Asian Journal of Chemistry; Vol. 24, No. 10 (2012), 4253-4256

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Isotherm Study and Interaction Consideration of Samarium(III) with New Modified Siliceous Support

ELHAM MONIRI[1,*], HOMAYON AHMAD PANAHI[2], MOHAMMADREZA MAHDAVI JALAL[3] and HOSSEIN GAFORIYAN[3]

[1]Department of Chemistry, Varamin (Pishva) Branch, Islamic Azad University, Varamin, Iran
[2]Department of Chemistry, Central Tehran Branch, Islamic Azad University, Tehran, Iran
[3]Department of Sea Chemistry, Faculty of Marin of Sciences and Technology, North Tehran Branch, Islamic Azad University, Tehran, Iran

*Corresponding author: E-mail: moniri30003000@yahoo.com

(*Received*: 17 May 2011; *Accepted*: 30 April 2012) AJC-11365

A new sorbent was prepared by surface grafting of polymer containing a functional monomer, poly[iminodiacetic acid-allylglycidyl-co-methylacrylamide] (poly(IDA/AGE-DMAA) onto a modified silica. The silica surface was modified by silylation with 3-mercaptopropyltrimethoxysilane followed by graft polymerization. The resulting sorbent has been characterized by FT-IR. The optimum pH value for sorption of the metal ion was 5. The equilibrium adsorption data of Sm(III) on modified sorbent were analyzed by Langmuir, Freundlich, Temkin and Redlich-Peterson models. Based on equilibrium adsorption data the Langmuir, Freundlich and Temkin constants were determined 55.06, 0.398 and 0.2, respectively at pH 5 and 20 ºC.

Key Words: Samarium, Isotherm study, Langmuir, Freundlich, Temkin, Redlich-Peterson model.

INTRODUCTION

Samarium is a silvery-white hard metal and found in a variety of minerals such as monazite, gadolinite, cerite, bastnasite and samarskite. These minerals contain different mixture of rare earth metals, which are the elements from lanthanum through lutetium in the periodic table. Samarium has a variety of commercial uses. It is used as a catalyst for certain organic reactions and in pyrophoric alloys for cigarette lighter flints. Samarium oxide is also used in special infrared absorbing glass and in the cores of carbon arc-lamp electrodes. Samarium can be taken into the body by drinking water, eating food, or breathing air. Due to the allowable low levels of Sm(III) in food and beverages and its very low concentrations in natural waters as described above, sensitive analytical methods like inductively couple plasma-atomic emission spectroscopy are required for determination of this metal[1-5].

The aim of this work is isotherm study of poly(IDA/AGE-DMAA)-grafted silica gel with samarium ions in solution. For this purpose, free-radical graft co-polymerization of N,N-dimethylacrylamide (DMAA) and a functional monomer containing metal chelating group, iminodiacetic acid-3-allyl-glycerol (AGE/IDA) onto silica surface modified with (3-mercaptopropyl)trimethoxy silane (MPTMS) is accomplished and then it's interaction with Sm (III) in solution were studied.

The pH measurements were made with a Metrohm model 744 pH meter (Zofingen, Switzerland). Infrared spectra were recorded on a Jasco Fourier transform infrared spectrometer (FT-IR-410, Jasco Inc., Easton, Maryland). Inductive couple plasma-atomic emission spectroscopy (ICP-AES), Varian, model Vista were used for concentration measurements of metal ions. Elemental analysis was carried out on a Thermo-Finnigan (Milan, Italy) model Flash EA elemental analyzer. Thermogravimetric analysis (TGA) was carried out by using a TGA-50H (Shimadzu Corporation, Kyoto, Japan).

EXPERIMENTAL

NaOH, HCl, H_2SO_4, HNO_3, NaOH, CH_3COOH, CH_3COONa, NaH_2PO_4, Na_2HPO_4, $Pb(NO_3)_2$, $Sm(NO_3)_3$, N,N-dimethylacrylamide (DMAA), 3-mercaptopropyltrimethoxy-silane and aluminum oxide were from Aldrich (Steinheim, Germany). 2,2'-azo*bis*(2-methylpropionittrile) was purchased from Acros (New Jersey, USA). Allyl glycidyl ether (AGE) was purchased from Fluka Chemica (Buchs Switzerland). Anhydrous 1,4-dioxane, silica gel 60 for column chromatography (0.2-0.5 mm), iminodiacetic acid and C_2H_5OH were products of Merck (Darmstadt, Germany).

The stock solution (500 mg L^{-1}) of Sm(III), were prepared by dissolving appropriate amounts of $Sm(NO_3)_3$, in deionized water. To adjust the pH of the solution, 10 mL of 0.1 M acetic

acid-acetate buffer (pH 3-6) or 0.01 M phosphate buffer (pH 6.0-7.5) were used wherever suitable.

Preparation of monomer (AGE/IDA): Iminodiacetic acid was neutralized with KOH solution to keep carboxylic acid from reacting with epoxy ring of AGE. Dipotassium salt of IDA solution (1 M, 50 mL) was added slowly to AGE at a 1:1 molar ratio. The mixture was kept at 65 ºC for 1 h under powerful stirring. When the reaction was finished, the oil-water mixture changed to a transparent water phase. The yellowish liquid monomer (IDA/AGE) was purified by pouring into acetone and dissolving in distilled water repeatedly.

Combination of mercapoto arm with silica: Details of the preparation and characterization of the poly [AGE/IDA-DMAA] was reported in the previous work[6]. The washed silica with HCl and/then distilled water was dried for 3 h at 150 ºC and kept at this temperature until the start of the reaction. At this point, 10 g hydroxylated silica particles were silylated by an anhydrous solution of 5 % of MPTMS in 1,4-dioxane. The silyation reaction was performed in the boiling solution for 24 h. Then, the silica particles were washed several times with 1,4-dioxane and dried under vacuum in a desiccator over dry calcium chloride.

Reaction modified silica with monomer: The free radical graft copolymerization of AGE/IDA and DMAA-onto MPTMS-modified silica particles was carried out in a temperature-controlled reactor with vigorous stirring under a nitrogen atmosphere. Silica particles, modified with MPTMS were placed into the degassed polymerization mixture (20 mL ethanol, 450 mg AGE/IDA, 2.07 mL N,N-DMAA and 53.7 mg 2,2'-azo*bis*(2-methyl-propionitrile) for 6 h at 75 ºC. The grafted silica sample was filtered immediately and washed with 100 mL of ethanol, water and again ethanol and dried under vacuum in a desiccator over dry calcium chloride. It was found that triple washing of grafted silica with ethanol and water was sufficient for removing any homopolymer that may have adsorbed. The grafted silica gel was characterized by FT-IR (Fig. 1).

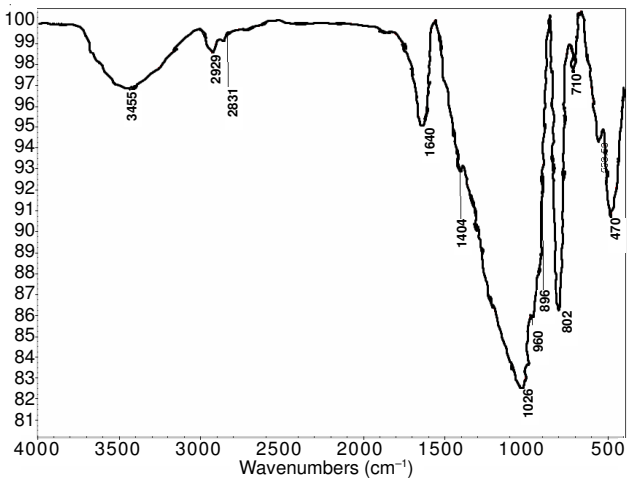

Fig. 1. FTIR of poly(IDA/AGE-DMAA)-grafted silica gel

Batch method of Sm(III) adsorption: A set of solutions (the volume of each 100 mL) containing 0.5 μg mL^{-1} of Sm(III) was taken. Their pH values were adjusted between the ranges 3-9 with 0.01 M acetate and/or phosphate buffer solutions. The 0.05 g of poly(IDA/AGE-DMAA)-grafted silica gel was added to each solution and the mixture was shaken for 4 h. The sorbent was filtered and the adsorbed metal ions were eluted with 0.5 M nitric acid (10 mL). The concentration of the metal ion in the eluate was determined by ICP-AES.

Isotherm adsorption study: Isotherm studies were conducted in a batch mode to determine the adsorption of Sm(III) on poly(IDA/AGE-DMAA)-grafted silica gel, using stoppered conical flasks. In these experiments, 100 mL of Sm(III) solution with a Sm concentration varying from 10 to 100 mg L^{-1}, were poured into each flask to which 0.1 g of poly(IDA/AGE-DMAA)-grafted silica gel was added. The solution-poly(IDA/AGE-DMAA)-grafted silica gel mixtures were stirred at 120 rpm at optimum pH range and ambient temperatures, using a shaker. The difference between the initial and the final value gives the amount of Co adsorbed per gram of the adsorbent. The amount of Sm(III) at equilibrium q_e (mg/g) on poly(IDA/AGE-DMAA)-grafted silica gel was calculated from the following equation:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg L^{-1}) are the liquid phase concentrations of Pb(II) at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent used.

RESULTS AND DISCUSSION

Characterization of poly(IDA/AGE-DMAA)-grafted silica gel: The grafted silica gel was characterized by FT-IR. FT-IR confirmed the presence of carbonyl and C-S groups at the surface of the grafted material.

Effect of pH: The degree metal sorption at different pH values was determined by batch equilibration technique. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the Sm(III) content (by ICP-AES) in supernatant liquid. The optimum pH range for the sorption of the metal ion is shown in Fig. 2. The maximum sorption was at pH 5.

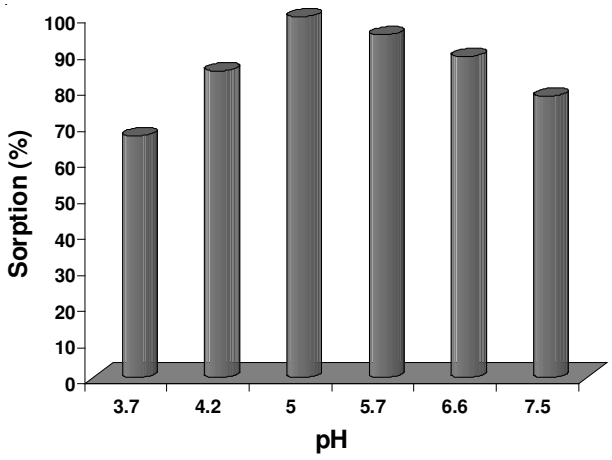

Fig. 2. Effect of pH sorption of Sm(III) onto poly(IDA/AGE-DMAA)-grafted silica gel

Isotherm studies: The equilibrium data were correlated by Langmuir, Freundlich, Temkin and Redlich-Peterson equations for samarium adsorption on poly(IDA/AGE-DMAA)-grafted surface.

Table-1 shows the values of R_L (0.018) were in the range of 0-1 at optimum pH which confirms the favorable uptake of the Pb(II) (Table-2).

TABLE-1
ISOTHERM PARAMETERS OBTAINED BY USING LINEAR METHOD

Langmuir isotherm model				
Temp.	q_{max} (mg/g)	K_L (L/mg)	R_L	R^2
20 ºC	11.312	55.06	0.0178	0.9923
Frendlich isotherm model				
Temp.	K_F (mg/g) $(L/mg)^{1/n}$		n	R^2
20 ºC	0.398		1.531	0.9841
Temkin isotherm model				
Temp.	A (L/g)	B (J/mol)	b (J/mol)	R^2
20 ºC	0.199	2.386	1021.3	0.9893
Redlich-Peterson isotherm model				
g	B $(dm^3/mg)^g$	A (dm^3/g)		R^2
1.03	0.015	0.2		0.9982

TABLE-2
PARAMETER R_L INDICATED THE SHAPE OF ISOTHERM

Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Langmuir Isotherm: Langmuir treatment is based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface, with a constant energy of adsorption and no transmigration of adsorbate in the plane of the surface. The isotherm plotted in Fig. 3 are well described by the linear form of the Langmuir equation[7]:

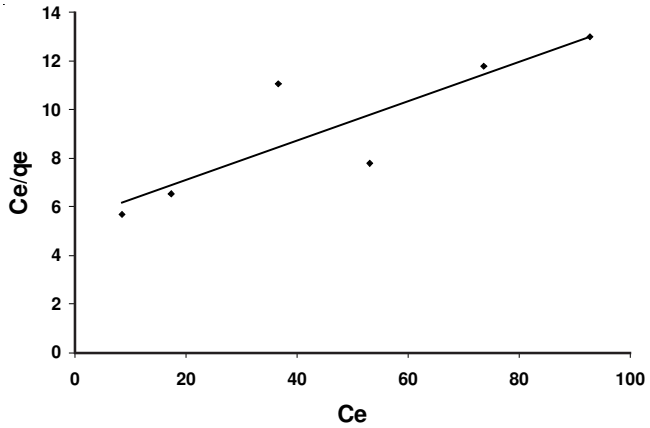

Fig. 3. Langmuir isotherm for Sm(III) adsorption onto poly(IDA/AGE-DMAA)-grafted silica gel at 20 ºC

$$q_e = q_{max} K_L \frac{C_e}{(1 + K_L C_e)} \quad (2)$$

The eqn. 2 can be rearranged to a linear form:

$$\frac{C_e}{q_e} = \left(\frac{1}{q_{max} K_L}\right) + \left(\frac{C_e}{q_{max}}\right) \quad (3)$$

where C_e (mg L^{-1}) is equilibrium concentrations of Co(II), q_e (mg g^{-1}) is amount of Sm(III) at equilibrium on poly(IDA/AGE-DMAA)-grafted silica gel, qmax is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg g^{-1}) and K_L is the Langmuir constant (L mg^{-1}) related to adsorption capacityand energy of adsorption, respectively. The data fitted well in the Langmuir equation as shown by the regression coefficient values (Table-1). The K_L and q_{max} values determined from the slopes and intercepts of the straight-line plot are given in Fig. 3. Conformation of the experimental data in to Langmuir isotherm model indicates the homogeneous nature of poly(IDA/AGE-DMAA)-grafted surface. The essential characteristics of a Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor R_L, given by the following equation[8].

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (4)$$

where C_0 is the initial metal concentration (mg/L) and K_L is the energy of interaction at the surface. Table-1 shows the values of R_L (0.023- 0.054) were in the range of 0-1 at optimum pH which confirms the favorable uptake of the Pb(II) (Table-2).

Freundlich Isotherm: The Freundlich equation is an empirical equation employed to the described heterogeneous systems, in which it is characterized by the heterogeneity factor 1/n. Hence, the empirical equation can be written as[16]:

$$q_e = K_F C e^{1/n} \quad (5)$$

A linear form of the Freundlich expression can be obtained by taking logarithms of the eqn. 5:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

where q_e is the amount of Sm(III) adsorbed per unit weight of the adsorbent (mg g^{-1}), C_e the equilibrium concentration (mg L^{-1}), K_F the Freundlich constant (mg g^{-1}) (L mg^{-1}) 1/n and 1/n is the heterogeneity factor. Linear plots of ln C_e and ln q_e shows that the adsorption of samarium on poly(IDA/AGE-DMAA)-grafted follows Freundlich model (Fig. 4). The value if 1/n between 0.1 and 1 (0.91) represents good adsorption of samarium on poly(IDA/AGE-DMAA)-grafted. The Freundlich equation predicts that the Sm(III) concentration on the adsorbent will increase as long as there is an increased in the Sm(III) concentration in the liquid.

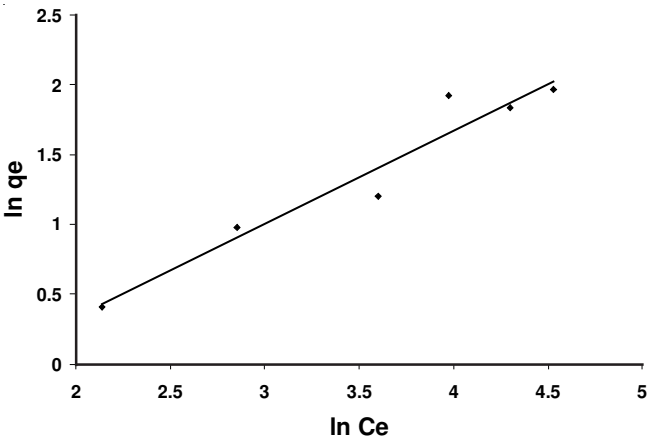

Fig. 4. Freundlich isotherm for Sm(III) adsorption onto poly(IDA/AGE-DMAA)-grafted gel at 20 ºC

Temkin isotherm: The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased.

The Temkin isotherm has been generally applied in the following form[9]:

$$q_e = \frac{RT}{b} \ln (AC_e) \quad (7)$$

And can be linearized:

$$q_e = B \ln A + B \ln C_e \quad (8)$$

where B = RT/b and b is the Temkin constant related to heat of sorption (J mol^{-1}). A is the Temkin isotherm constant (L g^{-1}), R the gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature (K). Therefore plotting q_e *versus* ln C_e (Fig. 5) enables one to determine the constants A and B. Temkin parameters calculated from eqns. 7 and 8 are listed in Table-1.

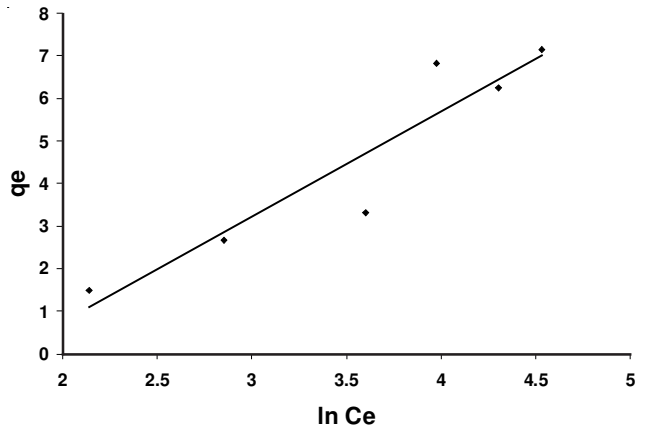

Fig. 5. Temkin isotherm for Sm(III) adsorption onto poly(IDA/AGE-DMAA)-grafted silica gel at 20 ºC

Redlich-Peterson isotherm: The Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (9)$$

It has three isotherm constants, namely, A, B and g ($0 < g < 1$), which characterize the isotherm. The limiting behaviour can be summarized as follows:

Where g =1

$$q_e = \frac{AC_e}{1 + BC_e} \quad (10)$$

i.e., the Langmuir form results.

Where constants A and B are much greater than unity[10]:

$$q_e = \frac{A}{BC_e^{g-1}} \quad (11)$$

i.e., the Freundlich form results.

Where g = 0

$$q_e = \frac{AC_e}{1 + B} \quad (12)$$

i.e., the Henry's Law form results.

Eqn. 9 can be converted to a linear form by taking logarithms:

$$\ln\left(A\frac{C_e}{q_e} - 1\right) = g \ln (C_e) + \ln (B) \quad (13)$$

Three isotherm constants, A, B and g can be evaluated from the linear plot represented by eqn. (13) using a trial and error procedure, which is applicable to computer operation. It was developed to determine the isotherm parameters by optimization routine to maximize the coefficient of determination, R^2, for a series of values of A for the linear regression of ln (C_e) on ln [$A(C_e/q_e) - 1$] and to obtain the best value of A which yields a maximum 'optimized' value of R^2 using the solver add-in with Microsoft's spreadsheet, Microsoft Excel.

The Redlich-Peterson isotherm constants, A, B and g as well as the coefficient of determination, R^2, for the sorption of Sm(III) onto poly(IDA/AGE-DMAA)-grafted silica gel using the linear regression is shown in Table-1. It can be seen that the values of g were close to unity, which means that the isotherms are approaching the Langmuir form and not the Freundlich isotherm. The result shows that the Langmuir isotherm best-fit the equilibrium data for adsorption of Sm(III) on poly(IDA/AGE-DMAA)-grafted silica gel.

Conclusion

A new method was developed for synthesize of solid support. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 11.3 (mg g^{-1}) at 20 ºC. The R_L values showed that the poly(IDA/AGE-DMAA)-grafted silica gel was favorable for the adsorption of Sm(III). Langmuir isotherm was proved to be best-fit isotherm for adsorption of Sm(III) on poly(IDA/AGE-DMAA)-grafted silica gel.

REFERENCES

1. T.R. Biju, *Crit. Rev. Anal. Chem.*, **30**, 179 (2000).
2. E. Greinacher, Industrial Application of Rare Earth Elements, in: ACS System, Symp. Ser. 164, American Society, Washington, DC (1981).
3. E.A. El-Sofany, *J. Hazard. Mater.*, **153**, 948 (2008).
4. T. Saito, H. Sato and T. Moteg, *J. Alloys Compd.*, **387**, 274 (2005).
5. C.B. Xia, Y.Z. Yang, X.M. Xin and S.X. Wang, *J. Radioanal. Nucl. Chem.*, **275**, 535 (2007).
6. H.A. Panahi, J. Morshedian, N. Mehmandost, E. Moniri and I. Yu. Galaev, *J. Chromatogr. A*, **1217**, 5165 (2010).
7. L. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
8. K.L. Hall, L.C. Eagleton, A. Acrivos and T. Vermeulen, *Ind. Eng. Chem. Fundam.*, **5**, 212 (1966).
9. H.M.A. Frendlich, *J. Phys. Chem.*, **57**, 385 (1906).
10. Y.S. Ho and A.E. Ofomaja, *Biochem. Eng. J.*, **30**, 117 (2006).