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ADSORPTION CAPACITY OF ACTIVATED CHARCOAL FOR LANTHANIDES (III) IONS

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The adsorption of lanthanides metals namely Sm^{3+}, Eu^{3+} and Gd^{3+} on activated charcoal has been studied as a function of pH at room temperature. Maximum adsorption was observed at pH value of 4. The adsorption mechanism has been described in term of hydrolysed species formed in aqueous solution at different pH. The adsorption of metal ions obeyed the Langmuir and Temkin isotherm models in the range of 1.0 to 6.0 g of metal ions per liter of solution. The values of adsorption capacities "Q" for Sm^{3+}, Eu^{3+} and Gd^{3+} ions have been calculated at different pH. The adsorption capacities obtained from Langmuir model are in agreement with the determined values of Temkin constants "A_T" from Temkin model. The determined adsorption capacities of the investigated metal ions varied in the order of $Gd^{3+} > Eu^{3+} > Sm^{3+}$ ions and were correlated with the charge density (Z/r) of the metal ions studied.

Keywords: Adsorption capacity, Activated charcoal, Lanthanide ions

1. Introduction

Interest in the adsorption of metal ions for recovery and preconcentration purposes has increased many folds in recent years. The adsorption process under certain conditions has a definite edge over other methods due to its simplicity, high enrichment factor, high recovery, rapid phase separation, low cost and ability to couple with different detection techniques in on-line and off-line modes. Activated charcoal has been used extensively for the removal of metal ions from solutions due to its high purity, large surface area, micro porous structure, high adsorption capacity and radiation stability [1–6]. The adsorption capacity of an adsorbent for a specific metal ion depends upon various factors like nature of adsorbent, oxidation state of the adsorbate, equilibration time and pH of the adsorption medium. Among these the pH of the medium is one of the most important factors [7] since it is responsible for the existing of different forms of metal ions, competitive interaction of H_3O^+ and H^+ ions, surface electric charge of the adsorbent and the competition of counter ions of acids and bases used for the adjustment of pH of the medium. For reasons cited above, the pH dependence of metal ions adsorption is a complex phenomenon and influences the metal ions adsorption on solids.

The adsorption of samarium (Sm^{3+}), europium (Eu^{3+}) and gadolinium (Gd^{3+}) ions is important from the point of view of purification, trace metal analysis and waste disposal treatment. The activated charcoal has been used for the adsorption of these metal ions from aqueous solutions [8–11]. The present communication is an extension of our earlier work and reports results of the adsorption of Sm^{3+}, Eu^{3+} and Gd^{3+} ions as a function of pH on the activated charcoal. The values of the adsorption capacities of these metal ions are calculated from the Langmuir isotherm equation at different pH and are correlated with the charge density (Z/r) of the metal ions.

2. Experimental

2.1. Reagents

A commercial activated charcoal, BDH, Product No. 33032, having BET surface area (nitrogen adsorption) 980 $m^2\ g^{-1}$, porosity 75.74 %; pore volume 1.43 $cm^3\ g^{-1}$, average particle diameter 3.7 ± 0.2 micron was used as such during this study. Nitrates of samarium, europium and gadolinium

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(99.999%) from Rare Earth Products and buffer solutions of different pH supplied by Fluka were used in this study. All pH measurements were made with a Metrohm 605 digital pH meter equipped with a combined glass/calomel electrode. Distilled and deionized water was used throughout.

2.2. Sorption measurements

10 mL of metal solutions of known concentration at different pH were taken in a 250 mL glass reagent bottles alongwith 100 mg of dried activated charcoal. The contents were equilibrated on a mechanical shaker for a specific time of 60 minutes. The solutions were filtered through Watman filter paper No. 40. The concentrations of metal ions in filtrate were measured by X–ray fluorescence spectrometer (Siemens SRS–200). The concentration of metal ions was corrected for the loss of metal ions through the adsorption on the walls of the glass bottles by running blank experiments i.e., without activated charcoal addition. The amount of metal ions adsorbed on activated charcoal at different pH was calculated using the following relationship:

$$C_{Ads} = \frac{C_I - C_{Eq}}{M} \times V \qquad (1)$$

where

C_{Ads} = amount of metal ions adsorbed on activated charcoal (g g^{-1})

C_I = initial concentration of metal ions in solution (g L^{-1})

C_{Eq} = concentration of metal ions in solution after equilibrium (g L^{-1})

M = amount of adsorbent (g)

V = volume of adsorbate solution (L)

3. Results and Discussion

The adsorption of samarium (Sm^{3+}), europium (Eu^{3+}) and gadolinium (Gd^{3+}) ions on activated charcoal was studied as a function of pH by employing batch technique at ambient temperature of 22 ± 1 °C. The initial concentrations of the metal solutions used were varied from 1.0 to 6.0 g of metal ions per liter of solution. All the reported results are the average of at least triplicate independent readings with a relative standard deviation of within ± 5%.

The adsorption isotherms of Sm^{3+}, Eu^{3+} and Gd^{3+} ions at different pH were obtained by plotting the amount adsorbed against equilibrium concentration of metal ions in solution and the results have been shown in Figures 1–3, which show that the adsorption of Sm^{3+}, Eu^{3+} and Gd^{3+} ions increases with the increasing pH upto 4 and

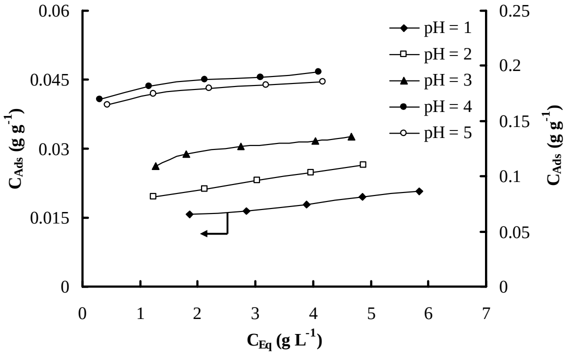

Figure 1. Adsorption isotherms of gadolinium ions on activated charcoal at different pH

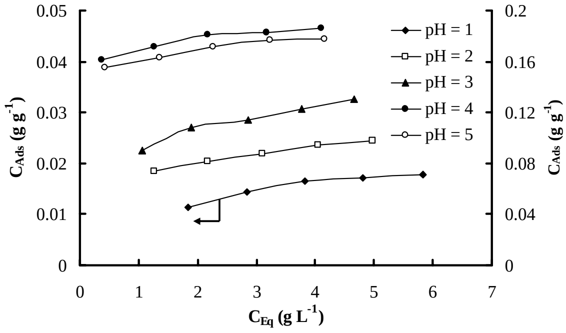

Figure 2. Adsorption isotherms of europium ions on activated charcoal at different pH

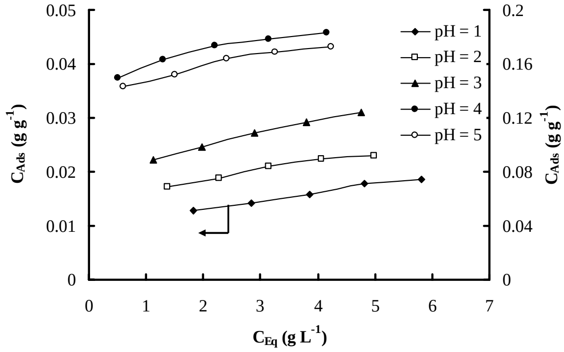

Figure 3. Adsorption isotherms of samarium ions on activated charcoal at different pH.

then starts decreasing with rise in pH. Maximum adsorption of Sm^{3+}, Eu^{3+} and Gd^{3+} ions occurs at pH 4. Further increase in pH resulted in the formation of insoluble precipitates. Similar results of maximum adsorption of cadmium ions at pH 4 to 4.5, on activated charcoal from different sources have been reported in literature [12, 13]. The adsorption behavior of metal ions on activated charcoal may be explained in terms of hydrolyzed species formed in solution at different pH and show different degree of activity. The metal ions studied exist as M^{3+} ions (where M^{3+} = Sm^{3+}, Eu^{3+} and Gd^{3+}), over the pH range 1–4. The competitive adsorption of H_3O^+ and M^{3+} ions an activated charcoal varies in accordance with the acidity of the solution. As the pH of the solutions increases from 1–4, the adsorption of H_3O^+ decreases whilst that of M^{3+} ions increases. Above pH 4, the metal ions (M^3) undergo hydrolysis resulting in the formation of hydroxyl ions such as $M(OH)^{2+}$, $M(OH)_2^+$ and $M(OH)_3$. These hydroxyl ions are weakly adsorbed relative to M^{3+} ions and hence the adsorption of gadolinium, europium and samarium ions on activated charcoal decreases. Above pH 5, the adsorption process could not be followed because of the formation of insoluble complexes in solution.

The adsorption data of Sm^{3+}, Eu^{3+} and Gd^{3+} on charcoal at different pHs were subjected to Langmuir isotherm model [14]. The Langmuir adsorption isotherm is based on the assumption that maximum adsorption corresponds to saturated monolayer of adsorbate molecules on the adsorbent surface, the energy of adsorption is constant and there is no transmigration of adsorbate in the plane of the surface. The Langmuir model is written as:

$$C_{Ads} = \frac{Q\,K\,C_{Eq}}{1 + K\,C_{Eq}} \qquad (2)$$

The linearized form of equation (2) is:

$$\frac{C_{Eq}}{C_{Ads}} = \frac{1}{K\,Q} + \frac{C_{Eq}}{Q} \qquad (3)$$

where

C_{Ads} = amount of metal ions adsorbed (g g^{-1})

C_{Eq} = equilibrium concentration of metal ions in solution (g L^{-1})

Q = adsorption capacity of metal ions (g g^{-1})

K = constant

In general Q and K are functions of pH, ionic media and ionic strength. The values of Q of ions may be computed graphically by using the linear equation (3) and the data in Figures 1–3. Straight lines were obtained by plotting C_{Eq}/C_{Ads} against C_{Eq} for metal ions adsorption on activated charcoal. Typical Langmuir plots for Gd^{3+} ions adsorption at different pH are shown in Figure 4. Similar plots were also obtained for Sm^{3+} and Eu^{3+} ions. The data revealed that the Langmuir adsorption model was obeyed over the entire concentration range studied. The values Q and K for Sm^{3+}, Eu^{3+} and Gd^{3+} ions were calculated from the slopes and intercepts of Langmuir plots respectively and are reported in Table 1.

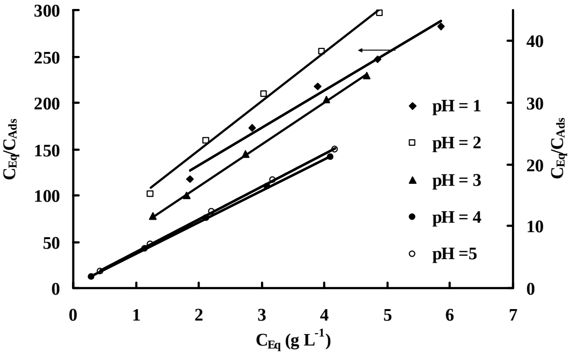

Figure 4. Langmuir plots for the adsorption of gadolinium ions on activated charcoal at different pH.

The adsorption data of Sm^{3+}, Eu^{3+} and Gd^{3+} on activated charcoal at different pHs were also subjected to Temkin isotherm model. The Temkin isotherm is an empirical relationship, which often gives a more satisfactory model of experimental data. Its linear form can be expressed as:

$$C_{Ads} = A_T + B_T \ln C_{Eq} \qquad (4)$$

where

C_{Ads} = amount of metal ions adsorbed (g g^{-1})

C_{Eq} = equilibrium concentration of metal ions in solution (g L^{-1})

A_T = constant related to adsorption capacity

B_T = constant related to intensity of adsorption

Table 1. Langmuir parameters for the adsorption of lanthanides ions on activated charcoal at different pH

pH	Adsorption capacities (g.g^{-1})			K		
	Sm^{3+}	Eu^{3+}	Gd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}
1.0	0.0241	0.0241	0.2481	0.5524	0.5131	0.7732
2.0	0.1085	0.1113	0.1256	1.1248	1.3565	1.2476
3.0	0.1433	0.1488	0.1475	1.2204	1.3566	2.2978
4.0	0.1893	0.1897	0.1962	5.7014	9.9830	12.5723
5.0	0.1804	0.1822	0.1884	4.6174	8.5597	11.4078

Table 2. Temkin parameters for the adsorption of lanthanides ions on activated charcoal at different pH

pH	A_T			B_T		
	Sm^{3+}	Eu^{3+}	Gd^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}
1.0	0.0093	0.0083	0.0124	0.0051	0.0057	0.0045
2.0	0.0614	0.0685	0.0752	0.0194	0.0180	0.0207
3.0	0.0837	0.0893	0.1067	0.0249	0.0260	0.0190
4.0	0.1603	0.1712	0.1802	0.0158	0.0105	0.0092
5.0	0.1494	0.1629	0.1722	0.0159	0.0103	0.0093

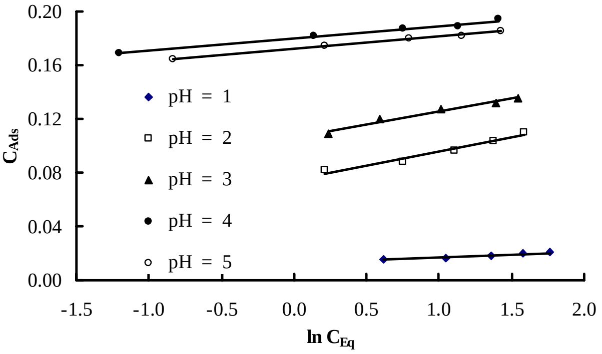

Figure 5. Temkin plots for the adsorption of gadolinium ions on activated charcoal at different pH.

Plots of C_{Ads} against lnC_{Eq} are straight lines. The values of A_T and B_T may be obtained from the intercept and slope of the straight line respectively. Typical Temkin plots for Gd^{3+} ions adsorption on activated charcoal at different pH are shown in Figure 5. Similar plots were also obtained for Sm^{3+} and Eu^{3+} ions indicating that the Temkin adsorption model was obeyed over the entire concentration ranges of metal ions studied. The determined values of constants A_T and B_T for Sm^{3+}, Eu^{3+} and Gd^{3+} ions have been reported in Table 2. The pattern of the determined Temkin constants is in accordance with the adsorption capacity data calculated from Langmuir model (Table 1). Perusal of the determined values of "Q" for Sm^{3+}, Eu^{3+} and Gd^{3+} ions obtained from Langmuir isotherms at different pH of the adsorption medium followed the sequence:

$$Gd^{3+} > Eu^{3+} > Sm^{3+}$$

The ionic radii of Sm^{3+}, Eu^{3+} and Gd^{3+} ions are 0.958, 0.947 and 0.938 Å [15], respectively, therefore, the determined values of the charge density (Z/r) of these ions varies in the following order:

$$Gd^{3+}\ (3.1983) > Eu^{3+}\ (3.1679) > Sm^{3+}\ (3.1315)$$

This indicates that Gd^{3+} ions is the most active ions and interact more strongly with the activated charcoal surface as compared to Eu^{3+}, which in turn is more interactive as compared to Sm^{3+} ions, thus giving maximum adsorption capacity for Gd^{3+} and minimum for Sm^{3+}. This also indicates a positive correlation with the adsorption capacity and charge density of the metal ions studied.

References

[1] E. A. Sigworth and S. B. Smith, J. Am. Water Works Assoc. **64**, No. 6 (1972) 386.

[2] B. M. Vanderborght and R. E. V. Grieken, Talanta **27** (1980) 417.

[3] D. Mohan, V. K. Gupta, S. K. Srivastava and S. Chander, Colloids and Surfaces A **177** (2001) 169.

[4] M. Seker, V. Sakthi and S. Rengaraj, J. Colloid Interf. Sci. **279** (2004) 307.

[5] S.I. Lyubechik, A. I. Lyubchik, O. L., Galushko, L. P. Tikhonova, J. Vital, I. M. Fonseca and S. B. Lyubchik, Colloids and Surfaces A **242** (2004) 151.

[6] K. Zhang, W. H. Cheung and M. Valix, Chemosphere **60** (2005) 1129.

[7] P. Benes and V. Majer, Trace chemistry of aqueous solutions, Elsevier Scientific publishing Company (1980) p. 175.

[8] R. Qadeer, J. Hanif, M. Saleem and M. Afzal, J. Chem. Soc. Pak. **14** (1992) 91.

[9] M. Saleem, M. Afzal, R. Qadeer and J. Hanif, Ads. Sci. Technol. **9** (1992) 1.

[10] R. Qadeer, J. Hanif, M. Saleem and M. Afzal, J. Radioanal. Nucl. Chem. **159** (1992) 155.

[11] M. Saleem, R. Qadeer, J. Hanif and M. Afzal, J. Radioanal. Nucl. Chem. **182** (1994) 415.

[12] R. Qadeer and N. Khalid, Sep. Sci. Technol. **40** (2005) 845.

[13] T. K. Budinova, K. M. Gergova, N. V. Petrov and V. N. Minkova, J. Chem. Tech. Biotechnol. **60** (1994) 177.

[14] B. E. Reed and M. R. Matsumoto, Sep. Sci. Technol. **28** (1993) 2179.

[15] D. R. Lide, Handbook of Chemistry and Physics, 83rd Edition, CRC Press LLC, Boca Raton (2002) p. 4-131.