged in the material, thus finding that at a concentration of 2.5 ppm the highest removal of cadmium is obtained, this being 85%. For the concentration of 3 ppm the removal percentage decreased drastically, which would indicate that the amount of ions available in solution to be sipped, are greater than the amount of available sites in 0.05 g of sorbent material.
Figure 1. Cd removal percentage at different times.

Figure 2. Cd removal percentage at different Cd concentration.

3.1.3. Doses of sorbent. Figure 3 shows the removal of cadmium as the amount of adsorbent material is increased, taking into account that the amount of free ions in the solution is the same in all cases, the behavior that occurs is to be expected, where as the amount of active sites in which these ions can lodge increases, the greater the removal percentage, having a removal of 100% when 0.05 g of material is contacted, itself as in the presence of excess available sites to host, there is a small decrease being less than 1%.

Figure 3. Cd removal percentage at different doses of ceramic system.

3.1.4. Test toxic waste. For these tests the pH of the test sample was adjusted from 1 to pH 4.5-5, with 5 M NaOH solution. According to the results shown in Table 1, it was observed that for 0.05 g of ceramic, the best percentage removal for cadmium (II) toxic waste solution was obtained. This value was: 99.6%, confirming that 0.05 g is the optimal amount used for these tests removal Cadmium (II).

Table 1. Cd removal percentage in toxic waste sample.

| Ceramic system | % Removal |
|---------------|-----------|
| 0.05          | 99.2      |

3.2. Analysis by scanning electron microscope

In Figure 4 the micrograph of the ceramic before the sorption process is shown. Table 2 contains EDS elementary analysis data of the surface of the sample. it is showing a high content of silicon and aluminum, and presence of metals such as K, Ca and Na, these cations can be displaced in sorption process generating active sites in which the Cd ion can enter.
Table 2. EDS of ceramic before removal tests.

| Element | Wt% |
|---------|-----|
| C       | 4.28|
| K       | 41.74|
| Na      | 0.41|
| Al      | 14.42|
| Si      | 28.46|
| Fe      | 7.33|
| Mg      | 1.35|
| Ca      | 0.57|

Figure 4. 100X micrograph of ceramic before removal tests.

After doing the removal process again an analysis of the morphology of the sample was performed. It is observed a change of material when it is exposed to different environments, in Figure 5 the micrograph of the sample after removal test is shown, there is evidence that there is no significant change in morphology, however in the EDS (see Table 3) there is the appearance of the Cd metal in the composition of the material, which is indicative that the removal process was carried out without causing damage to the structure of the material. For the ceramic after contact with toxic waste solutions, it is appearing an abrupt change in the morphology of the material as is seen in Figure 6. This fact evidencing agglomerate formation on the ceramic surface whose possible cause is the formation of salts product of the toxic wasted composition, in turn by means of the EDS (see Table 4) it is confirming the presence of several ions (Cr, Cd, P, Cl and K) that are on the ceramic surface.

Table 3. EDS of ceramic after removal tests with 2 mgCd/L.

| Element | Wt% |
|---------|-----|
| C       | 10.64|
| O       | 33.53|
| Al      | 7.55|
| Si      | 16.33|
| Cd      | 0.29|
| K       | 0.46|
| Fe      | 12.65|

Figure 5. 100X micrograph of ceramic after test with sample 2 mgCd/L.
Table 4. EDS of ceramic after removal tests with toxic waste.

| Element | Wt%  |
|---------|------|
| N       | 11.24|
| C       | 7.3  |
| O       | 43.53|
| Na      | 31.45|
| Al      | 0.59 |
| Cd      | 0.14 |
| Cr      | 0.08 |
| Fe      | 1.58 |
| Cl      | 2.09 |
| K       | 0.61 |

Figure 6. 100X micrograph of ceramic after testing with toxic waste sample.

4. Conclusion
The use of a ceramic material demonstrated that it is highly efficient, for the removal of cadmium present in residues with a mixture of several metals (from analysis of A.A.). Where its implementation for the toxic waste treatment, is a great contribution to the environment, because it achieves the decontamination of wastewater composed of heavy metals, in this case with cadmium, from the chemistry laboratories of the Universidad Industrial de Santander, Bucaramanga, Colombia.

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