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Comparative application of an irradiated and non-irradiated calcite-type material to improve the removal of Pb in batch and continuous processes

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ABSTRACT

The study compared the lead adsorption capacity of an irradiated and non-irradiated calcite-type material carried out in simulated wastewater. The adsorption capacity in the batch process was evaluated at different temperatures and initial concentrations. The equilibrium adsorption was fitted with the Langmuir and Dubinin – Radushkevich models. Kinetic results were described by the pseudo-second order and intraparticle-diffusion models. The thermodynamic parameters were evaluated as well. The highest adsorption capacity in the batch process (4.808 mg/g) was found at 40 °C, with 100 mg/L as initial concentration. The study was also conducted in a continuous mode using only the irradiated material, owing to its high adsorption capacity compared with the non-irradiated one. The effects of flow rate (5, 7.5 and 10 mL/min), initial concentration (60, 80 and 100 mg/L) and bed height (5, 7.5 and 10 cm) were evaluated. The highest adsorption capacity in the continuous process (4.602 mg/g) was achieved at 40 °C, with a 100 mg/L lead initial concentration solution, within a flow rate of 5 mL/min and a bed depth of 10 cm. The breakthrough time for a lead concentration at the exit of the column equal to 1 mg/L was 232.65 min. In this case, the effective mass transfer zone (MTZ) in the packed bed was 5.7 cm for a treated volume of 1163.25 mL and a lead removal of 86.98%. The column experimental results, in terms of the breakthrough curve, were better fitted with the Thomas and Yoon - Nelson models than with Dose – Reponse model.

1. Introduction

Although the pollution of water by heavy metals has been matter of study for many important groups of environmental researchers, it still remains as a large problem to be solved. Among heavy metals, people identify lead as the worst pollutant. Apart from that, it has been reported that lead, even in small quantities, can damage some vital organs of living organisms and cause serious illnesses to human beings, especially children. Today, many pediatric diseases are attributed to the exposure of children to a large number of chemical compounds dispersed in soil, air and water [1,2].

It is well known that exposure to lead causes severe damage to health, mainly in children but also in adults who are exposed to moderate concentrations; for example, damage in cardiovascular end points. Such exposure infers a causal relationship between lead exposure and hypertension [2].

In many underdeveloped countries with poor environmental regulations, where industries continue to discharge wastewater into rivers, there appears the opportunity to propose economic but effective processes to solve this problem, mainly in microindustries such as pottery, tannery and electroplating, among others [3,4].

The effective removal of heavy metal ions from wastewater is a goal of environmental departments in many industries and is also the subject of studies for many researchers. Adsorption is one of the technologies that has proved highly effective in removing metal ions from wastewater. This technology, unlike others such as electrocoagulation, chemical precipitation, nanofiltration, is safe and inexpensive, as long as the adsorbent is a waste material or does not require subsequent conditioning [5,6]. In several metal adsorption works, adsorbents of agro-industrial waste, called bioadsorbents, are commonly studied. Due to their nature and scarce physicochemical treatment, these bioadsorbents are considered low cost [7–10]. Inorganic, natural or synthetic materials, with or without physical-chemical treatments, are also used as adsorbents. This kind of materials are more promising owing to their

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high mechanical resistance, their insolubility in water and the possibility of being reused [11–14].

Gamma irradiation has a lot of applications in novel industrial processes. This technology is used commercially for food preservation, industrial applications handling organic and inorganic materials, as well as for quarantine purposes, particularly soil materials. When gamma irradiation is applied to solid inorganic materials, several effects are produced on their chemical structure as well as on their physical and chemical properties. For example, effects on the lattice and atomic dislocations are produced. Moreover, in specific applications it has been an adequate tool with great success, for example, hydrolysis of water into oxidizing and reducing species which may change the oxidation–reduction potential of soil water [15]. Even though there is a lack of investigations that address the application of gamma radiation as a modifier of adsorbent materials, in a previous work it was found that the adsorption capacity of a mineral increases slightly as the gamma radiation dose increases [11]. It is expected that structural changes on the irradiated solids would be responsible for the increase in the adsorption capacity. There are no adverse effects reported for humans who interact with gamma irradiated materials, owing to the nature of gamma rays, this is to say, the interactions of gamma rays with a solid material diminish their intensity in terms of the penetrated distance, their maximum effectivity is around 10 cm, but for longer distances, energy intensity gradually diminishes and eventually their effect disappears.

In environmental engineering, there are two ways to operate the process of adsorption of metal ions: batch and continuous operations. In batch processes, the process variables are perfectly controlled, so it is easy to reach equilibrium and obtain the kinetic, thermodynamic and transport parameters [16–18]. This information is then used to design the continuous processes, which are preferred to treat large volumes of effluent [19,20].

The equilibrium studies for adsorption processes can be modeledby means of equations such as Langmuir, Freundlich, Dubinin – Radushkevich, among others [21,22]. These models, also called adsorption isotherms, describe the interaction between the substance that must be absorbed and the adsorbent material. This interaction takes place on the surface of the adsorbent and, therefore, provides information on the adsorption capacity of the adsorbent material [23,24]. In most cases, the kinetics of adsorption processes can be described by simple models such as Lagergren's and Ho's, also known as kinetic models of pseudo-first order and pseudo-second order, respectively. Other models such as Elovich, intraparticle- diffusion and Bangham's kinetics models are also used [16,25,26]. In like manner, for the thermodynamic parameters, once the distribution coefficient is experimentally obtained for each temperature, by means of the Van't Hoff and Clausius – Clapeyron equations, standard enthalpy, standard entropy, standard free energy and isosteric heat of adsorption can be calculated [27–29]. All of these studies are carried out in batch process.

The continuous system has many advantages over the batch process and can therefore be used at an industrial scale. In this process, packed columns are used; either fixed bed or fluidized bed [30]. In order to model a continuous system, simplified equations are resorted to such as the Thomas model, the Yoon – Nelson model, the Adams – Bohart model, among others, which in many cases reproduce the column adsorption processes in a satisfactory manner [31–33].

In this work, non-irradiated and irradiated materials utilized as adsorbents to remove lead ions from simulated wastewater were compared. Furthermore, the equilibrium, kinetic and thermodynamic parameters were estimated in order to analyze the effect of experimental variables, such as equilibrium time, temperature, and initial concentration, in both kind of materials.

Adsorption was carried out in batch and continuous processes. In the batch process, the effects of gamma irradiation (0, 200kGy), temperature (20, 30 and 40 °C) and initial concentration (10, 20, 40, 60, 80 and 100 mg/L) were analyzed in order to find the maximum adsorption capacity and removal percentage. The kinetic of the process was modelled using pseudo-second order and intraparticle-diffusion models, while the equilibrium adsorption was modelled using the Langmuir and Dubinin – Radushkevich equations. The thermodynamic parameters of the adsorption process were also calculated. In the continuous process, the effects of initial concentration (60, 80 and 100 mg/l), flow rate (5, 7.5 and 10 ml/min) and bed depth (5, 7.5 and 10 cm) on the adsorption capacity and lead removal percentage in a fixed-bed column were studied. In this case, the process was successfully modelled by the Thomas, Yoon – Nelson and Dose – Reponse models.

2. Materials and methods

2.1. Preparation of non-irradiated and irradiated adsorbents

The natural material utilized in this work was extracted from mines located in Oaxaca, Mexico, and was purchased from an enterprise called Lumogral S.A. de C.V (located in Iztapalapa, Mexico City). This material was selected as adsorbent, because according to the seller it had been already utilized as a sieve in wastewater treatment plants in Mexico City. This shows low solubility in water and excellent mechanical properties, such characteristics were considered in order to explore its adsorption capacity to remove lead ions.

The material was trilled and sieved down to a particle size range of 0.149 - 0.177 mm. The non-irradiated adsorbent was obtained by washing the selected material at 40 °C in deionized water and drying it at 60 °C for 12 h in an electric oven. The irradiated adsorbent was obtained when the material was exposed to gamma radiation. The radiation process (200 kGy, 3.5 kGy/h) was performed at room temperature by using a Transelektro irradiator LGI-01 manufactured by IZOTOP Institute of Isotopes Co. Ltd., Budapest, Hungary.

The physicochemical characterization of this material (morphological surface, semi-quantitative elemental analysis and X-Ray diffraction) has been previously reported [11]. X-Ray analysis indicates that its chemical elements belong to calcite, calcium magnesium silicate and quartz.

2.2. Preparation of lead solutions

Aqueous solutions at a concentration of 100 mg/L of lead were prepared by dissolving dried salt (159.8 mg) of analytical grade lead nitrate [$Pb(NO_3)_2$] in deionized water (1 L). From this, other solutions at different concentrations (10, 20, 40, 60, 80 and 100 mg/L) were obtained by dilution. These aqueous lead solutions will be in contact with the adsorbent in the batch as well as in the continuous process. Once the material is saturated with lead ions, it is washed with an acidic aqueous solution to be reused, the leachates are confined in suitable containers for final disposal in authorized sanitary landfills.

2.3. Batch lead adsorption experiments

After the preparation of lead solutions, in 100 mL of such solution, 1.0 g of adsorbent was added. These heterogeneous mixtures were heated at constant temperature (20, 30 and 40 °C) and stirred with a shaker at 100 rpm (Lab-Line Incubator-Shaker, USA) until equilibrium was reached. Finally, separations of solid adsorbents were obtained by means of a filtration process. The concentrations of metals into the liquid solutions were analyzed by using Atomic Absorption Spectrophotometer (Perkin-Elmer model AA300), according to the standard method for lead detection [34].

The adsorption capacity, q (mg/g) was calculated with:

$$q = \frac{(C_0 - C_e)V}{w}$$

Where C_0 and C_e (mg/L) are the concentrations of lead at initial and equilibrium times, respectively; V (L) is the volume of the solution and