

Synthesis of some novel adsorbents for antimicrobial activity and removal of arsenic from drinking water

Hafiz Badaruddin Ahmad*, Gul E Yasmin*, Shafique Ahmad Arain**,†, Ijaz Ahmad Bhatti***, and Mazhar Hussain*

*Institute of Chemical Sciences, Bahauddin Zakariya University Multan, Pakistan

**Department of Chemistry, Shah Abdul Latif University, Khairpur, Pakistan

***Department of Chemistry, University of Agriculture, Faisalabad, Pakistan

(Received 26 March 2014 • accepted 11 September 2014)

Abstract—Arsenic contamination in drinking water is alarming for human beings; especially for those people who use ground water directly for drinking purposes. Attempts were made to design adsorbents for the removal of arsenic. Silica gel has been tested as adsorbent for such removal. After optimizing concentration, time and amount of adsorbent, Langmuir, Freundlich and D-R isotherms are drawn to determine different parameters for the evaluation of arsenic adsorption. Kinetics of adsorption is also calculated by using pseudo first order and pseudo second order rate equations. Zerovalent iron and manganese nanoparticles have been coated on silica gel and efficiency of removal of arsenic have been determined. Iron and manganese particles have been stabilized with polyvinyl alcohol (PVA). Similarly mixtures of iron-silver and manganese-silver nanoparticles have been synthesized by stabilizing with PVA, which show better efficiency than individual nanoparticles of iron and manganese coated silica gel. The newly synthesized adsorbents are very much effective for not only arsenic but also for antimicrobial activity. Concentration of arsenic in water has been determined spectrophotometrically using variamine blue as indicator.

Keywords: Arsenic, Contamination, Zerovalent, Herbicides, Mesoporous Alumina

INTRODUCTION

The contamination of natural and wastewater by different pollutants in the environment is a major concern worldwide and consequently much attention has been aroused in abatement of such pollutants [1-3]. Arsenic, which is notoriously toxic to humans and other living organisms [4,5], exists in -3, 0, +3 and +5 oxidation states [7]. In natural water, arsenic is primarily present in inorganic forms and exists in two predominant species, arsenate [As(V)] and arsenite [As(III)]. As(V) is the major arsenic species in surface water, while As(III) is the dominant arsenic in groundwater since it is favored under reducing conditions. As(III) is more toxic to biological systems than As(V) [8-10]. Pentavalent species predominate and are stable in oxygen-rich aerobic environments. Trivalent arsenites predominate in moderately reducing anaerobic environments such as groundwater [11]. Arsenic species in various pH ranges have been discussed [12,13]. Presence of arsenic in ground water is mostly due to minerals dissolving naturally from rocks and soil [14,15]. Moreover, biological and mining activities, geochemical reactions, volcanic emissions, use of arsenic additives, pesticides, herbicides and crop desiccants make the problem more serious for animals and humans [16]. Arsenic contaminated water may cause numerous diseases of skin and internal organs [14-19]. The World Health Organization (WHO), European Union, and several countries such as Turkey also lowered their recommended or required

arsenic limit to $10 \mu\text{g L}^{-1}$ in drinking water [20]. A variety of treatment processes have been studied for arsenic removal from water [21,22]. Various technologies are available, including chemical precipitation or coagulation, adsorption, lime softening, ion exchange, and membrane separation [23-31]. Although precipitation-coprecipitation with ferric and aluminum salts is one of the conventional methods for arsenic removal, handling and disposal of the waste sludge is a significant problem of this process [32]. Hydroponic technique has also been used for phytoextraction of arsenic [33]. Adsorption has emerged as an alternative to these traditional methods with the advantage of being technically easy, and with the potential for regeneration and sludge-free operation [34]. At the same time adsorption will provide an attractive technology if the adsorbent is cheap and ready for use. So far, many kinds of adsorbents such as Zr(IV) loaded orange waste gel, iron modified red mud, agricultural residue, rice polish [35], rice bran [36] iron modified calcined bauxite, zero valent iron [37], mesoporous alumina [38, 39], acid modified carbon black [40] and activated carbon from agrowastes [41] have been developed for the removal of arsenic. Functionalized graphene sheets and magnetite-graphene hybrid have been used for the removal of As(III) and As(V) [42,43]. Hybrid metal oxide has been successfully tested for the removal of aqueous solution of arsenic from industrial waste [44]. Immobilized small sized manganese dioxide sand has been utilized in the remediation of arsenic contaminated water [45]. Biosynthesis of manganese and zinc nanoparticles is available in literature [46]. In our present studies, we have attempted to design new adsorbents, metallic and bimetallic nanocomposites for antimicrobial activity and removal of arsenic from drinking water.

†To whom correspondence should be addressed.

E-mail: ashafique2010@gmail.com

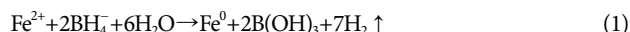
Copyright by The Korean Institute of Chemical Engineers.

EXPERIMENTAL

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, FeCl_3 , absolute ethanol, PVA, KMnO_4 , As_2O_3 and HCl (Merck), NaBH_4 (Sigma-Aldrich), silica gel, $\text{MnCl}_2 \cdot \text{H}_2\text{O}$, AgNO_3 , N_2H_4 , NaAsO_3 , CH_3COONa , KIO_3 , varamine blue, NaOH and KIO_3 (Fluka) were used without further purification throughout this study. All chemicals used were of analytical grade. Deionized water was used for preparation and dilution of reagents and samples.

1. Silica Gel Supported Nano Zero Valent Iron (Silica-nZVI)

Synthesis of nZVI is based on borohydride reduction of Fe(II) . In this study, iron (II) chloride tetra hydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) and sodium borohydride (NaBH_4) were used for iron (II) and borohydride sources, respectively. The proposed reaction is:



For the synthesis of nZVI (1.5 g), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (5.34 g) was dissolved in ethanol/water mixture (24 ml ethanol+6 ml deionized water) and stirred on a magnetic stirrer. On the other hand, 1 M sodium borohydride solution was prepared by dissolving NaBH_4 (3.78 g) in deionized water (100 ml). The final $\text{BH}_4^-/\text{Fe}^{2+}$ ratio was adjusted to 3:1, since excess borohydride was needed for better growth of nanoparticles. The borohydride solution was added from a burette dropwise to the iron(II) solution, while still stirring on magnetic stirrer. Black solid particles immediately appeared after the first drop of sodium borohydride solution. After adding the whole borohydride solution, the mixture was kept on stirring for another 10 minutes.

Silica gel (10 g) was added to this solution and stirred for an hour to get these nanoparticles adsorbed on silica gel. Silica gel supported nZVI were filtered and washed with methanol thrice (25×3 ml) and dried at room temperature. Similar procedure was applied for FeCl_3 (7.02 g) and $\text{MnCl}_2 \cdot \text{H}_2\text{O}$ (3.71 g).

2. Synthesis of PVA-metallic Nanocomposites

In a typical procedure, Mn-PVA nanocomposites were prepared by reacting aqueous solutions of PVA with that of $\text{MnCl}_2 \cdot \text{H}_2\text{O}$. PVA (1 g) was dissolved in deionized water (100 ml) to prepare its clear solution which was then mixed with aqueous solution of MnCl_2 (100 ml) and kept in oven for an hour at 80 °C. Silica gel (10 g) was added to the mixture (100 ml) and stirred vigorously for an hour to get adsorbed on silica gel. Few drops of hydrazine were added during stirring to reduce Mn^{+2} . Silica gel supported Mn-PVA nanocomposites were filtered and washed with methanol (25×3 ml) thrice and dried at room temperature. Similar reactions were carried out using FeCl_3 (0.01 M) and AgNO_3 (0.01 M).

3. Synthesis of PVA--bimetallic Nanocomposites

Mn-Ag-PVA nanocomposites were prepared by reacting aqueous solution of PVA with AgNO_3 (0.01 M) and $\text{MnCl}_2 \cdot \text{H}_2\text{O}$ (0.01 M). PVA solution (100 ml) was mixed with aqueous solution of MnCl_2 (0.01 M, 100 ml) and that of AgNO_3 (0.01 M, 100 ml). The solution was kept in an oven for an hour at 80 °C. Silica gel (10 g) was added to the mixture and stirred on a magnetic stirrer for an hour. Few drops of hydrazine were added during stirring for reduction of metal ions. Silica gel supported Mn-Ag-PVA nanocomposites were separated by Whatman filter paper and washed with metha-

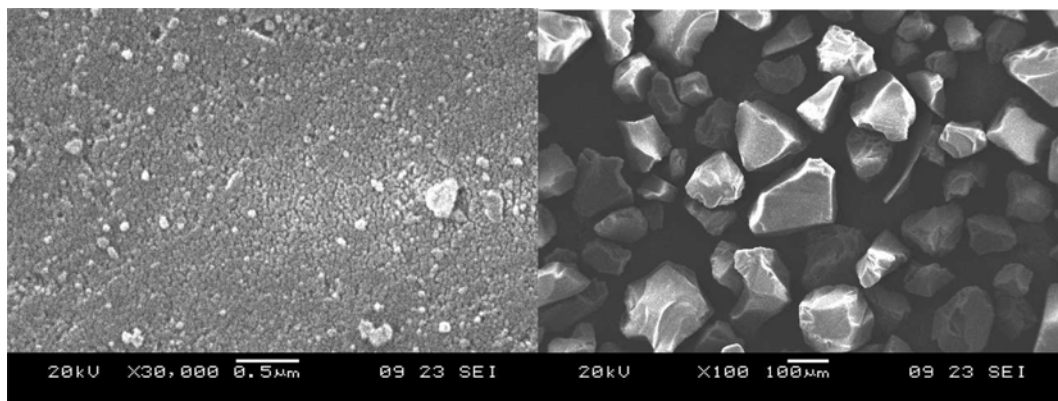


Fig. 1. SEM images of (silica-nZVI) and PVA stabilized (silica-nZVI) adsorbents.

Table 1. Synthesized adsorbents

Sr. No.	Code	Brief description
1	G.Y-2	Iron nano particles adsorbed on silica gel (using FeCl_2)
2	G.Y-3	Iron nano particles adsorbed on silica gel (using FeCl_3)
3	G.Y-4	Manganese nano particles adsorbed on silica gel
4	G.Y-5	Iron nano particles, stabilized with PVA, adsorbed on silica gel (using FeCl_2)
5	G.Y-6	Silver nano particles, stabilized with PVA, adsorbed on silica gel
6	G.Y-7	Manganese nano particles, stabilized with PVA, adsorbed on silica gel
7	G.Y-8	Iron nano particles, stabilized with PVA, adsorbed on silica gel (using FeCl_3)
8	G.Y-9	Iron and silver nano particles, stabilized with PVA, adsorbed on silica gel
9	G.Y-10	Manganese and silver nano particles, stabilized with PVA, adsorbed on silica gel

nol (25×3 ml) thrice and dried at room temperature. Similar reactions were carried out using FeCl₃ (0.01 M) and AgNO₃ (0.01 M) to prepare Fe-Ag-PVA nanocomposites and adsorbed on silica gel.

4. Determination of Arsenic Spectrophotometrically

Standard arsenic (III) stock solution was prepared by dissolving NaAsO₃ (0.1732 g) in deionized water (100 ml). Hydrochloric acid (0.4 M, 1 ml) and potassium iodate (2%, 1 ml) were added to the solution. The solution was gently shaken. Solution of variamine blue (0.05%) was prepared by dissolving variamine blue (0.05 g) in ethanol (25 ml) and making up to 100 ml with deionized water. Variamine blue (1 ml) and sodium acetate (2 M, 2 ml) were added to the solution. The absorbance of colored species was measured at 560 nm against the corresponding reagent blank [47].

Optimization of time and amount of adsorbents for maximum absorbance were calculated. Solutions of As₂O₃ (0.006 M, 0.01 M, 0.014 M, 0.018 M and 0.02 M) were prepared by following the above procedure. The solutions (25 ml) were treated with 0.6 g of synthesized adsorbents G.Y-9 and G.Y-10 one by one, by keeping it on magnetic stirrer for 30 minutes. Adsorption of arsenic was calculated by the change in molarity of the As₂O₃ solution.

Calculations were made by determining the final concentration of the solute in the solution (C_e). Amount of arsenic removed per gram by the treated silica gel was calculated. Results were analyzed for Freundlich, Langmuir and D-R adsorption isotherms (Eq. (2), (3) and (4)).

$$\ln(q_e) = \ln(K_f) + 1/n \ln(C_e) \quad (\text{Freundlich adsorption isotherm}) \quad (2)$$

$$C_e/q_e = 1/(K_L + a_L \cdot C_e/K_L) \quad (\text{Langmuir adsorption isotherm}) \quad (3)$$

The linear forms of Langmuir and Freundlich isotherm are expressed above, where K_L and a_L are Langmuir constants while K_f and n are Freundlich constants. Langmuir constants are calculated from slope and intercept when C_e is plotted against C_e/q_e, while Freundlich constants are calculated from slope and intercept when ln(C_e) is plotted against ln(q_e). The linear presentation of D-R isotherm equation is expressed by

$$\ln q_e = \ln X_m - K_{DR} \varepsilon^2 \quad (4)$$

$$\varepsilon = RT \ln [1 + 1/C_e] \quad (5)$$

where X_m is monolayer capacity of adsorbent and K_{DR} is constant related to adsorption potential. Graph is plotted between ln q_e and ε² and the values of K_{DR} and X_m are obtained from slope and intercept, respectively. The mean sorption energy is calculated by the following equation:

$$E = 1/\sqrt{2} K_{DR} \quad (6)$$

RESULTS AND DISCUSSION

Results obtained from the adsorption of arsenic on synthesized adsorbents are discussed in the following section.

1. Freundlich Isotherm

Plots of ln C_e versus ln q_e for G.Y-9 and G.Y-10 are shown in Figs. 2 and 3. The values of parameters (n and K_f) calculated from slope and intercept of these plots are listed in Table 2.

K_f refers to the adsorption capacity, while 'n' represents the inten-

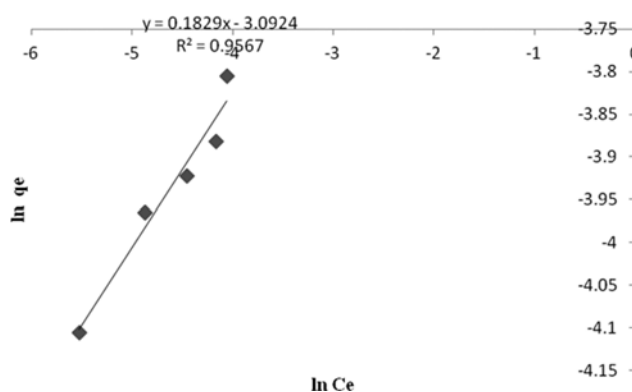


Fig. 2. Freundlich isotherm for the adsorption of As(III) on G.Y-9.

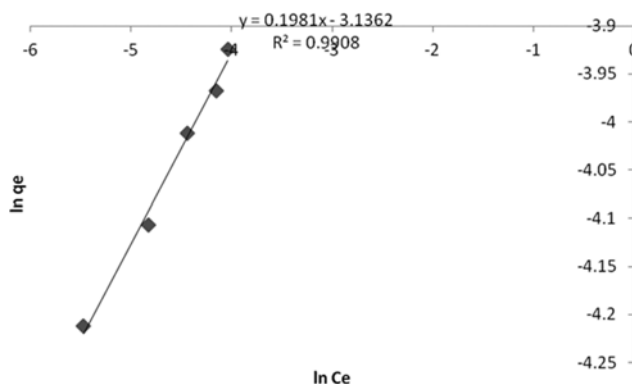


Fig. 3. Freundlich isotherm for the adsorption of As(III) on G.Y-10.

Table 2. Freundlich parameters for the adsorption of As(III) on G.Y-9 and G.Y-10

Sr. No	Adsorbents	n	K _f (mg/g)	R ²
1	G.Y-9	5.494	0.045	0.956
2	G.Y-10	5.05	0.043	0.990

sity of adsorption. It is also clear from Table 2 that the values of n for both the adsorbents are greater than unity. Higher values of n are indicative of the fact that adsorption of As(III) on these adsor-

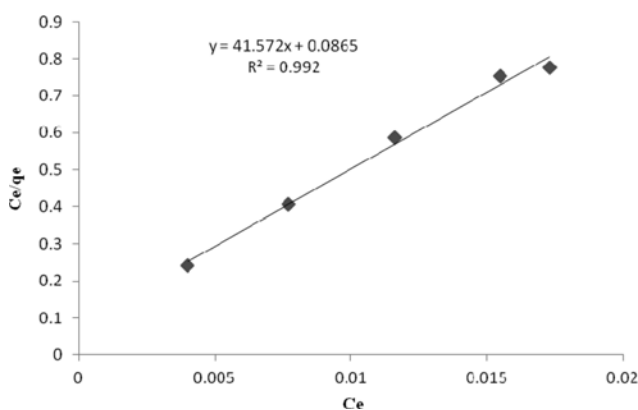


Fig. 4. Langmuir isotherm for the adsorption of As(III) on G.Y-9.

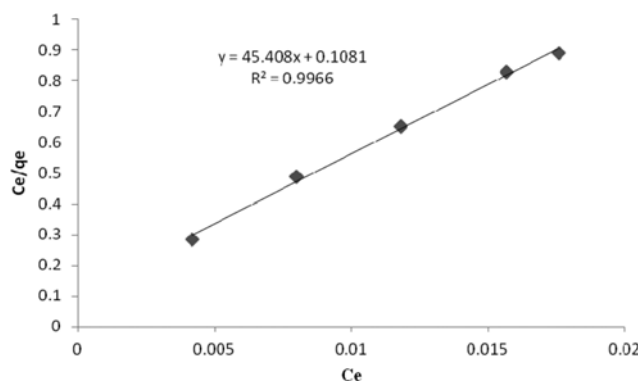


Fig. 5. Langmuir isotherm for the adsorption of As(III) on G.Y-10.

bents is favorable.

2. Langmuir Isotherm

Langmuir plots for G.Y-9 and G.Y-10 are shown in Figs. 4 and 5 and the values of parameters (K_L and a_L) are calculated from slope and intercept of these plots (Table 3).

In the Langmuir adsorption isotherm, the adsorption capacity q_m can be calculated as the inverse of slope.

$$q_m = K_L / a_L \quad (7)$$

The important characteristic of the Langmuir isotherm can be expressed in term of a dimensionless separation factor, R_L (Eq. (8))

$$R_L = 1 / (1 + K_L C_e) \quad (8)$$

3. Dubinin Radushkevich Isotherm

D-R isotherms for G.Y-9 and G.Y-10 are shown in Figs. 6 and 7. The values of K_{DR} , E and X_m are given in Table 4. The adsorption process accompanied with the energy (E) less than 8 kJ/mol was described to be of physical nature.

4. Kinetics of Adsorption

To clarify the kinetics of adsorption, pseudo-first and second-order were employed to experimental data using the linear form of rate equations (Eqs. (8) and (9)) [48].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (8)$$

where q_e and q_t (mg/g) are the amounts of As(III) adsorbed at equilibrium (mg/g) and at time t (min), respectively, and k_1 is the rate constant of the equation (min^{-1}). The adsorption rate constant k_1 can be determined experimentally by plotting $\ln(q_e - q_t)$ versus t for G.Y-9 and G.Y-10. It can be concluded from the R^2 values that the adsorption does not fit for first-order kinetic model. Experimental data were also tested for the pseudo-second-order kinetic model (Eq. (9)).

$$t/q_t = 1/k_2 q_e + t/q_e \quad (9)$$

where k_2 (g/mg min) is the rate constant of the pseudo-second-

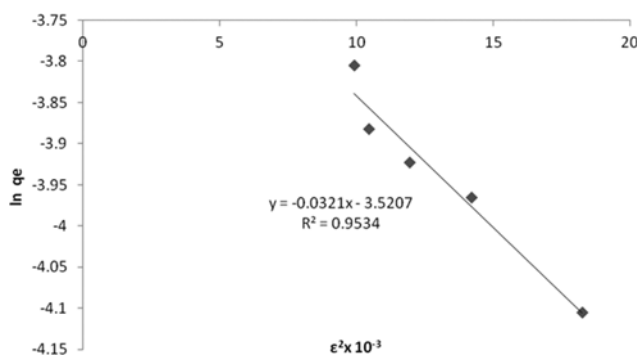


Fig. 6. Dubinin Radushkevich isotherm for the adsorption of As(III) on G.Y-9.

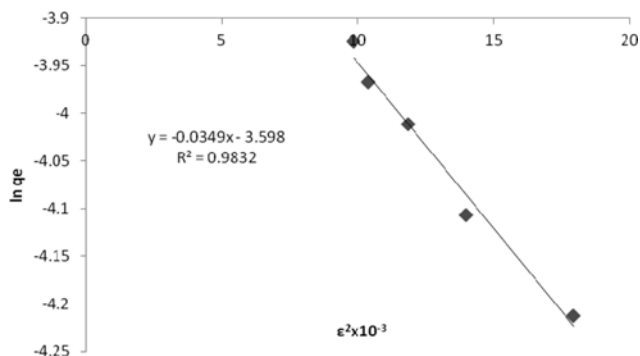


Fig. 7. Dubinin Radushkevich isotherm for the adsorption of As(III) on G.Y-10.

Table 4. Dubinin Radushkevich parameters for the adsorption of As(III) on G.Y-9, G.Y-10

Sr. No	Adsorbents	K_{DR}	X_m (mg/g)	E (kJ/mol)	R^2
1	G.Y-9	0.000032	0.0296	0.125	0.953
2	G.Y-10	0.000034	0.0274	0.121	0.983

order equation. Plots of t/q_t versus t for G.Y-9 and G.Y-10 are obtained. The experimental value of adsorption capacity q_e compares well with that of calculated from pseudo-second-order kinetic model. The value of correlation coefficients (R^2) for second order is also closer to unity as compared to first order (Table 5). Therefore, the adsorption of As(III) on the adsorbents G.Y-9 and G.Y-10 more appropriately follows the pseudo-second-order kinetic model.

5. Biological Activity

G.Y-6, G.Y-9, G.Y-10 were tested for the biological activity by agar media method.

6. Procedure

After the preparation of Agar media, it was placed in Petri-plates. Treated solutions (10 ml) of G.Y-6, G.Y-9, G.Y-10 were prepared.

Table 3. Langmuir parameters for the adsorption of As(III) on G.Y-9 and G.Y-10

Sr. No	Adsorbents	q_m (mg/g)	K_L (L/mg)	a_L (L/mg)	R_L (g/L)	R^2
1	G.Y-9	0.024	11.628	483.37	0.832 to 0.955	0.992
2	G.Y-10	0.022	9.26	420.37	0.86 to 0.962	0.996

Table 5. Kinetic parameters for the adsorption of As(III) on G.Y-9 and G.Y-10 at 298 K

Adsorbents	qe(exp) mg/g 1 st	qe(exp) mg/g 2 nd	qe(cal) mg/g 1 st	qe(cal) mg/g 2 nd	k ₁ 1 st	k ₁ 2 nd	R ² 1 st	R ² 2 nd
G.Y-9	0.135	0.112	0.007	0.098	0.021	0.186	0.671	0.948
G.Y-10	0.11	0.11	0.019	0.11	0.015	0.521	0.066	0.895

Table 6. Anti-fungal activity of G.Y-6, G.Y-9, G.Y-10 as growth rate on Agar media

Pathogens	Growth on G.Y-6 plates		Growth on G.Y-9 plates		Growth on G.Y-10 plates		Growth on controlled plates	
	Plate I	Plate II	Plate I	Plate II	Plate I	Plate II	Plate I	Plate II
<i>Candida albicans</i>	0.4 cm	0.45 cm	0.6 cm	0.6 cm	0.5 cm	0.5 cm	2.00 cm	2.00 cm
<i>Aspergillus niger</i>	0.35 cm	0.35 cm	0.55 cm	0.55 cm	0.5 cm	0.5 cm	2.00 cm	2.00 cm

About 100 μ L of each solution was poured in separate plates. Duplicate of each solution was prepared. The fungi, *Candida albicans* and *Aspergillus niger*, were added (one drop each) to each Petri-plate and kept in an incubator at 30 °C for 24 hours along with controlled plates. After 36 hours growth rates were noted for the synthesized adsorbents G.Y-6, G.Y-9, G.Y-10 (all were coated with silver nanoparticles), which showed antimicrobial activity (Table 6).

CONCLUSION

It is concluded that in just 30 minutes the synthesized adsorbents can effectively be used for the removal of As(III) from aqueous solution. Adsorption data is well described by the Langmuir model, which suggests that adsorbate molecules on the solid surface of adsorbents occur in monolayer. Positive value of 'n' in Freundlich isotherm shows that adsorption process is favorable. Mean sorption energy (less than 3 kJ/mol), calculated from DR model, indicates the physical nature of the adsorption process. Adsorption of As(III) on G.Y-9 and G.Y-10 follows pseudo-second-order kinetics, indicating that external and internal mass transfer are taking place simultaneously. Adsorbents show anti-microbial activity due the presence of silver nanoparticles. SEM images of (silica-nZVI) show the particles are dispersed homogenously throughout the gel, while the images of PVA stabilized (silica-nZVI) adsorbent show the particles are more pronounced and are in compact manner. This is the reason that PVA stabilized adsorbents are more effective for the removal of As(III) from aqueous solution.

REFERENCES

1. S. H. Lin and R. S. Juang, *J. Hazard. Mater.*, **92**, 315 (2002).
2. E. Erdem, N. Karapinar and R. Donat, *J. Colloid Interface Sci.*, **280**, 309 (2004).
3. Y. E. Yang, Y. S. Zhang, S. J. Kim and D. Y. Chung, *J. Hazard. Mater.*, **147**, 91 (2007).
4. M. P. Elizalde-Gonzalez, J. Mattusch, W. D. Einicke and R. Wennrich, *Chem. Eng. J.*, **81**, 187 (2001).
5. Y. H. Xu, T. Nakajima and A. Ohki, *J. Hazard. Mater.*, **92**(3), 275 (2002).
6. S. Maity, S. Chakravarty, S. Bhattacharjee and B. C. Roy, *Water Res.*, **39**(12), 2579 (2005).
7. B. K. Biswas, J. Inoue, K. Inoue, K. N. Ghimire, H. Harada, K. Ohto and H. Kawakita, *J. Hazard. Mater.*, **154**, 1066 (2008).
8. J. F. Ferguson and J. Davis, *Water Res.*, **6**, 1259 (1972).
9. W. R. Cullen and K. J. Reimer, *Chem. Rev.*, **89**, 713 (1989).
10. N. E. Korte and Q. Fernando, *Crit. Rev. Environ. Control.*, **21**, 1 (1991).
11. N. N. Greenwood and A. Earnshaw, *Chemistry of Elements*, Pergamon Press Oxford, Chapter 13 (1984).
12. S. K. Gupta and K. Y. Chen, *J. Water Pollut. Contr.*, **5**, 493 (1978).
13. M. M. Ghosh and J. R. Yuan, *Environ. Prog.*, **6**, 150 (1987).
14. S. Shevade and R. G. Ford, *Water Res.*, **38**, 3197 (2004).
15. R. M. Bena, H. Kazemian, M. G. Khansari, M. Hosseini and S. J. Shahtaheri, *Iran. J. Public Health*, **33**, 36 (2004).
16. D. Mohan and C. U. Pittman, *J. Hazard. Mater.*, **142**, 1 (2007).
17. C. J. Wyatt, V. L. Quiroga, R. T. O. Acosta and R. O. Mendez, *Environ. Res.*, **78**, 19 (1998).
18. M. P. Elizalde-Gonzalez, J. Mattusch and R. Wennrich, *J. Environ. Monit.*, **3**, 22 (2001).
19. S. W. Al Rmali, C. F. Harrington, M. Ayub and P. I. Haris, *J. Environ. Monit.*, **7**, 279 (2005).
20. S. Zhang, C. Liu, Z. Luan, X. Peng, H. Ren and J. Wang, *J. Hazard. Mater.*, **152**, 486 (2008).
21. E. O. Kartinen and C. J. Martin, *Desalination*, **103**, 78 (1995).
22. M. J. Bitner and J. D. Chwirka, *Proceedings of 39th New Mexico Water Conference*, Albuquerque, N.M., 251 (1994).
23. S. R. Wickramasinghe, B. Han, J. Zimbron, Z. Shen and M. N. Karim, *Desalination*, **169**, 231 (2004).
24. E. O. Kartinen and C. J. Martin, *Desalination*, **103**, 79 (1995).
25. T. Viraraghavan, K. S. Subramanian and J. A. Aruldos, *Water Sci. Technol.*, **40**, 69 (1999).
26. A. Zouboulis and I. Katsoyiannis, *Sep. Sci. Technol.*, **37**, 2859 (2002).
27. B. An, T. R. Steinwinder and D. Zhao, *Water Res.*, **39**, 4993 (2005).
28. M. M. Gholami, M. A. Mokhtari, A. Aameri and M. R. A. Fard, *Desalination*, **200**, 725 (2006).
29. M. B. Baskan and A. Pala, *J. Hazard. Mater.*, **166**, 796 (2009).
30. M. B. Baskan and A. Pala, *Desalination*, **254**, 42 (2010).
31. M. B. Baskan, A. Pala and A. Türkman, *Ekoloji*, **19**, 69 (2010).
32. K. Banerjee, G. L. Amy, M. Prevost, S. Nour, M. Jekel, P. M. Gallagher and C. D. Blumenschein, *Water Res.*, **42**, 3371 (2008).
33. S. Tiwari, B. K. Sarangi and R. A. Pandey, *Environ. Eng. Res.*, **19**(2), 145 (2014).

34. D. Ranjan, M. Talat and S. H. Hasan, *J. Hazard. Mater.*, **166**, 1050 (2009).
35. P. B. Bhakat, A. K. Gupta, S. Ayoob and S. Kundu, *Colloids Surf. A*, **281**, 237 (2006).
36. R. M. Thiyab and H. K. Abdul Hussein, *J. Kerbala Univ.*, **7**(1), 210 (2009).
37. H. L. Lien and R. T. Wilkin, *Chemosphere*, **59**, 377 (2005).
38. M. J. Yu, X. Li and W. S. Ahn, *Micropor. Mesopor. Mater.*, **113**, 197 (2008).
39. Y. Kim, C. Kim, I. Choi, S. Rengaraj and J. Yi, *Environ. Sci. Technol.*, **38**, 924 (2004).
40. D. Borah, S. Satokawa, S. Kato and T. Kojima, *J. Hazard. Mater.*, **162**, 1269 (2009).
41. F. O. Okeola and E. O. Odebunmi, *Adv. Natural Appl. Sci.*, **4**(3), 281 (2010).
42. A. K. Mishra and S. Ramaprabhu, *Desalination*, **282**, 39 (2011).
43. V. Chandra, J. Park, Y. Chun, J. W. Lee, I. Hwang and K. S. Kim, *ACS Nano*, **4**(7), 3979 (2010).
44. Y. J. Park, J. K. Yang, H. J. Choi and S. M. Lee, *Environ. Eng. Res.*, **17**(S1), S15 (2012).
45. D. Tiwari, C. Laldawngliana and S. M. Lee, *Environ. Eng. Res.*, **19**(1), 107 (2014).
46. S. S. Waghmare, A. M. Deshmukh, S. W. Kulkarni and L. A. Oswaldo, *Univ. J. Environ. Res. Technol.*, **1**, 64 (2011).
47. B. Narayana, T. Cherian, M. Mathew and C. Pasha, *Ind. J. Chem. Technol.*, **13**, 36 (2006).
48. M. E. Argun, S. Dursun, C. Ozdemir and M. Karatas, *J. Hazard. Mater.*, **141**(1), 77 (2007).