Proceedings of the 4th International Congress APMAS2014, April 24-27, 2014, Fethiye, Turkey

A Batch Adsorber Design for Rhodium Adsorption on Gallic Acid Formaldehyde Resin

M. CAN^{a,*}, E. BULUT^b, A. ÖRNEK^c ^aVocational School of Arifiye, 54580, Sakarya University, Turkey ^bSakarya University, Department of Chemistry, 54187 Sakarya, Turkey ^cKafkas University, Atatürk Vocational School of Healthcare, 36100 Kars, Turkey

The adsorption of rhodium (III) ions onto gallic acid formaldehyde resin in a batch adsorber has been studied. Adsorption experiments were carried out by agitating 1 g resin particles with 1000 ml of Rh (III) ion solution of the initial concentrations from 16.54 to 88.80 mg/l (293K, 1M HCl). Using Langmuir isotherm, a single stage batch adsorber was designed for different adsorbent mass/treated effluent volume ratios. An initial rhodium concentration of 100 g/m³ is assumed and the required amount of resin particles to recover metal ion content by 75%–99% at various volumes of effluents. For a single-stage adsorption system, thus the adsorbent demonstrated recovery capacity. For example, 1 m³ of solution is to be treated; the required masses of gallic acid resol resin are 25 kg for 75% rhodium removal. In order to recover 90% of the rhodium (III) at various volumes of solution which having different metal concentrations, the required amount of gallic acid resin was calculated. For example, 1 m³ of solution is to be treated to reduce the rhodium content by 90% increased from 75 to 76 kg with increase in the initial rhodium metal concentration from 0.1 to 100 g/m³. Through such a projection, a real single stage adsorption system can be designed.

DOI: 10.12693/APhysPolA.127.1311

PACS: 68, 81, 82

1. Introduction

Rhodium containing wastes has become a source of recycle because its low ore reserves and high utilization. It is difficult to follow the fate of metallic ions after they enter and pollute the ecosystem as they move from one ecological trophic layer to another [1].

Only few scientists have studied adsorption of rhodium ions onto various adsorbents. Reports include studies by Morisida at al, who investigated the rhodium (III) adsorption of the amine modified tannin polymer [2, 3];Akkaya *et al.* studied the adsorption of rhodium (III) onto poly(1,8-diaminonaphthalene) [4]; Ogata et al. designed an adsorber onto gibbsite [5]; Alam et al. studied the adsorption of Rh (III) onto various ion exchange resins [6]; Moon et al. studied the sorption of Rh (III) onto Amberlite XAD-4 impregnated with Aliquat 336 [7]; Couceiro et al. studied adsorption and desorption kinetics Rh (III) and Pt (IV) in turbid suspensions [8]; Sako et al. studied the adsorption and surface complexation modeling of Rh (III), Pd (II) and Pt (IV) onto semi-arid soils and sediment [9]; Ogata et al. designed an adsorber onto gibbsite. However, until now, as far as we can find, there isn't any report involving rhodium adsorption system design especially for batch systems involving polymer based adsorbents.

This paper presents mathematical models developed for predicting the optimized minimum operating time for the removal of specified amounts of Rh (III) ions from a fixed volume of solution using a novel gallic acid derived resol resin (GAR) particles. Data used for developing these models were obtained from batch kinetic studies of the adsorption Rh (III) ions using the GAR adsorbent. Both single stage adsorber models were used on the data.

2. Experimental

 $\rm RhCl_3\cdot 3H_2O$ and HCl purchased from Merck Company. AAS standard solutions for determination of PGM purchased form UltraScientific Company. All other reagents were analytical grade. Preparation of GAR polymer was explained in detail at our recent publication dealing synthesis and characterization of polymer [10]. The aqueous Rh (III) stock solution was prepared from solid RhCl_3\cdot 3H_2O in 1.0 M HCl. The Rh (III) solutions were prepared by dilution with ultra-pure water (Milli-Q, UK).

The rhodium (III) solution was prepared by diluting stock solutions to desired concentrations in 1 M HCl as 293 K. All adsorption experiments were carried out in a standard and strictly adhered to batchwise system. At the end of the adsorption period, 15 ml samples were centrifuged and the solutions were filtered through a 0.45 μ m Milipore filter paper to avoid any solid particle in the aqueous phase. Samples were measured using AAS. All the adsorption tests were performed at least twice so as to avoid wrong interpretation owing to any experimental errors. FAAS calibrated using 0, 4, 12 and 20 ppm standard solution for Rh (III) in 1 M HCl. Samples diluted to measurement limits for precise results. Amount of adsorbed metal ions was calculated from the concentrations in solutions before and after adsorption process. Results were taken from the average of three scans for each sample.

^{*}corresponding author; e-mail: mstfacan@gmail.com

The amount of metal adsorbed onto GAR, $q_e~(\rm mg/g),$ was calculated as follows:

$$q_e = (C_0 - C_t) V / W, (1)$$

where C_0 and C_t are the initial and time t liquid-phase concentrations of the metal (mg/l), respectively. V the volume of the solution (l) and W the weight of the dry GAR used (g). Each experiment was performed twice at least under identical conditions. Twice tests showed that the standard deviation of the measurement was $\pm 2.5\%$.

3. Results and discussions

Adsorption isotherms can be used to predict the design of single-stage batch adsorption systems and it is already been described by Ho and McKay [11]. Based on the best fitting isotherm, a single stage adsorber as shown in Fig. 1 was designed for different solution volumes. The design objective is to reduce the rhodium (III) solution of volume V, from an initial metal concentration of $C_0 - C_1$ (mg/l). The amount of adsorbent is M and the solute loading on the adsorbent changes from q_0 (mg/g) to q_1 (mg/g). At time t = 0, $q_0 = 0$ and as time proceeds the mass balance equated the rhodium adsorbed from the liquid to that picked up by the solid. The mass balance equation for the sorption system in Fig. 1 can be written as equation

$$V(C_0 - C_1) = M(q_1 - q_0) = Mq_1.$$
(2)

When system reaches to the equilibrium, C_1 and q_1 will change to C_e and q_e , respectively.



Fig. 1. Schematic representation of the single stage batch adsorber system.

From adsorption studies and from model results it was seen that the Langmuir model gave a more robust fit to equilibrium data from GAR particles [12]. Langmuir constants used further calculations can be seen at Table I. On this basis, the Langmuir isotherm equation was used to predict the amount of GAR particles required to remove a certain percentage of Rh (III) from various volumes of solutions.

With
$$q_e = \frac{K_L C_e}{1 + a_L C_e}.$$

(3)

Since the equilibrium studies confirm that the equilibrium data for Rh (III) onto GAR particles follows a Langmuir isotherm Eq. 3 substituted with q_e in Eq. 1 and it can be rearranged as

$$\frac{M}{V} = \frac{C_0 - C_1}{q_e} = \frac{C_0 - C_e}{\left[\frac{K_L C_e}{1 + a_L C_e}\right]}$$
(4)

Langmuir isotherm constants for Rh (III) TABLE I adsorption onto GAR particles.



Fig. 2. (a) Adsorbent mass (M) against volume of effluent (V) treated for various percentage of rhodium (III) removal at 100 g/m³ initial the rhodium ion concentration. (b) Adsorbent mass (M) against initial Rh (III) concentration for 90% metal removal at various volume of solutions (V) treated.

Figure 2a shows a series of plots derived from Eq. 4 for the adsorption of the Rh (III) ions onto GAR. An initial metal ion concentration of 100 g/m^3 is assumed and Fig. 2 shows the required amount of sawdust to reduce the color content by 75%–99% at various volumes

of solutions. For a single-stage adsorption system, thus the adsorbent demonstrated adsorption capacity of the metal ions containing solutions. For example, 5 m³ of solution is to be treated. The required masses of GAR are 95, 126, 177, 280, 589 and 3053 g of solution containing 100 g/m³ Rh (III) at 293K for 75%, 80%, 85%, 90%, 95%, and 99% rhodium removal, respectively.

Figure 2b shows the required amount of GAR to reduce the rhodium ion content by 90% at various volumes of solutions which have different Rh (III) concentrations. For example, 5 m³ of solution is to be treated, the required amounts of GAR to reduce the rhodium ions content by 90% increased from 277 to 279 kg with increase in the initial Rh (III) concentration from 0.1 to 50 g/m³. From Fig. 3, the amount of GAR required to remove 90% of rhodium ions from aqueous solution can be predicted for any initial Rh (III) concentration for a fixed volume of effluent (V). Through such a projection, a real single stage adsorption system can be designed.

4. Conclusions

In this study, mathematical model were applied for the adsorption of Rh (III) onto GAR particles using Langmuir isotherm data obtained experimentally via batch processes. The data from single-stage optimization models suggest that it will be useful for the design of adsorption plant for large-scale adsorption of Rh (III) by GAR particles from recycling streams. It is not feasible to removing 95% of Rh (III) ions in single-stage process. Pilot studies using this adsorbent are in progress to ascertain its full potential in the treatment of wastewater.

References

- E.I. Unuabonah, K.O. Adebowale, J. Chem. Technol. Biotechnology 84, 1726 (2009).
- [2] S. Morisada, T. Rin, T. Ogata, Y.-H. Kim, Y. Nakano, J. Appl. Polym. Sci. 126, E34 (2012).
- [3] M. Can, Research J. Chem. Environ. 17, 1 (2013).
- [4] T. Akkaya, M. Gülfen, U. Olgun, *React. Funct. Polym.* **73**, 1589 (2013).
- [5] F. Ogata, Y. Iwata, N. Kawasaki, *Toxicol. Environ. Chem.* 95, 890 (2013).
- [6] M.S. Alam, K. Inoue, K. Yoshizuka, *Hydrometallurgy* 49, 213 (1998).
- [7] J.K. Moon, Y.J. Han, C.H. Jung, E.H. Lee, B.C. Lee, *Korean J. Chem. Eng.* 23, 303 (2006).
- [8] F. Couceiro, A. Turner, G.E. Millward, Mar. Chem. 107, 308 (2007).
- [9] A. Sako, L. Lopes, A.N. Roychoudhury, *Appl. Geochem.* 24, 86 (2009).
- [10] M. Can, E. Bulut, M. Özacar, Ind. Eng. Chem. Res. 51, 6052 (2012).
- [11] G. McKay, M.S. Otterburn, J.A. Aga, *Water, Air, Soil Pollut.* 26, 149 (1985).
- [12] M. Can, Acta Phys. Pol. A, 149 (2014).