www.amlett.org, www.amlett.com, DOI: 10.5185/amlett.2012.icnano.138
"ICNANO 2011" Special Issue Published online by the VBRI press in 2012

Silver nano particles impregnated alumina for the removal of strontium(II) from aqueous solution

Rajesh Kumar, Thomas N. Abraham and Surendra K. Jain*

Water Quality Management, Desert Environmental science and Technology Division, Defence Laboratory, Ratanada Palace, Jodhpur 342011(Raj), India

*Corresponding author. Tel:(+91) 291-2567510 E-mail: skj_dl97@rediffmail.com

ABSTRACT

This study was carried out for removal of strontium (II) from aqueous solutions using silver nano particle impregnated alumina. The silver nano particle impregnated alumina was prepared by reduction method and characterized using UV-Vis spectroscopy, X-ray diffraction and scanning electron microscopy (SEM). The aim was to find the capability of the material for the removal of strontium from contaminated water under different conditions such as initial concentration of strontium, contact time and neutral pH. The adsorption isotherms were prepared, correlated to Freundlich and Langmuir models and it was found that the adsorption data could be fitted better by Freundlich model than Langmuir one. Copyright © 2012 VBRI press.

Keywords: Adsorption isotherm; strontium ion; silver nano particle impregnated alumina.

Rajesh Kumar joined Defence R&D Organisation at Defence Laboratory, Jodhpur, India as a scientist in 2005. He received his M.Sc. and Ph.D. degrees in Organic Chemistry from University of Rajasthan, Jaipur, India. His research interests include the synthesis and characterization of nano materials and chelating agents for water purification application. More than 35 international papers and one patent are in his credit.

S. K. Jain is Scientist at Defence Laboratory, Jodhpur (India), Defence R&D Organisation from 1982. He received his M.Sc. and Ph.D. degrees in Organic Chemistry from University of Rajasthan, Jaipur, India. Topics of his research interests are Desalination, Water Quality Monitoring and Water treatment. His research interest also synthesis and characterization of Nano materials and polymers for water purification application. More than 25 international papers and 8 patents are in his credit.

Introduction

The presence of toxic metal ions in the environment is a cause of concern due to their acute and long term toxicity **[1]**. The contamination of drinking water with radionucleides such as cesium, strontium and also the radioactive degraded products during the nuclear war is another emerging threat to both military as well civilian populations. The main source of these radionucleides is radioactive wastes from nuclear power plants, research facilities and the use of radioisotopes in industry and diagnostic medicine **[2-5]**. The drinking of radionuclide contaminated water can lead to irreversible damage to the entire living beings. Therefore the removal of radionuclides from water is a necessary requirement.

There are several methods such as precipitation, filtration, evaporation, nanofiltration ion exchange using organic resins and adsorption **[6-8]** for the removal of radionucleides from drinking water. The sorption of radionuclides onto modified alumina, TiO_2 (Anatase and Rutile), attapulgite and other minerals has been investigated in last decade **[9-11]**. However, the resins and other adsorbents have drawback due to their ability to swell. Such behavior makes them incompatible with the final waste forms.

A considerable number of synthetic inorganic material **[12]** and organic adsorbent such as natural and modified zeolites**[13]**, bentonite **[14]** and ion exchanger polyacrylamide cerium titanate polymer**[15]** and titanium tungstate **[16]** have been identified which have a strong affinity for radionuclides over a wide pH range. However, the removal efficiencies of metal ions of these adsorbents were low. The adsorptions of radionuclides on other materials such as carbon nanotubes have been studied **[17, 18]**. Nonmodified carbon nanotubes show insufficient adsorption efficiency due to their poor dispersion property. Therefore, researchers carried out investigation for new promising radionuclide adsorbents **[19]**.

Our laboratory has already developed water purification system for waste water treatment **[20, 21]**. For the up gradation of the system it is recommended to develop novel adsorbent for removal of strontium

radionuclides. Now our R&D is focusing on developing novel adsorbent for removal of radionuclides from contaminated water. Under this objective, we have analyzed silver nano particle impregnated alumina for the development of highly efficient adsorbent for such radioactive nuclei removal.

In this paper we describe the synthesis of silver nano particles by reduction method followed by a novel approach of impregnation of the synthesized silver nano particles in alumina. The synthesized material was evaluated for removal of the strontium (II) from aqueous solution. The process parameters such as neutral pH, contact time and initial concentration of strontium ions were evaluated for the maximum removal.

Experimental

Materials and instruments

All atomic absorption spectrometer (AAS) (Analytik-Jena-Nova-400) measurements were carried out on flame mode with single beam. UV-Vis absorption spectra were recorded using a Analytik Jena SPECORD S600 UV-Vis spectrometer. X-ray diffraction pattern were recorded on a Panalytical X'pert PRO Diffractometer with a Cu Kα source. The pH measurements were made on a digital pH meter (HACH, sension 1, model 51935-00) equipped with a gel-filled pH electrode. The meter was calibrated with the buffers of 3, 7 and 10.

Chemicals and solutions

All of the reagents used were of analytical-grade. All the solutions were prepared with ultrapure water (resistivity: 18.2 MΩ.cm,) from an Elix analytical reagent-grade water purification system. Silver nitrate $AgNO_3$ (Sigma Aldrich, UK) and trisodium citrate $C_6H_5O_7Na_3$ (Sigma Aldrich, UK) of analytical grade purity, were used as starting materials without further purification. Calibration standard solutions and internal standards were prepared from commercial metal standard solutions. Analytic grade nitric acid (Fisher) was used as acid for the preparation of all the calibration standard solutions and analytical solutions.

Standard working solutions 1000 mg/L of strontium were prepared from $SrCl_2.6H_2O$ Suprapur^R (Merck, Germy) and solutions of varying initial concentrations were prepared from a 1000 mg/L by serial dilution using distilled deionized water.

Synthesis and impregnation of silver nanoparticles on alumina

The silver colloid was prepared by chemical reduction method according to the description of Lee and Meisel **[22]**. In typical experiment 500 ml of $1x10^{-3}$ M $AgNO_3$ was heated to boiling. To this solution 5 ml of 1 % trisodium citrate was added drop by drop. During the process solution was mixed vigorously. Solution was heated until color's change is evident (pale yellow). After 2 hours heating the solution was removed and stirred until cooled to room temperature. Supported silver nanoparticles were prepared by the following method. As prepared solution of silver nano particles in hot condition, 5gm of alumina were soaked, stirred and kept for a minimum period of 6h to ensure saturable adsorption of nanoparticles on the alumina (Checked by taking the absorbance of nanoparticles solution). After it silver impregnated alumina were washed and dried.

Adsorption studies with batch method

Batch adsorption experiments were carried out in glass bottles (100 mL) containing silver nanoparticle impregnated alumina (100 mg) with 10 mL of Sr (II) ions of desired concentration at 30±1 ^{0}C. The bottles were shaken for 10-120 min and solutions containing Sr(II) ions were filtered using Whatman filter paper (No. 42). After each experiment, the residual concentration of Sr(II) ions was determined by AAS. The amount of metal ion adsorbed by silver nanoparticle impregnated alumina (Q_e mmol/g) was calculated according to the following equation:

$$Q_e = (C_i - C_e) \times V/m \qquad (1)$$

where C_i and C_e are initial and equilibrium concentration (μg/L), respectively. V (L) and m (g) are volume of the sample solution and mass of the silver nanoparticle impregnated alumina. The observed adsorption data were fitted with Langmuir and Freundlich models.

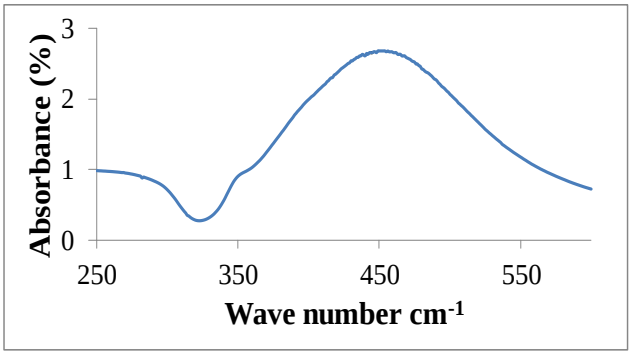

Fig. 1. UV-Vis adsorption spectrum of silver nanoparticle.

Results and discussion

Characterization of silver nanoparticles

Silver nanoparticles were prepared by reduction method. The formation of the silver nanoparticles was monitored using UV-Vis spectroscopy. The adsorption spectrum reveals the formation of silver nanoparticles by exhibiting the typical surface adsorption maxima at 420-470 nm **(Fig. 1)**.

XRD analysis was also performed to confirm the crystal phase of silver nanoparticles. **Fig. 2** shows x-ray diffraction pattern of the silver nanoparticles supported on alumina. The reflection peaks can be indexed to face-centred cubic silver, as indicated by diffraction peaks (111), (200), (220) and (311).

The morphology of silver nanoparticles was determined by Scanning electron microscopy (SEM). SEM photograph **(Fig. 3)** indicates that the nanoparticles with spherical morphology are well dispersed.

Adsorption isotherm

The adsorption isotherms of Sr(II) onto silver nanoparticles impregnated alumina from aqueous solution is shown that the adsorption capacity of Sr(II) onto silver nanoparticles impregnated alumina increases with increasing the initial Sr(II) concentration increased and continued up to 2000 µg/L and level off thereafter. The initial Sr (II) concentrations (1000, 2000, 3000, 4000 and 5000 µg/L) have been used for investigation of the adsorption isotherm. The equilibrium concentrations are obtained after 60 min. of contact time.

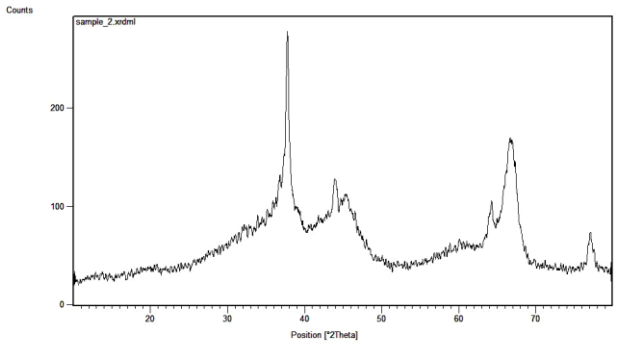

Fig. 2. XRD pattern silver nanoparticles impregnated alumina

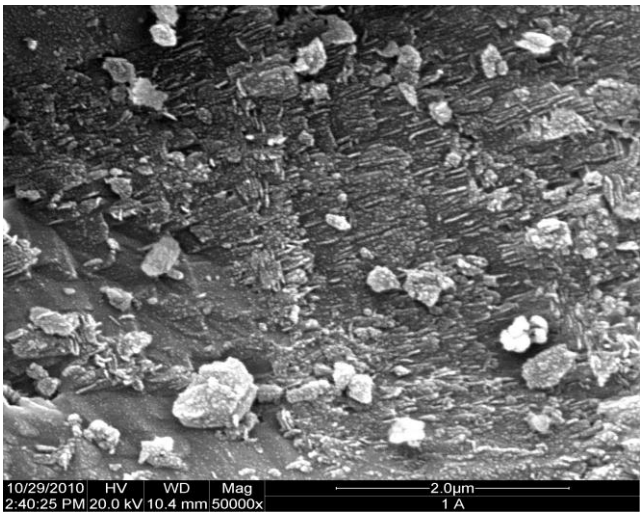

Fig. 3. SEM image of silver nanoparticle impregnated alumina

Langmuir **[23]** and Freundlich **[24]** models are employed to describe the adsorption process. The Langmuir isotherm model is given as

$$C_e/Q_e = 1/(q_m b) + C_e/Q_m \qquad (2)$$

where C_e is the equilibrium concentration obtained from the initial concentration upon a certain period of contact time with the silver nanoparticles impregnated alumina, Q_e is the amount of Sr(II) adsorbed per gram of silver nanoparticles impregnated alumina (µg/g) at equilibrium, and Q_m is the maximum adsorption capacity (µg/g). *b* is the Langmuir parameter related to energy of adsorption. Q_e is derived from the equation 1. The linear plot of C_e/Q_e vs C_e gives the intercept and slope corresponding to $1/(Q_m b)$ and $1/Q_m$, respectively, from which both Q_m and *b* are derived. A plot of C_e/Q_e vs C_e should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium. Freundlich isotherm can be expressed as

$$\log Q_e = 1/n \log C_e + \log K \qquad (3)$$

where *K* and 1/*n* are Freundlich constants, indicating the sorption capacity and sorption intensity, respectively. C_e is the equilibrium concentration of Sr(II) in aqueous solution and Q_e is the sorption capacity. The plot of $\log Q_e$ against $\log C_e$ gives the intercept and slope corresponding to $\log K$ and $1/n$, respectively, from which both *K* and *n* are obtained.

Table 1. Langmuir and Freundlich parameters of Sr(II) adsorption.

Langmuir Model			Freundlich Model		
Q_m (µg/g)	b (L/µg)	R^2	K	1/n	R^2
1666	0. 0006	0.9531	0.2508	0.9412	0.9948

The regression equations parameters Q_m, K, 1/n and the correlation coefficient are summarized in **Table 1**. It is seen that the Freundlich model is more suitable to fit the adsorption data than Langmuir model since the correlation coefficients are higher than 0.99. The numerical value of 1/n <1 indicates that adsorption is fitted Freundlich model and multilayer adsorption on the surface.

Conclusion

The silver nano particle impregnated alumina was successfully carried out by reduction method followed by a novel approach of impregnation. The formation of silver nanoparticle on alumina has been confirmed of coloured colloidal solution of silver nanoparticles having strong adsorption band between 420-470 nm followed by X-ray diffraction pattern studies. Impregnated alumina (100mg) was also evaluated for removal of the strontium (II) (1 ppm) from aqueous solution and maximum removal 82% obtained at pH 7 in 60 minutes. The adsorption isotherms were correlated to Freundlich and Langmuir models and it was found that the adsorption data could be fitted better by Freundlich than Langmuir model one. Impregnated alumina can be used as good adsorbent for the removal of the strontium ions from polluted water according to results.

Acknowledgements

We gratefully acknowledge the support, encouragement and valuable suggestion which we received from Dr S.R. Vadera, Director, Defence laboratory. The authors thank Dr. Manoj Patra for XRD analysis.

Reference

1. Patterson, J.W. *Industrial Wastewater Treatment Technology*, 2nd Ed. Butterworth- Heinemann, London, **1985**.
2. Kemp, R. V.; Bennett, D. G.; White, M. *J. Environ. Int.* **2006**, *32*, 1021.
DOI: http://dx.doi.org/10.1016/j.envint.2006.06.010
3. Andrade, C.; Martinez, I.; Castellote, M.; Zuloaga, P. *J. Nuc. Mater.* **2006**, *358*, 82.
DOI: http://dx.doi.org/10.1016/j.jnucmat.2006.06.015
4. Plecas, I.; Dimovic, S. *Progress Nuc. Energy*, **2006**, *48*, 629.

DOI: http://dx.doi.org/10.1016/j.pnucene.2006.06.012
5. Melville, G.; Liu S.F.; Allen, B. *J. Appl. Radi. Isot.* **2006**, *64*, 979. **DOI**: http://dx.doi.org/10.1016/j.apradiso.2006.04.005
6. Abdel Raouf, M.W. *J. Chem. Techno. Biotech.* **2003**, *79*, 22. **DOI**: http://dx.doi.org/10.1002/jctb.737
7. Wang, X.; Xu, D.; Chen, L.; Tan, X.; Zhou, X.; Ren, A.; Chen, C. *Appl. Radi. Isot.* **2006,** *64*, 414. **DOI**: http://dx.doi.org/10.1016/j.apradiso.2005.08.010
8. Khedr, M. G. *Desalination and water Treatment* **2009**, *2*, 342. **DOI**: 10.5004/dwt.2009.333
9. Tan, X.L.; Wang, X.K.; Geckeis, H.; Rabung, T.H. *Environ. Sci. Technol.* **2008**, *42*, 6532. **DOI**: 10.1021/es8007062
10. Tan, X. L.; Fan, Q. H.; Wang, X. K.; Grambow, B. *Environ. Sci. Technol.* **2009**, *43*, 3115. **DOI**: 10.1021/es803272f
11. Fan, Q. H.; Tan, X. L.; Li, J. X.; Wang, X. K.; Wu, W. S.; Montavon, G. *Environ. Sci. Technol.* **2009**, *43*, 5776. **DOI**: 10.1021/es901241f
12. Nilchi, M.; Ghanadi, N.; Khanchi, A. *J. Radioanal. Nuc. Chem.* **2000**, *245*, 589. **DOI**: 10.1023/A:1006773631000
13. Borai, E.H.; Harjula, R.; Malien, L.; Paajanen, A. *J. Hazard. Mater.* **2009**, *172*,416. **DOI**: http://dx.doi.org/10.1016/j.jhazmat.2009.07.033
14. Klika, Z.; Kraus, L.; Vopalka, D. *Langmuir* **2007**, *23*, 1227. **DOI**: 10.1021/la062080b
15. Chen, C.; Hu, J.; Xu, D.; Tan, X.; Meng, Y.; Wang, X. *J. Coll. Interf. Sci.* **2008**, *323*, 33. **DOI**: http://dx.doi.org/10.1016/j.jcis.2008.04.046
16. Ibrahim, G. M. *Desalination and water Treatment* **2010**, *13*, 418. **DOI**: 10.5004/dwt.2010.999
17. Shao, D.; Jing, Z.; Wang, X.; Li, J.; Meng, Y. *J. Phys. Chem. Lett.* **2009**, *113*, 860. **DOI**: 10.1021/jp8091094
18. Rao, G.P.; Lu, C.; Su, F. *Sep. Purif. Tech.* **2007**, *58*, 224. **DOI**: http://dx.doi.org/10.1016/j.seppur.2006.12.006
19. Anilan, B.; Gedikbey, T.; Akar, S.T. *Clean-Soil, Air, Water* **2010**, *38(4)*, 344. **DOI**: 10.1002/clen.201000009
20. Kumar, R.; Abraham, T. N.; Jain, S. K. *J. Water reuse and Desalination* **2011**,*1(2)*,113. **DOI**:10.2166/wrd.2011.020
21. Misra, R.K.; Jain, S.K.; Khatri, P.K. *J. Hazard. Mater.* **2011,** 185, 1508. **DOI**: http://dx.doi.org/10.1016/j.jhazmat.2010.10.077
22. Lee, P. C.; Meisel, D. *J. Phys. Chem.* **1982**, *86*, 3391. **DOI**: 10.1021/j100214a025
23. Langmuir, I. *J. Am. Chem. Soc.* **1916**, *38*, 2221. **DOI**: 10.1021/ja02268a002
24. Freundlich, H.M.F. Z. Phys. Chem. **1906**, *57*, 385.

