Silica monolith with mesopore structure: synthesize, characterization and application for cadmium removal from wastewater

Hakimeh Sharififard[1*], Raziye Hayati[2], Solmaz Hayati[3]

[1]Chemical Engineering Department, Yasouj University, Yasouj, I.R. Iran
[2]Materials Engineering Department, Yasouj University, Yasouj, I.R. Iran
[3]Chemical Engineering Department, Yasouj University, Yasouj, I.R. Iran

ABSTRACT

One of the most important issues in today's world is the pollution of water with toxic and dangerous metals. Cadmium is one of the toxic metals that enter the surface and groundwater through various industrial wastewaters. In this paper, polyethylene oxide-based silica monolith was synthesized with a uniform porous structure and was used to remove cadmium ions from the aqueous medium. The chemical and physical properties of silica monolith were characterized by SEM, BET, and FTIR techniques. The results of BET and SEM analysis showed that the monolith has a mesopore structure with a specific surface area of 543 m^2g^{-1}. The synthesized silica monolith was used as an adsorbent for cadmium removal in a batch adsorption process and the effects of operating parameters including pH, adsorbent concentration, cadmium initial concentration, and contact time were investigated. The Central Composite Design method was used to optimize the effects of operating parameters. The results of the experimental design showed the importance of pH and adsorbent concentration parameters. The analysis of equilibrium data indicated that the maximum adsorption capacity of the monolith for cadmium is 153 mg g^{-1}. The kinetic data were analyzed with various models and results indicated the importance of chemical adsorption. The results of regeneration and reuse of monolith as an adsorbent showed that the synthesized monolith has a high ability to adsorb heavy metal ions from an aqueous solution and can be an option for water treatment at industrial scale.

KEYWORDS

Silica monolith, Mesopores, Cadmium, Adsorption, Optimization.

* Corresponding Author: Email: Hakimeh.sharifi@gmail.com, h.sharififard@yu.ac.ir

1. Introduction

One of the most important issues in today's world is environmental pollution with toxic and hazardous metals [1-3]. One of the most common heavy metals is cadmium, which is widely used through the combustion of fossil fuels, the production of cement, color, and batteries, and electroplating. It enters the environment through the effluents of these industries. The presence of cadmium in water, even at very low concentrations, is extremely harmful to the environment, humans and even aquatic life [4]. The maximum permitted cadmium concentration in drinking water is 0.003 mg/L [5]. Studies in recent years have shown that the adsorption is a cost-effective and high-efficiency method for the separation of heavy metals from wastewater [6]. The adsorbent is one of the important factors in the performance of the adsorption process. The adsorbent should have a high specific surface area, high porosity, suitable functional groups, and high mechanical and chemical strength. Silica or SBA-15 is one of the materials that has received much attention today due to its high strength properties and good porosity. SBA-15 is a porous material with mesoporous structure [7-11]. However, most of the silica mesopore materials are synthesized in the form of powder, which their structural and porosity properties are usually reduced during the process due to their adhesion and agglomeration, and this problem is particularly severe when used in industrial applications. A review of the current research indicates that little research has been done on the synthesis of monolithic silica mesophore so far, its application as a cadmium adsorbent from the aquatic environment has not been reported. Therefore, in this research work, silica monoliths were synthesized and the effect of process parameters on the efficiency of cadmium adsorption process was investigated and then the kinetics and equilibrium of adsorption were investigated.

2. Methodology

Silica monoliths were synthesized from polyethylene oxide according to the method presented in Sachse et al. paper [12]. In order to characterize the morphology, porosity structure and surface chemistry of synthesized monolith, FTIR, SEM, and BET were used. Also, pH_{ZPC} value was determined [6]. In order to optimize the adsorption of cadmium with silica monolith, central composite design (CCD) was used and the effects of solution pH, adsorbent concentration (g L^{-1}), and cadmium initial concentration (mg L^{-1}) were investigated. According to CCD method, 20 experiments were performed and the removal percentage was selected as a response for analyzing data. Also kinetic and equilibrium experiments were performed and analyzed with different kinetic methods and isotherms. The regeneration experiments were performed with 0.1 M EDTA solution at five cycles.

3. •Discussion and Results

The results of SEM and BET analysis showed that the synthesized monolith has a mesoporous structure with a surface area of 540 m^2g^{-1}. The value of pH_{ZPC} was 4.19. The results of the FTIR analysis confirmed the existence of Si-OH and Si-O-Si bands. Results of ANOVA showed that pH and adsorbent concentration parameters had the most influence on cadmium removal with silica monolith. Also, the interaction between pH-adsorbent concentration and cadmium concentration-adsorbent had a significant effect on the cadmium separation process. Results showed that the cadmium adsorption increased with increasing pH. At pH <4.19, the silica monolith surface has a positive charge and its surface charge is negative at pH> 4.19. Also, the cadmium ions present in the solution as Cd^{2+}. Therefore, at pH<4.19 due to electrostatic repulsion, the cadmium adsorption is low. Then with increasing pH and increasing the negative charge of the monolith surface, the amount of cadmium adsorbed increased. The optimum condition for cadmium adsorption are: pH=5.99, adsorbent concentration: 1.39 g L^{-1} and initial concentration=84.34 mg L^{-1}.

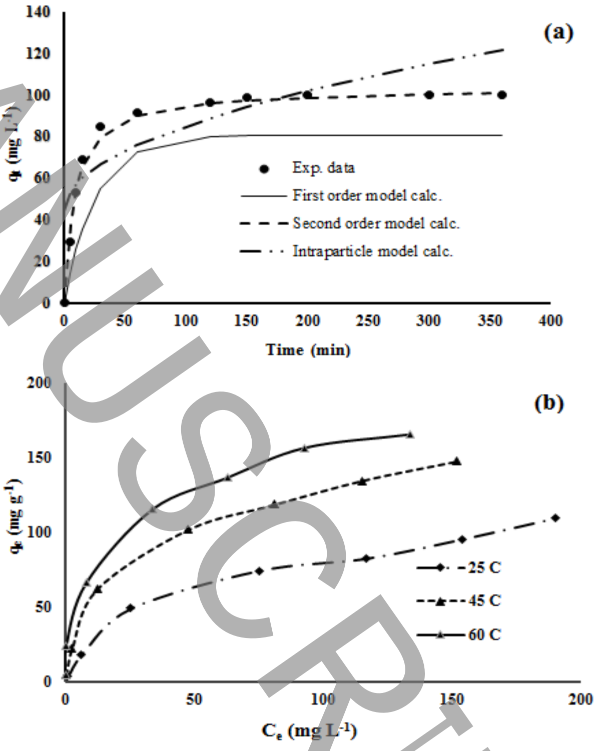

Figure 1. (a): Kinetics data; (b): Equilibrium data

Figure 1 (a) presents the kinetics data with different kinetics models. Results show that the pseudo- second-order model has very good agreement with the experimental data. Figure 1 (b) presents the equilibrium isotherms for cadmium adsorption with silica monolith. Data shows the endothermic nature of cadmium adsorption process. The analyzing of data with various isotherms indicate that the Langmuir model fits better with the data. These results indicate the predominance of chemical adsorption. The maximum adsorption capacity of silica for cadmium was 153 mg g^{-1} which is comparable with other adsorbent reported in papers [13-16]. The results of regeneration tests showed that the cadmium removal percentage has decreased from 100 to 73.5% after 5 cycles.

4. Conclusions

Silica monolith was synthesized and used to separate cadmium from aqueous solution. The results of the characterization analyzes showed that the synthesized monolith has a uniform mesoporous structure. The results of the experimental design showed that pH and adsorbent concentration are important parameters. Kinetics and equilibrium analysis of the adsorption process showed that the predominant mechanism is chemical adsorption. By analyzing the equilibrium data at different temperatures, the maximum adsorption capacity of monosil for cadmium was 153 mg cadmium per g of monosil. It was also found that the adsorption process of cadmium with monosil is endothermic.

5. References

[1] Hogan, M.C., "Heavy metal: encyclopedia of earth", National Council for Science and the Environment, Washington, 2010.

[2] Adriano D.C., "Trace elements in the terrestrial environment", Springer-Verlag, New York 1986.

[3] Appenroth K.J., "Definition of Heavy Metals and Their Role in Biological Systems", Soil Heavy Metals, Vol. 19, pp. 19-29, 2010.

[4] Zaini M.A.A., Okayama R., Machida M., "Adsorption of Aqueous Metal Ions on Cattle-manure- compost Based Activated Carbons", Journal of Hazardous Materials, Vol. 170, pp. 1119–1124, 2009.

[5] World Health Organization, "Guidelines for drinking water quality: recommendations", World Health Organization, Geneva, 2008.

[6] Hashemi Z., Sharififard H., Lashanizadegan A., "Grape stalks biomass as raw material for activated carbon production: synthesis, characterization and adsorption ability", Materials Research Express., Vol. 5, pp. 055603, 2018.

[7] D'Amore A., "Special topics on materials science and technology –The Italian panorama", CRC Press, Leiden, 2009.

[8] Dasgupta S., Nanoti A., Gupta P., Jena D., Goswami A.N., Garg M.O., "Carbon Di-Oxide Removal with Mesoporous Adsorbents in a Single Column Pressure Swing Adsorber", Separation Science and Technology, Vol. 44(16), pp. 3973-3983, 2009.

[9] Yan X., Zhang L., Zhang Y., Yang G., Yan Z., "Amine-Modified SBA-15: Effect of Pore Structure on the Performance for CO2 Capture", Industrial & Engineering Chemistry Research, Vol. 50(6), pp. 3220-3226, 2011.

[10] Olea A., Sanz-Perez E.S., Arencibi, R., Sanz R., Calleja G., "Amino-functionalized pore-expended SBA-15 for CO2 adsorption", Adsorption, Vol. 19, pp. 589-600, 2013.

[11] Gargiulo N., Peluso A., Aprea P., Pepe F., Caputo D., "CO2 Adsorption on Polyethylene mine Functionalized SBA-15 Mesoporous Silica: Isotherms and Modeling", The Journal of Chemical & Engineering Data, Vol. 59(3), pp. 896-902, 2014.

[12] Sachse A., Galarneau A., Fajula F., Di Renzo F., Creux F., Coq B., "Functional silica monoliths with hierarchical uniform porosity as continuous flow catalytic reactors", Microporous and Mesoporous Materials, Vol. 140, pp. 58-68, 2011

[13] Aghababaei A., Ncibi M.C., Sillanpaa M., "Optimization Removal of Oxytetracycline and Cadmium from Contaminated Waters Using Chemically Activated and Pyrolyzed Biochars from Forest and Wood- processing Residues", Bioresource Technology, Vol. 239, pp. 28-36, 2017.

[14] Fosso-Kankeu E., Mittal H., Waanders F., Sinha Ray S., "Thermodynamic Properties and Adsorption Behaviour of Hydrogel Nanocomposites for Cadmium Removal from Mine Effluents", Industrial & Engineering Chemistry Research, Vol. 48, pp. 151-161, 2017.

[15] Bhanjana G., Dilbaghi N., Singhal N.K., Kim K.H., Kumar S., "Copper Oxide Nanoblades as Novel Adsorbent Material for Cadmium Removal", Ceramic International, Vol. 43(8), pp. 6075-6081, 2017.

[16] Roushani M., Saedi Z., Baghelani Y.M., "Removal of cadmium ions from aqueous solutions using TMU-16-NH2 metal organic framework", Environmental Nanotechnology, Monitoring and Management, Vol. 7, pp. 89-96, 2017.

↑ please level both columns of the last page as far as possible. ↑