



Studies on the removal of arsenic (III) from water by a novel hybrid material

Sandip Mandal, T. Padhi, R.K. Patel*

Department of Chemistry, NIT, Rourkela 769008, India

ARTICLE INFO

Article history:

Received 31 January 2011
Received in revised form 10 May 2011
Accepted 31 May 2011
Available online 6 June 2011

Keywords:

Arsenic
Hybrid material
BET
Isotherms
AAS

ABSTRACT

The present work provides a method for removal of the arsenic (III) from water. An ion-exchanger hybrid material zirconium (IV) oxide-ethanolamine (ZrO-EA) is synthesized and characterized which is subsequently used for the removal of selective arsenic (III) from water containing 10, 50, 100 mg/L of arsenic (III) solution. The probable practical application for arsenic removal from water by this material has also been studied. The various parameters affecting the removal process like initial concentration of As (III), adsorbent dose, contact time, temperature, ionic strength, and pH are investigated. From the data of results, it is indicated that, the adsorbent dose of 0.7 mg/L, contact time 50 min after which the adsorption process comes to equilibrium, temperature (25 ± 2) , solution pH (5–7), which are the optimum conditions for adsorption. The typical adsorption isotherms are calculated to know the suitability of the process. The column studies showed 98% recovery of arsenic from water especially at low concentration of arsenic in water samples.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Arsenic in different form is found in all segment of the environment. The occurrence of arsenic in the environment, its toxicity, health hazards, and the techniques used for speciation analysis are well documented in literature [1]. Arsenic and its compounds are considered as highly toxic substances. The compounds of arsenic are generated from pesticides, dyes and drugs industries, glassware production industries etc. Relatively high concentration of arsenic in the aquatic system has many implications on health of humans, animals, and plants. Drinking of arsenic contaminated water for long periods of time causes cancers in skin, lung, urinary bladder, and kidney. It also causes changes in pigmentation of skin, skin thickening (hyperkeratosis), neurological disorders, muscular weakness, loss of appetite, and nausea. Acute poisoning by arsenic typically causes vomiting, abdominal pain, and bloody "rice water" diarrhoea, arsenic in natural water is a worldwide problem [2]. Arsenic pollution has been reported recently in USA, China, Chile, Bangladesh, Taiwan, Mexico, Argentina, Poland, Canada, Hungary, New Zealand, Japan, and India. Because of these health effects, World Health Organization (WHO) established a guideline of 0.01 mg/L as the maximum permissible arsenic content in potable water [3]. Concentrations of arsenic in tailings of mines may be up to 200 mg/L. Considerable efforts are being made to eliminate arsenic from wastewater. There are few reported methods for removal of arsenic from water like chemical precipitation, oxida-

tion, reverse osmosis, ion exchange, membrane filtration, froth flotation, solvent extraction, and adsorption, but none of them is widely accepted because of cost or maintenance of the process [4].

2. Experimental

2.1. Reagents and chemicals

All chemicals used for this study are of Analytical grade and are obtained from Merck. The measuring cylinder, volumetric flask and conical flask and other glassware used are of borosil and tarson. Zirconium oxychloride octahydrate (CDH, India), ethanolamines (E. Merck) are used for the synthesis of the hybrid material. Standard solution of arsenic (III) is prepared from sodium arsenite (NaAsO_2), and suprapure HCl (30%, v/v) (E. Merck) is also used, pH meter (ElicoLI 612, India) is used for measurement of pH. AAS (Perkin Elmer PE analyst Atomic Absorption Spectrometer) is used for the determination of the concentration of arsenic (III). BET (Quantachrome Autosorb I), XRD (Shimadzu XRD-6000 diffractometer), SEM (JEOL JSM-6480LV scanning electron microscope), and FTIR (Shimadzu IR Prestige-21 FTIR instrument) are used for the characterization of the material before and after adsorption, TGA-DTA (Shimadzu TGA 60H) used for thermal analysis, Particle size analyzer (Malvern Nano ZS 90).

2.2. Synthesis of the hybrid material

The synthesis of zirconium (IV) oxide-ethanolamine (ZrO-EA) hybrid material is prepared by using a 0.1 M aqueous solution of zirconium oxychloride, which is mixed with a 0.1 M aqueous solution of ethanolamine in different volume ratios (v/v) at pH 3–10

* Corresponding author. Tel.: +91 943745438; fax: +91 661 2462651.

E-mail addresses: sandipmandal9@gmail.com (S. Mandal), rkpatel@nitrkl.ac.in (R.K. Patel).

Table 1
Synthesis of various samples of zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material.

Sample composition no.	Zirconium oxychloride solution (M)	Ethanolamine solution (M)
Composition 1	0.1	0.2
Composition 2	0.3	0.6
Composition 3	0.4	0.8
Composition 4	0.5	1.0
Composition 5	0.6	1.2

(Table 1). The pH of the solution is adjusted using 0.1 M HCl/NaOH solution. The white colored gel so obtained is allowed to stand for 24 h at room temperature for complete precipitation. The gel is separated from the mother liquor by decantation and washed with distilled water several times to ensure a pH 7 of the effluent wash. The material is then dried at 50 °C in an oven for 24 h and it is collected in granular form with shiny appearance. A preliminary investigation is done with 10 mg/L arsenic (III) solution with fixed quantity of adsorbent, at pH 7 and ambient temperature (25 °C) of the medium to know the arsenic (III) removal capacity of the material zirconium (IV) oxide-ethanolamine (ZrO-EA). The material prepared with 0.8 M solution of ethanolamine showed comparatively better results, which is selected for further detail studies.

2.3. Characterization of zirconium (IV) oxide-ethanolamine hybrid material

These samples are characterized by FTIR, SEM, XRD, and CHN elemental analysis.

2.4. Batch experiments

The arsenite sorption experiments from its aqueous solution by zirconium (IV) oxide-ethanolamine (ZrO-EA) is carried out using standard 10 mg/L, 50 mg/L, and 100 mg/L As (III) solution in absence of other competing ions. The adsorption experiments are carried out in a series of 250 mL glass conical flask with stopper by adding 0.1–1.0 g of zirconium (IV) oxide-ethanolamine in 100 mL of arsenic (III) solution. Stoppers are provided to avoid change in concentration due to evaporation. All the adsorption experiments are carried out at ambient temperature (25 ± 2 °C). After continuous stirring, over magnetic stirrer at about 400 rpm for a predetermined time interval, the solid is separated by filtration through Whatman-42 filter paper. The remaining As (III) concentration is determined by AAS (Perkin Elmer PE Analyst Atomic Absorption Spectrometer). All the sample and standards are maintained at same temperature to avoid interference due to difference in temperature. pH of the solution is maintained by the addition of required amount of 0.1 M NaOH or 0.1 M HCl. The variable parameters such as contact time, pH, affecting the removal of arsenic (III) ion have been varied widely in order to optimize the adsorption process. In order to know the effect of other competing ions on arsenic sorption, study of the effect of anions like sulfate, nitrate, chloride, carbonate, and bicarbonate ions. Standard solutions are prepared from the corresponding salts solutions. The experimental condition for initial arsenite concentration is kept at 10 mg/L.

3. Results and discussion

3.1. Characterization of zirconium (IV) oxide-ethanolamine hybrid material

The present study is an attempt to explore the synthesis of zirconium (IV) oxide-ethanolamine (ZrO-EA) hybrid mate-

Table 2
Chemical stability of ZrO-EA hybrid material in various acid, alkali, and salt solutions.

Solvent (20 mL)	Amount dissolved ZrO-EA (mg)
1 M HCl	0.21
2 M HCl	0.38
4 M HCl	0.86
1 M HNO ₃	0.65
2 M HNO ₃	1.21
4 M HNO ₃	1.49
1 M H ₂ SO ₄	Completely
2 M H ₂ SO ₄	Completely
4 M H ₂ SO ₄	Completely
1 M NaOH	0.45
2 M NaOH	0.84
4 M NaOH	1.23
1 M KOH	1.23
2 M KOH	1.48
4 M KOH	1.86
1 M NH ₄ OH	1.24
2 M NH ₄ OH	Completely
4 M NH ₄ OH	Completely
2 M NaNO ₃	0.04
2 M KNO ₃	0.09

rial and its application for the removal of arsenic (III) from synthetic solution. A number of samples of zirconium (IV) oxide-ethanolamine are prepared by adding different molar solution of ethanolamine (0.1–1.0 M) and their arsenic (III) ion exchange capacity is determined by batch experiments. The anion exchange capacity of the hybrid material depends on the concentration of ethanolamine. The anion exchange capacity is found to be maximum when the hybrid material is prepared with 0.8 M solution of ethanolamine. Ethanolamine is toxic in nature but not carcinogenic [5]. Ethanolamine is stable with zirconium oxychloride because it forms a polymeric matrix, which is supported by the chemical stability as shown in Table 2. Zirconium oxychloride cannot be used alone. The material reported here is having a high surface area as compare to zirconium oxychloride alone. The advantages of using ZrO-EA hybrid material are: (1) it has high adsorption capacity, (2) highly stable, and (3) the whole reaction process is feasible in room temperature. So, the zirconium (IV) oxide-ethanolamine hybrid material prepared with 0.8 M ethanolamine is used for further studies. The material is obtained in the form of granular with shiny appearance. The particle size of the hybrid material was analyzed and it is found to be 160 nm (Fig. 1). The thermal stability of the material is found to be very high, which may be due to its hybrid nature, which is supported by TGA-DTA (Fig. 2). The thermogravimetric analysis (TGA) curve shows rapid weight loss up to a temperature 550 °C. However, on increasing the temperature, a sharp deflection in the TGA curve was noticed at 200–280 °C, which is attributed to the decomposition of organic molecule present in the matrix at higher temperature. Correlating the data with differential thermal analysis (DTA), an exotherm was also noticed at the same temperature, that is, at 158.86 °C, which further supported the stability. An endothermic peak noticed at 100 °C in the DTA

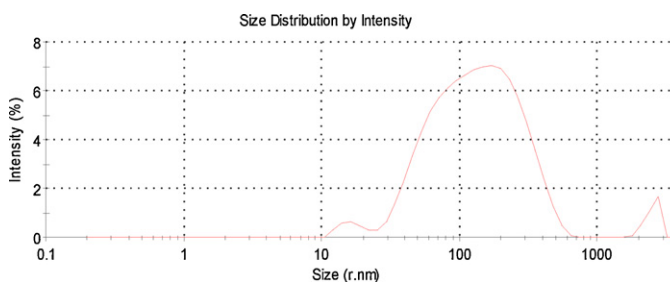


Fig. 1. Particle size analysis of ZrO-EA hybrid material.

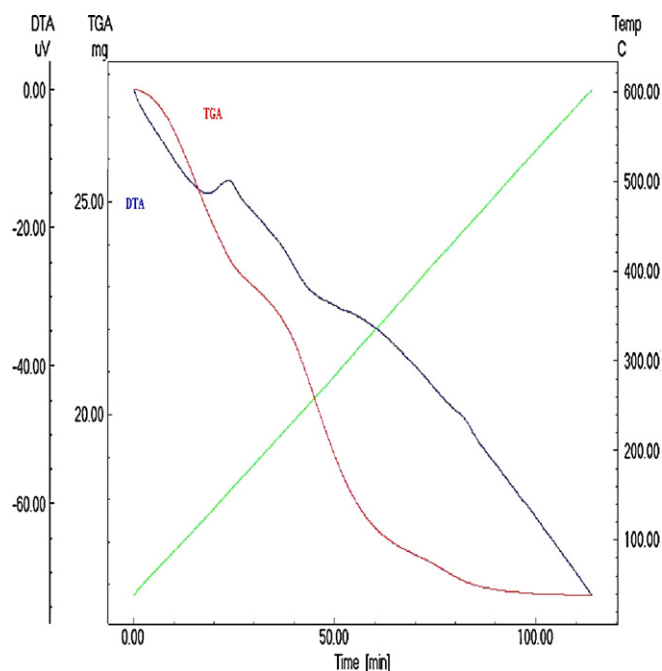


Fig. 2. Differential thermal analysis and thermogravimetric analysis of ZrO-EA hybrid material up to 650 °C.

Table 3
Effect of concentration of eluent on ion exchange capacity of arsenic (III) ion.

Concentration of eluent (M)	As (III) ion exchange capacity (Mequiv./g(dry))
0.2	0.98
0.4	1.67
0.6	2.34
0.8	3.41
1.0	4.23
1.2	4.23
1.4	4.23

curve indicates the loss of water molecules present as free/bonded form in the core of the matrix. From the TGA and DTA analysis it is confirmed that the material is stable even after 550 °C. Thermogravimetric analysis, therefore, strongly indicates that the organic molecule ethanolamine could be present in the matrix or it may also remain adsorbed on the surface of the material. In order to know the chemical stability, the material was kept in 20 mL of different mineral acids, bases, and salt solutions of different concentration for 24 h and the supernatant liquid was analyzed for zirconium and ethanolamine (Table 2). The material exhibits high chemical stability, and was found that the material was quite stable in most of the mineral acids and salt solutions.

The extent of elution is found to depend on the concentration of eluent. Arsenic ion exchange capacity for different eluent concentration is studied at ambient temperature and represented in Table 3. The optimum concentration of the eluent is found to be 1.0 M for arsenic (III) ion. The minimum volume required to complete the elution is found to be 120 mL. On the basis of the chemical analysis (Table 4) and elemental analysis (Table 5) of

Table 4
Results of chemical analysis of zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material.

Elements/ions/compounds	Weight	Number of moles	Molar ratio
Zirconium oxychloride octahydrate	0.1277	0.866×10^{-3}	1
Ethanolamine	0.3225	1.2702×10^{-3}	3

Table 5
Results of CHN analysis of zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material.

Elements	Percentage (%)
Carbon	31.90
Hydrogen	8.56
Oxygen	10.44
Nitrogen	8.10
Others	41

zirconium (IV) oxide-ethanolamine (ZrO-EA) hybrid material, the number of moles of zirconium, and ethanolamine are found to be 0.866×10^{-3} , 1.2702×10^{-3} , respectively. The molar ratio of zirconium and ethanolamine is calculated and found to be ratio 1:3 so, from the above discussion, the tentative empirical formula for the material can be suggested as $[(ZrOCl_2)(C_2H_7NO)_3] \cdot nH_2O$.

The value of n was found to be 6.414 using Alberti equation [6,7]

$$18n = \frac{X(M + 18n)}{100} \quad (i)$$

Scanning electron micrographs of the sample is presented in Fig. 3. It is evident from the SEM micrograph (a) before adsorption and (b) after adsorption, that the material is porous in nature and adsorbed arsenic (III) ion in the surface of the hybrid material. The XRD pattern of the sample is presented in Fig. 4. No specific peaks are obtained indicating that the sample is poorly crystalline. XRD is analyzed using software, but a very low intensity peak of zirconium oxide is found. The XRD structure shows that the crystal system is anorthic, 2 theta peak obtained at 10.159° with d-spacing 8.7000 the density is 2.95 and volume of the cell is 338.47, the h,k,l values are 0,0,1 it is supported by the JCPDES file number 24-14 94. BET surface area is obtained to know the specific surface area and is found to be $201.62 \text{ m}^2/\text{g}$. FTIR study of the sample was carried out (Fig. 5) in order to know the presence of different groups and probable structures of the material. The presence of band at 3593.31 cm^{-1} is due to $-OH$ group, which indicates the presence of water of crystallization. Further, the presence of a peak at 1621.57 cm^{-1} in ZrO-EA is due to the $-NH$ bending vibration band. This peak is found to be shifted with slight broadening after adsorption, which is an indication of bonding between the protonated nitrogen and the arsenite. The peak at 733.16 cm^{-1} in ZrO-EA is assigned to metal-oxygen bonding. After adsorption shift of this peak is noticed with decreased intensity indicates the arsenic adsorption. From the spectral and other studies it indicates that the material have a probable structure, which is represented in Fig. 6.

3.2. Removal study of arsenic (III) ion

All the experiments are done in batch mode.

3.2.1. Effect of adsorbent dose

The effect of adsorbent dose on the removal of arsenic (III) is studied in neutral condition (pH 7), at ambient temperature ($25 \pm 2^\circ\text{C}$) and contact time of 30 min for initial arsenic (III) concentration of 10 mg/L, 50 mg/L, and 100 mg/L. The results are presented in Fig. 7. It is evident from Fig. 7 that the removal of arsenic (III) increases from 88.89% to 99.90%, 88.22% to 98.25% and 87.12% to 98.16% for 0.1–1.0 g/100 mL of zirconium (IV) oxide-ethanolamine (ZrO-EA) hybrid material respectively with initial arsenic (III) concentration of 10 mg/L, 50 mg/L, and 100 mg/L. It is observed that after dosage of 0.7 mg/100 mL, there is no significant change in percentage of removal of arsenic (III). It may be due to the overlapping of active sites at higher dosage. Therefore, due to the conglomeration of exchanger particles there is no any appreciable increase in the effective surface area. So, 0.7 mg/100 mL is considered the optimum dose and is used for further study. The maximum removal

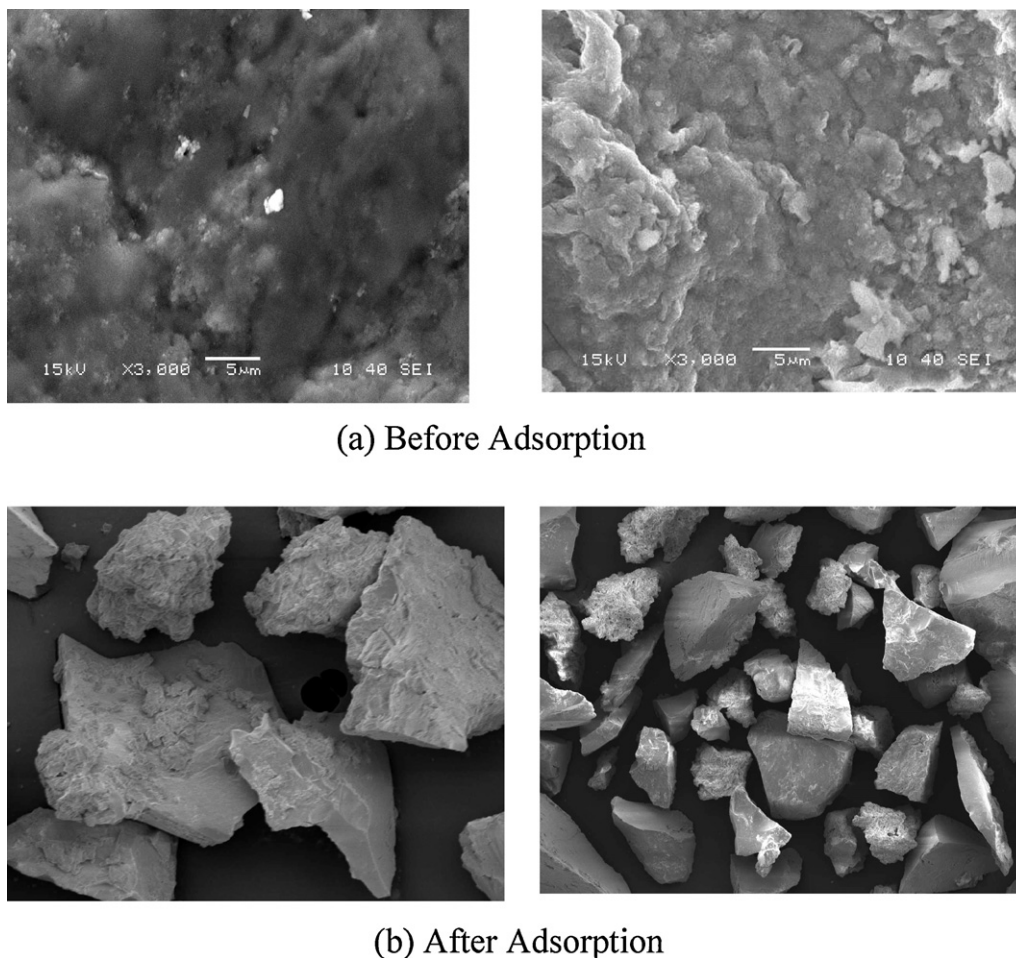


Fig. 3. SEM micrographs of zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material. (a) Before adsorption and (b) after adsorption.

of arsenic (III) is found to be about 98% in average and hence the removal process is effective to bring the concentration of arsenic (III) very close to Indian permissible limit IS:10,500 (50 ppb).

3.2.2. Effect of pH

Percentage removal of arsenic (III) at different pH is studied in batch experiments using 0.7 mg of adsorbent in 100 mL synthetic solution, at ambient temperature ($25 \pm 2^\circ\text{C}$), contact time of

30 min for initial arsenic (III) concentration of 10 mg/L, 50 mg/L, and 100 mg/L. The results are presented in Fig. 8. The pH of the solution after adsorption is measured and is found to increase or decrease slightly without any regular trend (Table 6). It is evident from the graph that there is no removability at pH lower than 2 and almost 98.98% removal was achieved at pH higher than 7 but below 9. This decrease of arsenic (III) uptake at alkaline pH could be mainly due to two factors; the electrostatic repulsion of arsenic (III) ion to the negatively charged surface of the zirconium (IV) oxide-ethanolamine (ZrO-EA) hybrid material and the competition for active sites by excessive amount of hydroxyl ions.

3.2.3. Effect of contact times

Adsorption of arsenic (III) at different contact time is studied for initial arsenic (III) concentration of 10 mg/L, 50 mg/L, and 100 mg/L at pH 7 keeping all other parameters constant. The result is represented in Fig. 9. It is clear from Fig. 9 that more than 95% removal takes place within 10 min and equilibrium is reached after 50 min. The change in the rate of removal might be due to the fact that initially all adsorbent sites are vacant and also the solute concentration gradient is high. Later the arsenic (III) uptake rate by adsorbent is decreased significantly, due to the decrease in the number of adsorption sites as well as arsenic (III) concentration. Decreased arsenic removal rate, particularly, towards the end of experiments, indicates the possible monolayer formation of arsenic (III) ion on the outer surface.

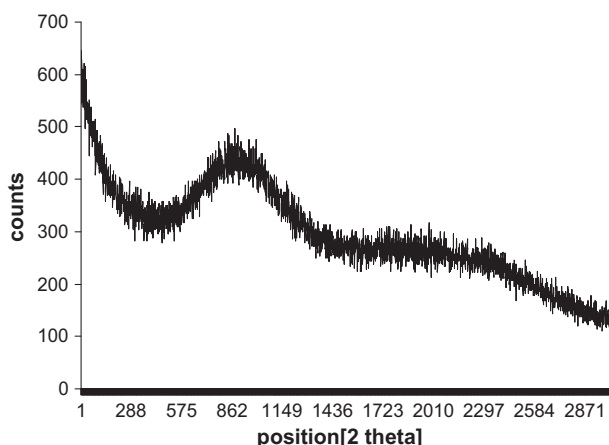


Fig. 4. XRD pattern of zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material.

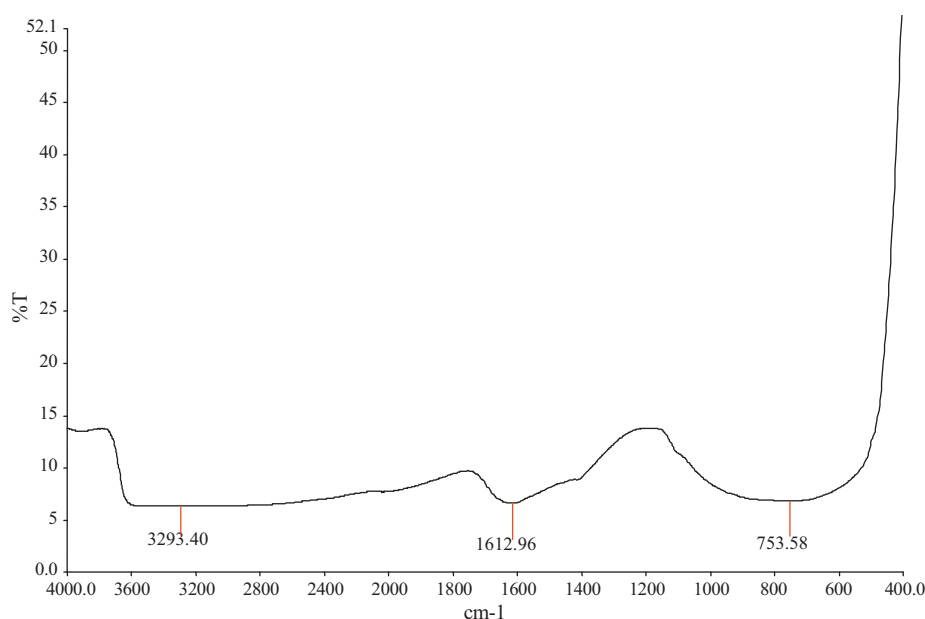


Fig. 5. FTIR spectrum of zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material.

Table 6

Change in pH during the removal process.

Initial concentration of 10 mg/L		Initial concentration of 50 mg/L		Initial concentration of 100 mg/L	
Initial pH	Final pH	Initial pH	Final pH	Initial pH	Final pH
2.0	2.0	2.4	2.4	1.8	1.8
3.8	3.21	2.7	3.8	2.2	2.6
4.52	5.63	3.5	4.8	4.8	5.2
6.5	7.2	5.6	7.1	6.8	8.2
8.2	9.4	7.8	9.12	8.9	10.2
10.12	11.23	10.6	11.5	10.6	11.4

3.2.4. Adsorption kinetics

Adsorption of arsenic (III) ion is rapid for the first 10 min and its rate slowed down as it approaches towards equilibrium. The rate constant K_{ad} for sorption of arsenic (III) is studied by Lagergren

rate equation [8,9] for initial concentration of 10 mg/L, 50 mg/L, and 100 mg/L by the following equation

$$\log (q_e - q) = \log q_e - K_{ad} \left(\frac{t}{2.303} \right) \quad (ii)$$

where q_e and q (both in mg/g) are the amounts of arsenic (III) adsorbed at equilibrium and at time t , respectively, the plots of $\log (q_e - q)$ versus t at different time interval is almost linear, which indicates the validity of Lagergren rate equation of first order kinetics. The adsorption rate constant (K_{ad}), is calculated from the slope and shown in Fig. 10. The adsorption rate constant (K_{ad}), calculated from the slope of the above plot is presented in Table 7.

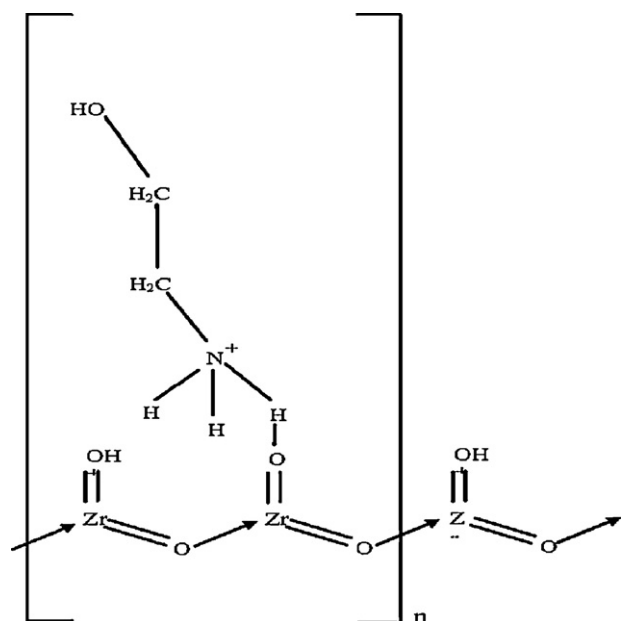


Fig. 6. Structure of zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material.

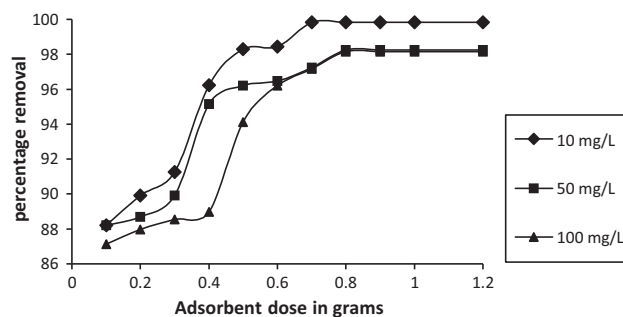


Fig. 7. Adsorbent dose versus percentage removal of arsenic (III) with initial concentration of 10 mg/L, 50 mg/L, and 100 mg/L.

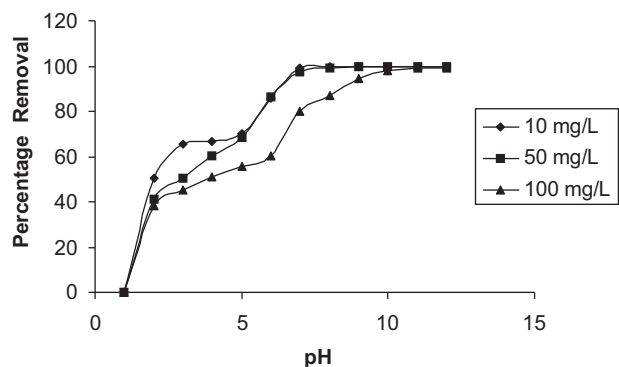


Fig. 8. Percentage removal of arsenic (III) of initial concentration of 10 mg/L, 50 mg/L, and 100 mg/L versus pH of the synthetic solution.

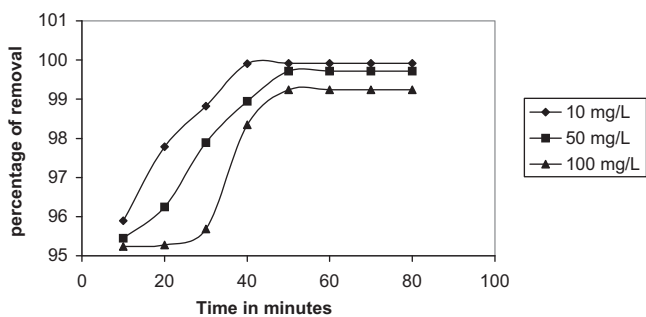


Fig. 9. Time versus percentage removal of arsenic (III) with initial concentration of 10 mg/L, 50 mg/L, and 100 mg/L.

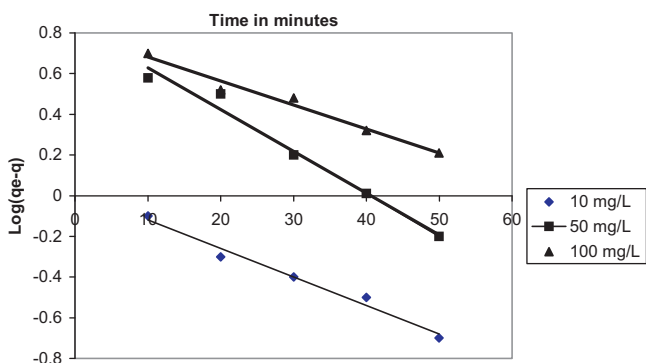


Fig. 10. Adsorption kinetics, time versus $\log(q_e - q)$ with initial arsenic (III) concentration of 10 mg/L, 50 mg/L, and 100 mg/L.

3.2.5. Effect of temperature

The effect of temperature on the adsorption of arsenic (III) with initial concentration 10 mg/L, 50 mg/L, and 100 mg/L is studied using optimum adsorbent dose (0.7 mg/100 mL). The results are represented as percentage removal of arsenic (III) versus temperature (Fig. 11). The percentage removal of arsenic (III) with initial concentration 10 mg/L increased from 84.99% to 99.83%, for 50 mg/L increased from 88.56% to 99.90% and for 100 mg/L increased from 89.90% to 99.92% for 25–45 °C temperature, respectively. It can be clearly seen from Fig. 11 that, at the temperature of 25 °C the

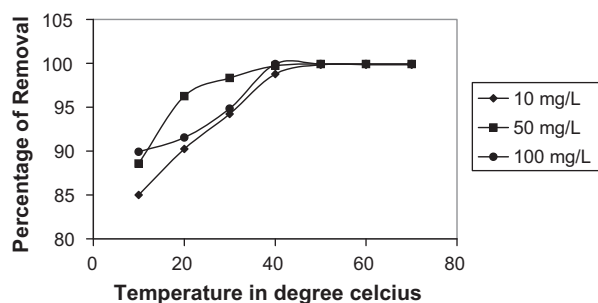


Fig. 11. Temperature versus percentage removal of arsenic (III) with initial concentration of 10 mg/L, 50 mg/L, and 100 mg/L.

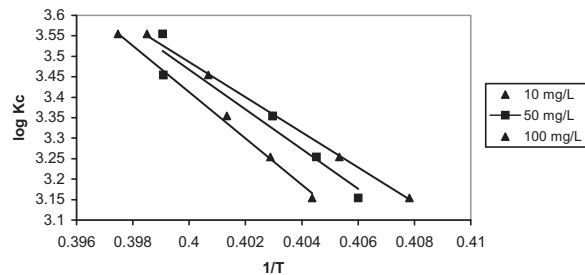


Fig. 12. Van't Hoff plots, $\log K_C$ versus $1/T$.

removal was almost 95%, and with increase in temperature the percentage removal increase slowly and reached almost 99.82%. The continuous increase in percentage removal indicated that the adsorption is endothermic in nature.

Further, it is supported by the value of thermodynamic parameters. The change in free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of adsorption are calculated by using the following equations [10,11]:

$$\log K_C = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (\text{iii})$$

$$\Delta G = \Delta H - T(\Delta S) \quad (\text{iv})$$

where ΔS and ΔH are the changes in entropy and enthalpy of adsorption respectively.

A plot of $\log K_C$ versus $1/T$ for initial arsenic (III) concentration of 10 mg/L, 50 mg/L, and 100 mg/L is found to be linear (Fig. 12). The K_C Value is calculated by using the following equation [11,12]

$$K_C = \frac{C_1}{C_2} \quad (\text{v})$$

where C_1 is the amount of arsenic (III) ion adsorbed per unit mass of adsorbent and C_2 is the concentration in aqueous phase. Values of ΔH and ΔS are calculated from slope and intercept of Van't Hoff Plot represented in Table 8. The positive value of entropy (ΔS) indicates the increase in randomness of the ongoing process and hence good affinity of arsenic (III) with the hybrid material. Negative value of ΔG at each temperature indicates the feasibility and spontaneity of ongoing adsorption. A decrease in values of ΔG with increase in temperature suggests more adsorption of arsenic (III) at higher temperature, which indicates the endothermic nature of the process. It is once again confirmed by the positive value of enthalpy

Table 7
Rate constants (K_{ad}) obtained from the graph for different initial concentration.

Initial concentration (mg/L)	Slope	Intercept	Rate constant (K_{ad})	Correlation coefficient (R^2)
10	-0.0145	0.021	0.023862	0.98102
50	-0.0208	0.844	0.028452	0.97266
100	-0.0118	0.832	0.014561	0.97561

Table 8
Thermodynamic parameters using synthetic arsenic (III) solution of 10 mg/L, 50 mg/L, and 100 mg/L.

Initial arsenic (III) concentration (mg/L)	ΔH (kJ mol ⁻¹)	ΔS (kJ/K mol)	ΔG (kJ mol ⁻¹)					R^2
			10 °C	20 °C	30 °C	40 °C	50 °C	
10	0.0536	7.264	-17.759	-17.869	-17.975	-18.077	-18.176	0.9993
50	0.0430	7.405	-18.264	-18.264	-18.330	-18.510	-19.268	0.9357
100	0.0404	7.705	-19.014	-19.084	-19.158	-19.266	-19.345	0.9943

(ΔH). Positive value of enthalpy (ΔH) suggests that entropy is responsible for making ΔG value negative. So, the adsorption process is spontaneous since the entropy contribution is much larger than that of enthalpy.

3.2.6. Effect of initial arsenic (III) concentration

The adsorption of arsenic (III) onto hybrid material is studied by varying initial arsenic (III) concentration using optimum adsorbent dose (0.7 mg/100 mL) at ambient temperature (25 ± 2 °C) and contact time of 30 min. The results are represented in graphical form as percentage removal versus initial arsenic (III) concentration in Fig. 13. The initial arsenic (III) concentration is increased from 10 mg/L to 100 mg/L and the corresponding removal gradually increases from 99.52% to 99.92%. It is clear from Fig. 13, that there is an increase in removal percentage with increase in initial arsenic (III) concentration, due to the fact that at higher adsorbate concentration, the free sites available approaches saturation. From the above data, it is clear that the removal method can be implemented to remove arsenic (III) from water present in any concentration.

3.2.7. Adsorption isotherm

The adsorption data are fitted to linearly transformed Langmuir isotherm. The linearized Langmuir equation, which is valid for monolayer sorption onto a surface with finite number of identical sites, is given by [13,14] the following equation

$$\frac{1}{q_e} = \frac{1}{q_0 b C_e} + \frac{1}{q_0} \quad (\text{vi})$$

where q_0 is the maximum amount of the arsenic (III) ion adsorbed to the hybrid material to form a complete monolayer on the surface, (adsorption capacity), C_e denotes equilibrium adsorbate concentration in solution, and q_e is the amount adsorbed per unit mass of adsorbent, and b is the binding energy constant. The linear plot of $1/C_e$ versus $1/q_e$ (Fig. 14) with $R^2 = 0.972$ indicates the applicability of Langmuir adsorption isotherm. The values of Langmuir parameters, q_0 and b were 0.250019952 mg/g and 0.035717136 L/mg, respectively. In order to predict the adsorption efficiency of the

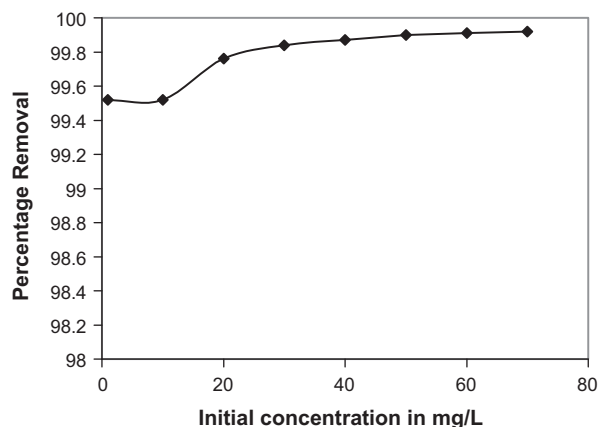


Fig. 13. Initial arsenic concentration versus percentage removal.

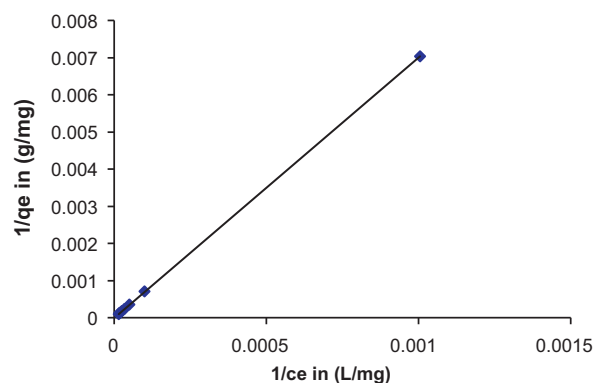


Fig. 14. Langmuir adsorption isotherm, $1/C_e$ versus $1/q_e$.

adsorption process, the dimensionless equilibrium parameter is determined by using the following equation [15,16]

$$r = \frac{1}{1 + bC_0} \quad (\text{vii})$$

where C_0 is the initial concentration, values of $r < 1$ represent favorable adsorption and the r -values for initial concentration of 10 mg/L, 50 mg/L, and 100 mg/L are found to be 0.965515, 0.8715, and 0.7212, respectively. These values indicated a favorable system. It is known that the Langmuir adsorption isotherm constants do not give any idea about the adsorption mechanism. In order to understand the adsorption type, equilibrium data were tested with Dubinin–Radushkevich isotherm [12].

The linearized D–R equation can be written as

$$\ln q_e = \ln q_m - K\varepsilon^2 \quad (\text{viii})$$

where ε is Polanyi potential, and is equal to $RT \ln(1 + 1/C_e)$, where q_e is the amount of arsenic (III) adsorbed per unit mass of adsorbent, q_m is the theoretical adsorption capacity, C_e is the equilibrium concentration of arsenic (III), K is the constant related to adsorption energy, R is the universal gas constant and T is the temperature in Kelvin. The plot of $\ln q_e$ against ε^2 shown in Fig. 15, is almost linear

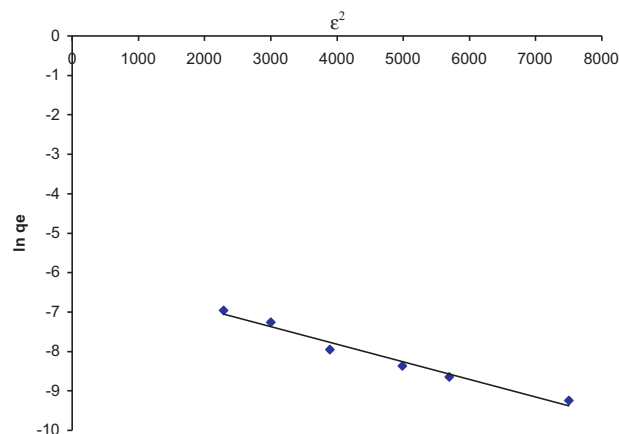


Fig. 15. D–R adsorption isotherm, $\ln q_e$ versus ε^2 .

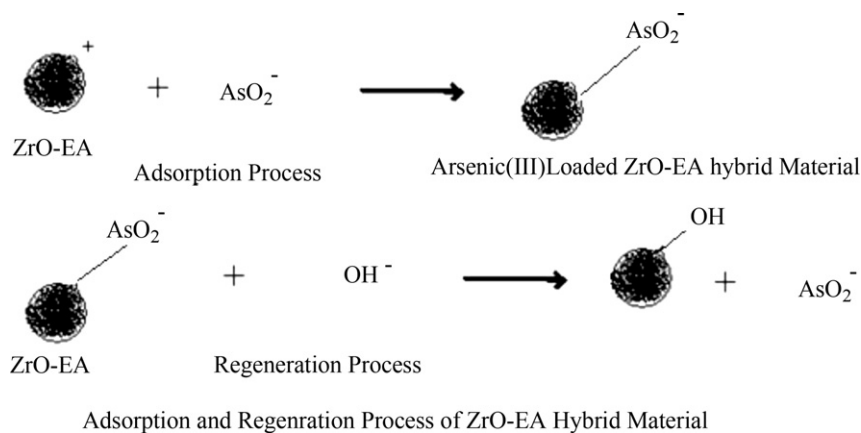


Fig. 16. Adsorption and regeneration mechanism.

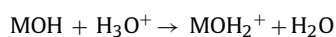
with correlation coefficient, $R^2 = 0.972$. D–R isotherm constants K and q_m are calculated from the slope and intercept of the slope of the plot, respectively. The value of K is found to be 2.0479×10^{-3} and that of q_m is 0.09813. The mean free energy of adsorption (E) was calculated from the constant K using the relation [12]

$$E = (-2k)^{-1/2} \quad (\text{ix})$$

It is defined as the free energy change when one mole of ion is transferred to the surface of the solid from infinity in the solution. The value of E is found to be $49.43 \text{ kJ mol}^{-1}$. The value of E is very useful in predicting the type of adsorption and if the value is less than 8 kJ mol^{-1} then the adsorption is physical in nature and if it is in between 8 and 16 kJ mol^{-1} , then the adsorption is chemisorptions or due to exchange of ions [12]. In the present study the value is found to be much higher than 16 kJ mol^{-1} . This indicates that the adsorption arsenic (III) may also be controlled by ion exchange (chemical interaction) with amine present in the hybrid material in addition to electrostatic attraction and hydrogen bonding.

3.3. Mechanism of adsorption of arsenic (III) on ZrO-EA hybrid material

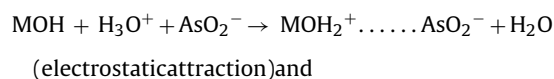
The mechanism of any adsorption process is an important component in understanding the process as well as to know the characteristics of the material, which help to design a new adsorbent for future applications (Fig. 16). A mechanism for the adsorption of arsenic (III) by ion-exchanger hybrid material zirconium (IV) oxide-ethanolamine (ZrO-EA) has been proposed by taking the results obtained from the experimental investigations and computing the results using mathematical/theoretical models. At lower pH of the medium, surface sites are positively charged and, therefore, attract negatively charged arsenite by an electrostatic interaction process. The materials under hydration, the zirconium surface completes the coordination shells with the available OH group [17,18]. On the variation of pH, these surface active OH groups may further bind or release H^+ where the surface remains positive due to the reaction:



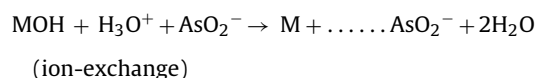
Thus, when $\text{pH} < 7.00$, the overall arsenite adsorption mechanism can be represented in three different forms:

- (i) electrostatic interaction between positively charged center (nitrogen) and negatively charged arsenite molecule in solution,

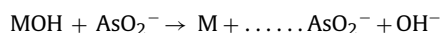
- (ii) electrostatic attraction between positively charged surface hydroxyl group and arsenite



- (iii) ion-exchange reaction between positively charged metal center and arsenite:



Further, when the pH of the medium remains relatively in a neutral range, ($\text{pH} 7.00$), the arsenic (III) adsorption onto the neutral solid surface can be described by a ligand or ion exchange reaction mechanism, which is represented as:



The above-proposed mechanism is supported by notable increase of pH in equilibrium solution. A possible mechanism has been outlined for the newly synthesized adsorbent zirconium (IV) oxide-ethanolamine (ZrO-EA) hybrid material. The modeling of the specific adsorption of AsO_2^- on any material surface depends on a number of external factors such as temperature, pH, initial AsO_2^- concentration, as well as the density of surface functional groups available for coordination. In light of the above-mentioned mechanism of adsorption, it may be further noted that zirconium (IV) oxide-ethanolamine (ZrO-EA) hybrid material showed adsorption capacity at a wide pH range, which could be useful for commercial exploitation purpose. The role of ethanolamine in the material is 2-fold. First, the attachment of ethanolamine to the structure develops nucleophilicity. Second, the attachment of the ethanolamine could be responsible for the development of porosity in the structure and for imparting a large specific surface area after the process of drying. Further, the ethanolamine may also combine with the zirconium to form a layer where the neighboring particles could be interconnected.

3.4. Effect of competitive ions

Drinking water contains many other ions such as sulfate, chloride, nitrate, etc., along with arsenite, which may compete with arsenic for active sorption sites. In order to study the effect of interfering ions, the adsorption studies were carried out in presence of 0.1 M salt solutions of sulfate, nitrate, chloride, carbonate, and bicarbonate ions separately. The experimental condition for initial arsenic concentration was kept at 10 mg/L , the results of

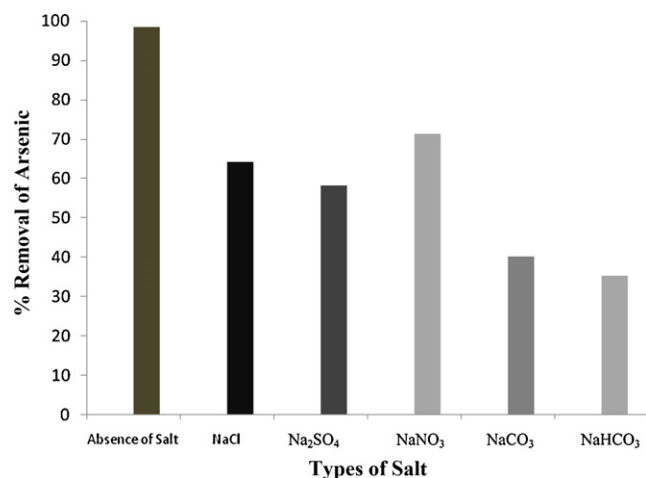


Fig. 17. Effect of the presence of anions on removal of arsenic (III) (initial concentration = 10 mg/L; optimum dose = 0.7 mg/L; contact time = 24 h). (■) Adsorption of arsenic in the absence of salt; (■) adsorption of arsenic in the presence of 0.1 M sodium chloride (NaCl); (■) adsorption of arsenic in the presence of 0.1 M sodium sulfate (Na₂SO₄); (■) adsorption of arsenic in the presence of 0.1 M sodium nitrate (NaNO₃); (■) adsorption of arsenic in the presence of 0.1 M sodium carbonate (NaCO₃); (■) adsorption of arsenic in the presence of 0.1 M sodium bicarbonate (NaHCO₃).

the observation showed graphically (Fig. 17). From the adsorption experiments results, and it was observed that NO₃⁻, Cl⁻, SO₄²⁻, HCO₃⁻ and CO₃²⁻ ions show negative effect on removal of arsenic. However, the experimental result showed that the presence of CO₃²⁻ and HCO₃⁻ showed practically no removal of arsenic (III). This may be because of the change in pH as well as the competing effect of these co-anions. The pH of the arsenic (III) solution was 8.1, 7.0, 7.5, 10.5, 10.2, respectively, for NO₃⁻, Cl⁻, SO₄²⁻, HCO₃⁻ and CO₃²⁻ while the pH of the arsenic (III) solution was 7.1 without addition of salts/anions. This indicates that addition of salt resulted in increased pH of arsenic (III) solution. From our experiments on effect of pH (Section 3.2.2) it was observed that the adsorption of arsenic (III) decreases in alkaline pH is also explained. Another observation was found that in the absence of anions, ZrO-EA release was a very negligible amount (below detection limit), while at alkaline pH and in the presence of anions ZrO-EA release increased marginally from 0.69 to 1.69 mg/L, this indicates that active zirconium sites available at alkaline pH will be relatively less for adsorption of arsenic (III). The overall effect, therefore, is decrease in the removal of arsenic (III) from water mainly due to the increased pH of the solution and competing effect of anions as well as lesser active ZrO-EA sites available for adsorption process.

3.5. Desorption and regeneration of adsorbent

Regeneration and reuse of the adsorbent material carries utmost importance, which directly affects the cost factor and hence its utility in continuous batch adsorption processes. Only the adsorbent materials that can be reused have practical value in real system. The reusability capacity of arsenic (III) adsorbent was performed with oven dried used ZrO-EA to determine its reusability. As can be seen from Fig. 18, the used adsorbent has slightly less adsorption capacity as compared to fresh ZrO-EA. The arsenic (III) removal decreases by 8, 9.6, and 15.2%, respectively, after 1st, 2nd, and 3rd use of adsorbent. However, it may be possible to regenerate the adsorbent by the alkali-acid treatment. In the presence study, anion exchange carried out at pH 8, 10, and 12 with NaOH and the optimum pH is found to be 12. To evaluate the efficacy of the prepared adsorbent material (ZrO-EA) with respect to various other available materials, a comparative assessment was made with

Table 9 Comparative evaluation of various low-cost hybrid adsorbents with present adsorbent ZrO-EA for arsenic (III) removal.

Adsorbent	Type of water	pH	Concentration/ range	Surface area (m ² /g)	Temperature (°C)	Model used to calculate adsorption capacity	Capacity (mg/g) As (III)	References
Ferric chloride impregnated silica gel	Drinking/wastewater	7.0	1 mg/L	840	20–23	-	4.50	[19]
MnO ₂ -loaded resin	Drinking water	7–8.5	3–150 mg/L	-	22	-	53	[20,21]
Bead cellulose loaded with iron oxyhydroxide (BCF)	Ground water	7.0	1–100 mmol/L	-	250 ± 0.5	Langmuir	99.6	[22]
Monoclinic hydrous zirconium oxide (Zr resin)	Drinking water	9–10	1 × 10 ⁻³ M	373	25	Langmuir	112.4	[23]
Zr resin	Drinking water	8.0	0–5 mmol/L	-	25	Langmuir	79.42	[24]
Iron (III)-loaded chelating resin	Aqueous solution	9.0	-	-	25	Langmuir	62.93	[25]
Zirconium (IV)-loaded chelating resin (Zr-LDA)	Spring water	9.0	-	7.3	25	Langmuir	49.15	[26]
Hybrid (polymer/inorganic) fibrous sorbent (FIBAN-As)	Drinking water	7.7	-	-	20	Langmuir	75.67	[27]
Poly (ethylene mercaptoacetamide) (PEM)	-	8.0	-	-	24	Langmuir	31.56	[28]
ZrO-EA (zirconium (IV)-ethanolamine based hybrid material)	Drinking water/waste water/tap water	7.0–8.0	0.7 mg	201.62	27 ± 2	Langmuir	98.0	Present material

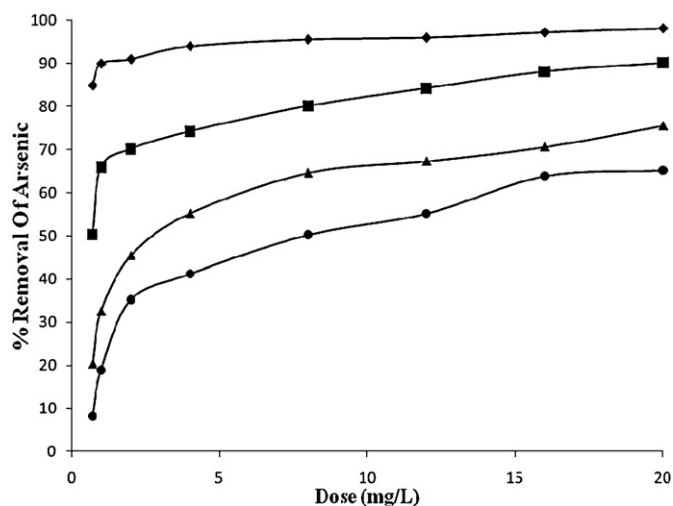


Fig. 18. Reusability of adsorbent for removal of arsenic (III). (♦) Fresh adsorbent; (■) 1st reuse; (▲) 2nd reuse; (●) 3rd reuse.

respect to available literature data [19–35] (Table 9). The studies on optimization regeneration process are under progress.

4. Conclusion

Zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material is an efficient ion exchanger, which has been synthesized from zirconium oxychloride octahydrate and ethanolamine by coprecipitation method. Synthesis is ascertained by the results of various characterization methods like SEM, XRD, FTIR, TGA-DTA, and BET. The hybrid material exhibits specific surface area of 201.62 m²/g. The adsorption of arsenic (III) from aqueous solution by the hybrid material is spontaneous. Adsorption of arsenic (III) is found to follow first order kinetics. The effect of anions is also studied and it is found that NO₃⁻, Cl⁻, SO₄²⁻, HCO₃⁻ and CO₃²⁻ ions show negative effect on removal of arsenic. However, the experimental result showed that the presence of CO₃²⁻ and HCO₃⁻ showed practically no removal of arsenic (III). Regeneration study of the ion exchanger is also carried out and it is found that the ion exchanger could be easily regenerated with sodium hydroxide at pH 12. The maximum removal of arsenic (III) is found to be about 98% in average at pH 7 and hence the removal process is effective to bring the concentration of arsenic (III) very close to Indian permissible limit IS:10,500 (50 ppb). Further studies are being carried out with zirconium (IV) oxide-ethanolamine (ZrO-EA) hybrid material to make it low cost effective along with other high efficiency adsorbent for removal of arsenic and other ions from the water effectively.

Acknowledgements

The Authors are thankful to Prof. P.C. Panda, Director, Dr. B.G. Mishra (HOD), Department of chemistry, and other staff members of the department, National Institute of Technology, Rourkela, for providing necessary facilities and help in carrying out the research work. The authors are also thankful to MOEF, Government of India for its financial assistance.

References

- [1] B.K. Mandal, K.T. Suzuki, Arsenic round the world: a review, *Talanta* 58 (2002) 201–235.
- [2] W.R. Penrose, Arsenic in the marine and aquatic environments: analysis, occurrence and significance, *Crit. Rev. Environ. Contr.* 4 (1974) 465.
- [3] WHO, World Health Organization, Arsenic in drinking water, 2008 (May 2001 October 26).
- [4] C.K. Jain, I. Ali, Arsenic: occurrence, toxicity and speciation techniques, *Water Res.* 34 (2000) 4304–4312.
- [5] R.E. Reitmeier, V. Sivertz, H.V. Tartar, Some properties of monoethanolamine and its aqueous solutions, *J. Am. Chem. Soc.* 62 (1940) 1943–1944, Coden: JACSAT ISSN: 0002-7863.
- [6] G. Alberti, E. Torracca, A. Conte, Stoichiometry of ion exchange materials containing zirconium and phosphate, *J. Inorg. Nucl. Chem.* 28 (2) (1966) 607–613.
- [7] R.S. Jayasree, V.P. Mahadevan Pillai, V.U. Nayar, I. Odnevall, G. Keresztury, Raman and infrared spectral analysis of corrosion products on zinc NaZn₄Cl(OH)₆SO₄·6H₂O and Zn₄Cl₂(OH)₄SO₄·5H₂O, *Mater. Chem. Phys.* 99 (2006) 474–478.
- [8] N. Das, P. Pattanaik, R. Das, Defluoridation of drinking water using activated titanium rich bauxite, *J. Colloid Interface Sci.* 292 (2005) 1–10.
- [9] M.G. Sujana, R.S. Thakur, S.B. Rao, Removal of fluoride from aqueous solution by using alum sludge, *J. Colloid Interface Sci.* 206 (1998) 94–101.
- [10] P.V. Messina, P.C. Schulz, Adsorption of reactive dyes on titania-silica mesoporous materials, *J. Colloid Interface Sci.* 299 (2006) 305–320.
- [11] C. Namasivayam, R.T. Yamuna, Adsorption of direct red 12 B by biogas residual slurry: equilibrium and rate processes, *Environ. Pollut.* 89 (1995) 1–7.
- [12] E. Eren, B. Afsin, Investigation of a basic dye adsorption from aqueous solution onto raw and pre-treated bentonite surfaces, *Dyes Pigments* 76 (2008) 220–225.
- [13] American Academy of Pediatrics, Committee on Drugs. Treatment guidelines for lead exposure in children (RE9529), *Pediatrics* 96 (1995) 155–160. <http://www.aap.org/policy/00868.html>.
- [14] D. Bryce-Smith, H.A. Waldron, Lead pollution, disease and behaviour, *Community Health* 6 (1974) 168–175.
- [15] M. Mahramanlioglu, I. Kizilcikli, I.O. Bicer, Adsorption of fluoride from aqueous solution by acid treated spent bleaching earth, *J. Fluorine Chem.* 115 (2002) 41–47.
- [16] M. Islam, R.K. Patel, Evaluation of Removal efficiency of fluoride from aqueous solution using quick lime, *J. Hazard. Mater.* 143 (2007) 303–310.
- [17] A.K. De, P. Chakraborty, Synthetic inorganic ion exchangers XXI. Electrochromatographic separations of metal ions on lanthanum antimonite-impregnated paper, *Electrophoresis* 2 (5–6) (2005) 330–332.
- [18] G. Alberti, U. Costantino, Crystalline insoluble acid salts of tetravalent metals. X. Fibrous thorium phosphate, a new inorganic ion-exchange material suitable for making (support-free) inorganic sheets, *J. Chromatogr.* 50 (1970) 482.
- [19] Y. Isao, K. Hiroshi, U. Keihei, Selective adsorption of arsenic ions on silica gel impregnated with ferric hydroxide, *Anal. Lett.* 9 (12) (1976) 1125–1133.
- [20] V. Lenoble, C. Chabroulet, R. Al Shukry, B. Serpaud, D. Vieronique, J.-C. Bollinger, Dynamic arsenic removal on a MnO₂-loaded resin, *J. Colloid Interface Sci.* 280 (1) (2004) 62–67.
- [21] V. Lenoble, C. Laclautre, B. Serpaud, D. Vieronique, J.-C. Bollinger, As(V) retention and As(III) simultaneous oxidation and removal on a MnO₂-loaded polystyrene resin, *Sci. Total Environ.* 326 (1–3) (2004) 197–207.
- [22] X. Guo, F. Chen, Removal of arsenic by bead cellulose loaded with iron oxyhydroxide from groundwater, *Environ. Sci. Technol.* 39 (17) (2005) 6808–6818.
- [23] T.M. Suzuki, M.L. Tanco, D.A.P. Tanaka, H. Matsunaga, T. Yokoyama, Adsorption characteristics and removal of oxy-anions or arsenic and selenium on the porous polymers loaded with monoclinic hydrous zirconium oxide, *Separ. Sci. Technol.* 36 (1) (2001) 103–111.
- [24] T.M. Suzuki, J.O. Bomani, H. Matsunaga, T. Yokoyama, Preparation of porous resin loaded with crystalline hydrous zirconium oxide and its application to the removal of arsenic, *React. Funct. Polym.* 43 (1–2) (2000) 165–172.
- [25] H. Matsunaga, T. Yokoyama, R.J. Eldridge, B.A. Bolto, Adsorption characteristics of arsenic (III) and arsenic (V) on iron (III)-loaded chelating resin having lysine-N^ε, N^δ-diacetic acid moiety, *React. Polym.* 29 (1996) 167–174.
- [26] T. Balaji, T. Yokoyama, Matsunaga, Hideyuki, adsorption and removal of As(V) and As(III) using Zr-loaded lysine diacetic acid chelating resin, *Chemosphere* 59 (8) (2005) 1169–1174.
- [27] O.M. Vatutsina, V.S. Soldatov, V.I. Sokolova, J. Johann, M. Bissen, A. Weisenbacher, A new hybrid (polymer/inorganic) fibrous sorbent for arsenic removal from drinking water, *React. Funct. Polym.* 67 (2007) 184–2001.
- [28] P.M. Styles, M. Chanda, G.L. Rempel, Sorption of arsenic anions onto poly(ethylene mercaptoacetamide), *React. Funct. Polym.* 31 (2) (1996) 89–102.
- [29] D. Mohan, C.U. Pittman Jr., Arsenic removal from water/wastewater using adsorbents—a critical review, *J. Hazard. Mater.* 142 (2007) 1–53.
- [30] R.T. Yang, *Adsorbents: Fundamentals and Applications*, Wiley-Interscience, 2003, ISBN 0-471-29741-0.
- [31] S. Paraeniemi, S. Hannonen, H. Mustalahti, M. Ahlgren, Zirconium loaded activated charcoal as an adsorbent for arsenic, selenium, and mercury, *Fresen. J. Anal. Chem.* 349 (7) (1994) 510–515.
- [32] M. Hodi, K. Polyak, J. Hlavay, Removal of pollutants for drinking water by combined ion-exchange and adsorption methods, *Environ. Int.* 21 (1995) 325–331.
- [33] H. Genc, J.C. Tjell, D. McConchie, O. Schulling, Adsorption of arsenate from water using neutralized red mud, *J. Colloid Interface Sci.* 264 (2003) 327–334.
- [34] L.V. Rajakovic, M.M. Mitrovic, Arsenic removal from water by chemisorption filter, *Environ. Pollut.* 75 (1992) 279–287.
- [35] E. Deschamps, V.S.T. Ciminelli, W.H. Holl, Removal of As (III) and As (V) from water using a natural Fe and Mn enriched sample, *Water Res.* 39 (2005) 5212–5220.