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Mercury(II) adsorption by a novel adsorbent mercapto-modified bentonite using ICP-OES and use of response surface methodology for optimization

Tekin Şahan *, Funda Erol, Şakir Yılmaz

Van Yuzuncu Yil University, Faculty of Engineering, Department of Chemical Engineering, 65080 Van, Turkey

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ABSTRACT

The presence of mercury(II) ions in aqueous media is a major concern due to toxicity and the threat to public health and ecological systems. Thus, the development of novel adsorbents that are highly efficient and selective is of critical importance for the removal of mercury(II) ions from aqueous media. The adsorption of mercury(II) from aqueous media by a new adsorbent, 3-mercaptopropyl trimethoxysilane-modified bentonite (B-SH), and the optimization of adsorption parameters was investigated in this study. B-SH was used as a novel sorbent for mercury(II) adsorption, and the analysis of adsorption conditions was performed by response surface methodology (RSM). The characterization of B-SH was executed using Brunauer, Emmett and Teller (BET), Fourier Transform Infrared (FTIR) Spectroscopy, Energy-dispersive X-ray spectroscopy (EDX), and X-ray diffraction (XRD) analyses. The most important parameters for Hg(II) adsorption were initial pH, initial mercury(II) concentration (C_o), temperature (T (°C)), and adsorbent dosage (g). The RSM results showed that the optimal adsorption conditions yielding the best response were 6.17, 36.95 mg/L, 37.28 °C, and 0.19 g, for pH, C_o, T (°C), and adsorbent dosage, respectively. At optimum adsorption conditions obtained by program, the maximum adsorption capacities and the adsorption yield were 19.30 mg/g and 99.23%, respectively. Among the adsorption isotherm models (the Langmuir, Freundlich and Dubinin-Radushkevich), the adsorption data showed a better fit to the Langmuir isotherm model. The thermodynamic studies revealed that the adsorption process was spontaneous, feasible and endothermic. According to these results, B-SH has high mercury(II) adsorptive removal potential from aqueous media. In addition, a new adsorbent has been added to the literature for the uptake of toxic metals like mercury.

1. Introduction

Due to rapid increases in industrialization over the last century, heavy metal contamination in aqueous environments has become a major concern for ecosystems, defined as geographic areas where plants, animals, and other organisms exist [1–3]. Heavy metals including mercury (Hg), chromium (Cr), nickel (Ni), arsenic (As), cadmium (Cd), and lead (Pb) have highly toxic effects, and can enter the aqueous environment as industrial waste from varied sources such as batteries, metal plating, alloys, the metallurgical industry, mining, oil refining, pulp and paper mills, and rubber processing [4]. Wastes resulting from activities such as electrical-electronics manufacturing, chloroalkali manufacturing, and sulfide ore roasting operations contain significant amounts of Hg. Due to its toxic effects on living organisms, long-term intake of Hg can cause health problems affecting the central nervous system, reproduction, the liver, and kidneys, as well as cause sensory and psychological diseases [5,6]. Hg accumulation in aqueous environments, resulting from municipal wastes and manufacturing of organic compounds containing Hg, is a potential risk to human health because of the uptake of Hg by plants and their subsequent introduction into the food chain [7]. Due to this risk, the uptake of Hg from aquatic media is an issue of great significance for public health.

Thus far, conventional separation methods such as electrochemical processes, filtration, ion exchange, chemical oxidation or reduction, and chemical precipitation, have been used effectively for heavy metal removal from aqueous environments [7–10]. Disadvantages associated with these methods, such as high costs, slow turnaround time, and consumption of chemicals, have restricted their applicability. Adsorption has generated interest in recent years because it is a relatively inexpensive, simple, and effective method to remove heavy metal from wastewater [10–14]. The use of adsorbents based on clay minerals for heavy metal removal from aqueous environments has attracted great attention, as they possess properties critical for the adsorption process, are readily available, abundant in nature, cheap, and produce environmentally friendly waste. In addition, the high cation exchange capacity and the high surface area of clays make them suitable for use as adsorbents for the adsorption of heavy metals [15]. Furthermore, the silanol and

* Corresponding author.
E-mail address: tekinsahan@yyu.edu.tr (T. Şahan).

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aluminol groups on clay minerals allow for surface modifications with different chemicals to increase their adsorption affinity for different contaminants [16,17].

Bentonite is a clay composed primarily of montmorillonite, a subclass of the smectite mineral group [18]. This group of clay minerals has a structurally net negative charge because of the isomorphic substitution of cations in the crystal structure. These negative charges can be neutralized by hydrated cations. The exchangeability of these cations increases with decreasing cation counter ion charge and cation polarizability and increasing hydrated radius. The exchangeable ions on the clay surface are of great importance to the sorption process, as they can be replaced by positively charged pollutants. Thus, these types of clay minerals have a high capacity to adsorb cations such as toxic heavy metals [19]. During the past two decades, many researchers have studied the characterization, preparation, and sorption properties of the phase systems of clay minerals such as bentonite, vermiculite, zeolite and kaolinite, as indicated in various review articles [20–22]. Clay minerals have been often used in adsorption studies because of their high specific surface area and the low cost of these sorbent materials. A number of studies related to the adsorption of different adsorbates onto bentonite have already been presented in the literature [23–26].

Conventionally, optimization has been carried out by monitoring the effect of one parameter on the process at a time. Based on this traditional method, only the parameter to be examined is varied, while the others are fixed at a certain value. However, this process has many disadvantages: it neither clarifies the interactive effects among the parameters examined, nor does it produce statistical data explaining more detailed influence of the parameter on the response (the experimental result). In addition, this method requires a lot of experiments, consuming large amounts of time and chemicals [27]. In recent years, response surface methodology (RSM), a strong optimization procedure, has been largely utilized to overcome these shortcomings and optimize the most effective process conditions in the presence of fewer experimental data. This method has been studied for the purpose of optimization in recent years [14,28,29]. In this approach, the advantages can be listed as extra chemical and time consumption for each parameter, as well as less cost [30–32]. RSM employs a mathematical algorithm based on experimental results generated from experiments designed by a program, and validation of the quadratic model is derived from statistical techniques. Linear or quadratic polynomial functions are utilized to define the system under investigation and, ultimately, to determine (by displacing and modeling) experimental conditions up to optimization. In RSM, the independent variables that affect the system are selected based on the aim and experience of the researcher by means of a literature search. Next, the experimental design is selected and the experiments are performed according to the selected experimental matrix and the experimental data obtained undergo mathematical-statistical treatment using a polynomial function. The suitability of the model is then assessed and optimal values are obtained for each variable studied [27]. The principal advantage of RSM is that it is a mathematical model which incorporates experimental data and all the parameters for optimization can be changed simultaneously. As a result, in RSM, the number of experiments required for optimization is less than that required by traditional methods.

The aims of the present work are to define the optimal points for the most important Hg(II) adsorption parameters using a popular method, RSM, and to investigate the utilization of 3-mercaptopropyl trimethoxysilane-modified bentonite (B-SH) as an efficacious adsorbent for the removal of Hg(II) ions from aqueous solutions. In this study, the effect of adsorption parameters like initial pH, initial Hg(II) concentration (C_o), temperature (T (°C)), and adsorbent dosage (g) was investigated on adsorption yield. Furthermore, the optimization of the adsorption conditions affecting Hg(II) adsorption onto B-SH was successfully conducted by central composite design (CCD) in RSM.

2. Experimental methods

2.1. Preparation and modification of the adsorbent

Raw bentonite samples obtained from the Kütahya region of Turkey were used in this study. The main component is calcium-montmorillonite. The bentonite samples were ground with a grinder and sieved to attain the required grain size (<125 μm). The chemical composition of the raw bentonite sample was determined in a previous study [24] and was 71.90% SiO_2, 13.85% Al_2O_3, 0.68% Fe_2O_3, 0.09% TiO_2, 2.42% CaO, 1.27% MgO, 0.39% Na_2O, 1.62% K_2O, and 7.50% ignition loss.

To modify the surface of the bentonite with a mercapto agent, 3-mercaptopropyl trimethoxysilane (MPTMS) (Sigma-Aldrich, Germany) was used as the modifying agent, with toluene (Merck, Germany) as the solvent. The method was as follows: 15 g bentonite and 15 mL 3-mercaptopropyl trimethoxysilane were activated in a reflux for 6 h at 60 °C in the presence of 30 mL toluene solvent. The resulting solid was washed with toluene to eliminate organosilane compounds from the bentonite surface after filtering by using a filter paper (Whatman, No. 42) and then dried in an oven at 100 °C [33,34]. It was subsequently stored in desiccators until later utilization.

2.2. Analyses and adsorption experiments based on batch system

A Hg(II) stock solution (250 mg/L) was prepared by dissolving the calculated and weighed quantity of $Hg(NO_3)_2.1H_2O$ (purity 99%, Sigma-Aldrich, Germany) in 500 mL of ultra-pure water. The desired Hg(II) concentrations (5, 22.5 and 40 mg/L) were made by the dilution of this stock solution. The initial pH of prepared solutions was adjusted to the desired level with negligible volumes of 0.1 M HNO_3 (Merck, Germany) and NaOH (Merck, Germany) solutions. Then, adsorption experiments were performed by adding the required dosage of the adsorbent.

Each adsorption experiment generated by CCD program in RSM was performed on a magnetic stirrer with temperature-controller with 100 mL Hg(II) solution in 250 mL erlenmeyer flasks. All the batch tests were carried out at fixed agitation speed and contact time (800 rpm, 2 h). After adsorption, the residual concentration of Hg(II) was analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) with a ThermoFisher Scientific iCAP 6300 model instrument (ThermoFisher Scientific, Waltham, USA). The amount of Hg(II) adsorption per unit mass of adsorbent and removal percentage of Hg(II) were calculated from the following equations [35].

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

$$\%Adsorption = \frac{(C_o - C_e)}{C_o} x100 \quad (2)$$

where q_e (mg/g) is adsorption capacity, C_o (mg/L) is the initial concentration of Hg(II) in solution and C_e (mg/L) is final concentration of Hg(II) in solution, V (L) is the volume of solution, and m (g) is the mass of B-SH.

2.3. CCD for experimental design approach

CCD which is the most popular program in RSM was chosen to optimize the four parameters known to have the greatest effect: initial pH, C_o, T (°C), and adsorbent dosage (g). A total of 30 experiments were generated in CCD using the $2^k + 2k + 6$ equation for four independent variables ($k = 4$; Initial pH, C_o (mg/L), T (°C), and adsorbent dosage (g)). This experimental set produced by CCD was completed to investigate the influence of independent parameters on the Hg(II) adsorption. To define experimental error, six replications were made at the median values. The CCD design is made up of four factors, each at three levels (−*1*, *0*, *+1*) (Table S1). *−1* and *+1* codes corresponded to the lowest and