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STUDIES ON THE REMOVAL OF ARSENIC (III) FROM WATER BY A NOVEL HYBRID MATERIAL

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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 minutes 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.

Key words: Arsenic, hybrid material, BET, Isotherms, AAS.

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" diarrhea, arsenic in natural water is a worldwide problem [2]. Arsenic pollution has been reported recently in the 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 0.01mg/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, oxidation, 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 (v/v 30%) (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), 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. (Table1). The pH of the solution is adjusted using 0.1 M H Cl / Na OH solution. The white colored gel so obtained is allowed to stand for 24 hour 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 hour and it is collected in granular form with shiny appearance. A preliminary investigation is done with 10 mg L^{-1} 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 0.8M 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 10mg/L, 50mg/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 gram 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^{-1}.

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 material 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 exchanger 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 0.8M 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 advantage of using the 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 (Figure 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 (Figure 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 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 ^{0}C. Thermo gravimetric analysis, therefore, strongly indicates that the organic molecule ethalonolamine 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 24h and the supernatant liquid was analyzed for zirconium and Ethanolamine(Table 2). The material exhibit 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 Zirconium (IV) oxide ethanolamine (ZrO-EA) hybrid material, the number of moles of Zirconium, and Ethanolamine are found to be 0.866 $\times$ 10^{-3}, 1.2702 $\times$ 10^{-3}, respectively. The molar ratio of Zirconium and Ethanolamine is calculated and found to be 1:3.ratio so, from the above discussion, the tentative empirical formula for the material can be suggested as $[(ZrOCl_2)\,(C_2H_7NO)_3].\ nH_2O$.

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

$$18n = X\,(M + 18n)/100 \qquad \text{(i)}$$

Scanning electron micrographs of the sample is presented in (Figure 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 (Figure 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 ^{o} 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 m^2/g. FTIR study of the sample was carried out (Figure 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 the (Figure 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±2 ^{o}C) and contact time of 30 minute for initial arsenic (III) concentration of 10mg/L, 50mg/L and 100mg/L. The results are presented in (Figure 7). It is evident from the (Figure 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/100ml of Zirconium (IV) oxide ethanolamine (ZrO-EA) hybrid material respectively with initial arsenic (III) concentration of 10mg/L, 50mg/L and 100mg/L. It is observed that after dosage of 0.7mg/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 isn't any appreciable increase in the effective surface area. So, 0.7mg/100ml is considered the optimum dose and is used for further study. The maximum removal 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:10500 (50 ppb).

3.2.2. Effect of pH

Percentage removal of arsenic (III) at different pH is studied in batch experiments using 0.7mg of adsorbent in 100 mL synthetic solution, at ambient temperature (25±2 ^{o}C) , contact time of 30 minute for initial arsenic (III) concentration of 10mg/L, 50mg/L, and 100mg/L. The results are presented in (Figure 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 10mg/L, 50mg/L and 100mg/L at pH 7 keeping all other parameters constant. The result is represented in (Figure 9). It is clear from the (Figure 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.

3.2.4. Adsorption Kinetics

Adsorption of arsenic (III) ion is rapid for the first 10 minutes 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, 50mg/L, and 100 mg/L by the following equation.

$$\log(q_e - q) = \log q_e - k_{ad}\left(\frac{t}{2.303}\right) \qquad \text{(ii)}$$

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 the (Figure 10). The adsorption rate constant (K_{ad}), calculated from the slope of the above plot is presented in (Table 7).

3.2.5. Effect of Temperature

The effect of temperature on the adsorption of arsenic (III) with initial concentration 10mg/L, 50 mg/L and 100 mg/L is studied using optimum adsorbent dose (0.7 mg/100mL). The results are represented as percentage removal of arsenic (III) versus temperature (Figure 11). The percentage removal of arsenic (III) with initial concentration 10mg/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 to 45° C temperature respectively. It can be clearly seen from the (Figure 11) that, at the temperature of 25° C the 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]:

$$\log K_C = \frac{\Delta S}{2.303R} - \frac{\Delta \mathrm{H}}{2.303R\mathrm{T}} \qquad \text{(iii)}$$

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

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

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

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

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 (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 (0.7mg/100ml) at ambient temperature (25±2 ^{o}C) and contact time of 30 min. The results are represented in graphical form as percentage removal versus initial arsenic (III) concentration in (Figure 13). The initial arsenic (III) concentration is increased from 10mg/L to 100 mg/L and the corresponding removal gradually increases from 99.52 % to 99.92 %. It is cleared from the (Figure 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,

$$\frac{1}{q_e} = \frac{1}{q_o b C_e} + \frac{1}{q_o} \qquad \text{(vi)}$$

Where q_o 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 (Figure 14) with R^2 = 0.972 indicates the applicability of Langmuir adsorption isotherm. The values of Langmuir parameters, q_o and b were 0.250019952 mg/g and 0.035717136 L/mg, respectively. In order to predict the adsorption efficiency of the adsorption process, the dimensionless equilibrium parameter is determined by using the following equation [15, 16].

$$r = \frac{1}{1 + bC_o} \qquad \text{(vii)}$$

Where C_o 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 100mg/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

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

Where ε is Polanyi potential, and is equal to RT ln (1 + 1/ C_e), where qe 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 (Figure 15), is almost linear 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]

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

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 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, 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 16kJ

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.

3.2.8 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 (Figure 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:

$$MOH + H_3O^+ \longrightarrow MOH_2^{\ +} + H_2O$$

Thus, when 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

$$MOH + H_3O^+ + AsO_2^{--} \longrightarrow MOH_2^{\ +} \cdots\cdots AsO_2^{--} + H_2O$$

(Electrostatic attraction) and

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

$$MOH + H_3O^+ + AsO_2^{--} \longrightarrow M+\ldots\ldots AsO_2^{--} + 2H_2O \text{ (ion-exchange)}$$

Further, when the pH of the medium remains relatively in a neutral range, (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:

$$MOH + AsO_2^{--} \longrightarrow M+ \ldots\ldots AsO_2^{--} + OH^-$$

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.

3.2.9 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^{-1}, the results of the observation showed graphically (Figure 17).From the adsorption experiments results, and it was observed that NO_3^-, Cl^-, SO_4^{2-}, HCO_3^- and CO_3^{2-} ions show negative effect on removal of arsenic. However, the experimental result showed that the presence of CO_3^{2-} and HCO_3^- 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 were 8.1, 7.0, 7.5, 10.5, 10.2, respectively, for NO_3^-, Cl^-, SO4 $^{2-}$, HCO_3^- and CO_3^{2-} 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 as 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.

3.2.10 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 (Figure 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 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 co-precipitation 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 m^2/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 NO_3^-, Cl^-, SO_4^{2-} , HCO_3^- and CO_3^{2-} ions show negative effect on removal of arsenic. However, the experimental result showed that the presence of CO_3^{2-} and HCO_3^- 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:10500 (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.

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Table Caption (S)

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

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

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

Table 4: Results of chemical analysis of Zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid Material

Table 5: Results of CHN analysis of Zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid Material

Table 6: Change in pH during the removal process

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

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

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

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

Solvent(20 ML)	*Amount Dissolved(mg) ZrO-EA*
1M HCL	0.21
2 M HCL	0.38
4 M HCL	0.86
1 M HNO_3	0.65
2M HNO_3	1.21
4M HNO_3	1.49
1M H_2SO_4	completely
2M H_2SO_4	completely
4M H_2SO_4	completely
1 M NaOH	0.45
2M NaOH	0.84
4M NaOH	1.23
1M KOH	1.23
2M KOH	1.48
4M KOH	1.86
1M NH4OH	1.24
2 MNH4OH	completely
4M NH4OH	completely
2M $NaNO_3$	0.04
2M KNO_3	0.09

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

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

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

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

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^{-1})*	*Temperature (° C)*	*Model used to calculate adsorption capacity*	*Capacity (mg/g) As(III)*	*References*
Ferric Chloride impregnated Silica gel	Drinking/wastewater	7.0	1mg/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 mercaptoacetimide) (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

Figure Caption (s)

Figure 1: Particle Size analysis of ZrO-EA hybrid material

Figure 2: Differential Thermal Analysis and Thermogravimetric analysis of ZrO-EA hybrid material

Figure 3: SEM micrographs of Zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material (a) Before Adsorption (b) After Adsorption

Figure 4: XRD pattern of Zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material

Figure 5: FTIR Spectrum of Zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material

Figure 6: Structure of Zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material

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

Figure 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

Figure 9: Time versus percentage removal of Arsenic (III) with initial concentration of 10 mg/L, 50 mg/L and 100 mg/L

Figure 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

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

Figure 12: Van’t Hoff plots, log Kc versus 1/T

Figure 13: Initial arsenic concentration versus percentage removal

Figure 14: Langmuir adsorption isotherm, $1/C_e$ versus $1/q_e$

Figure 15: D-R adsorption isotherm, ln qe versus ε^2

Figure 16: Adsorption and Regeneration mechanism

Figure 17: Effect of the presence of anions on removal of arsenic (III)

Figure 18: Reusability of adsorbent for removal of arsenic (III)

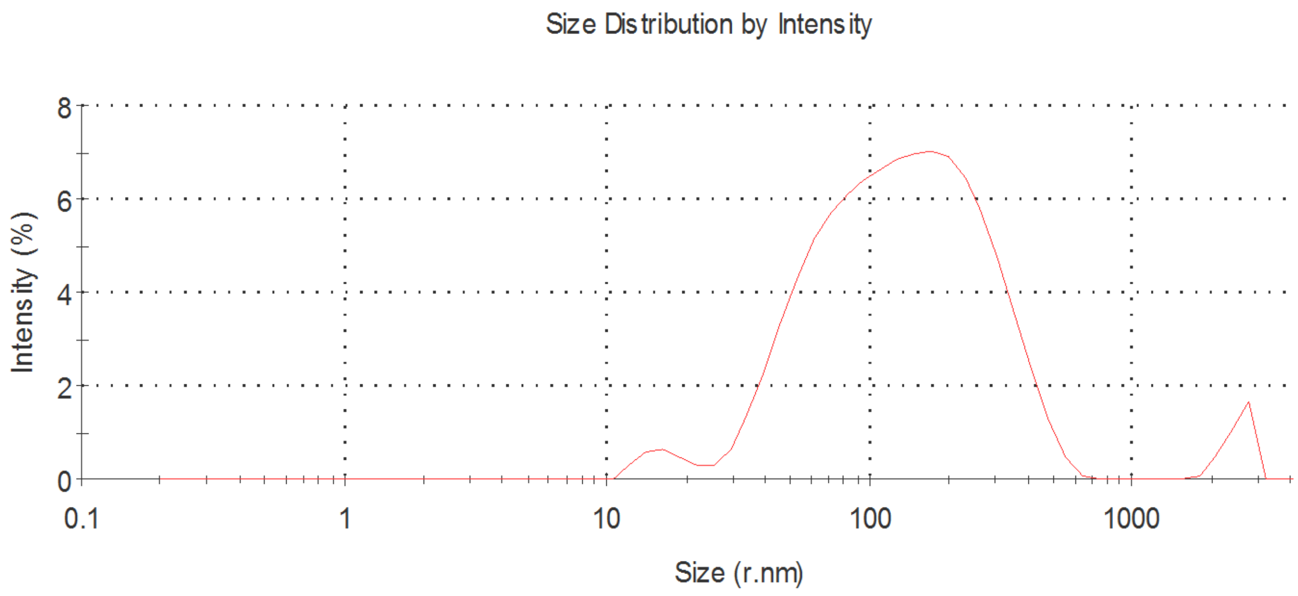


Figure 1: Particle Size analysis of ZrO-EA hybrid material

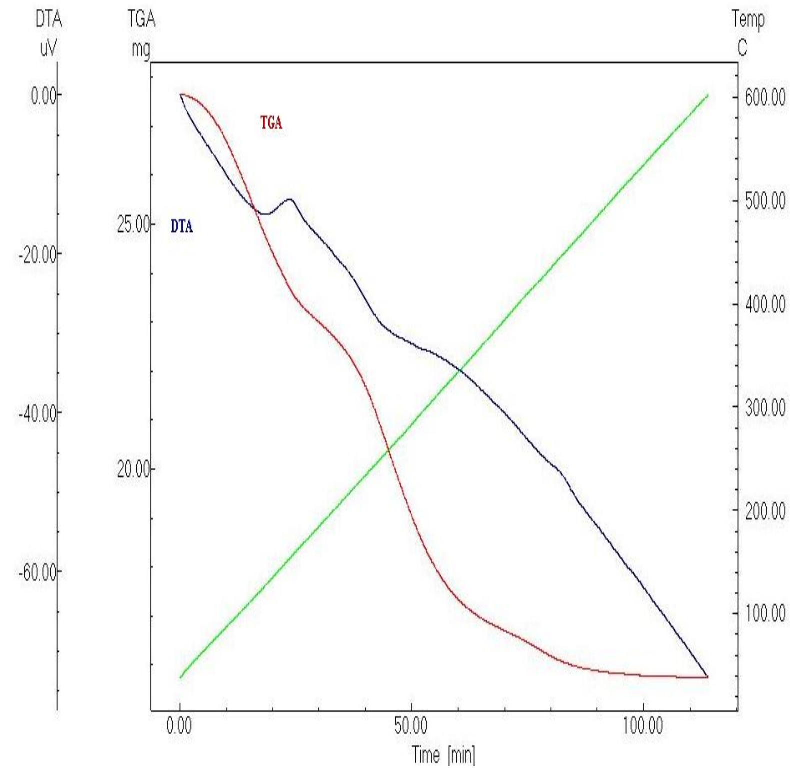
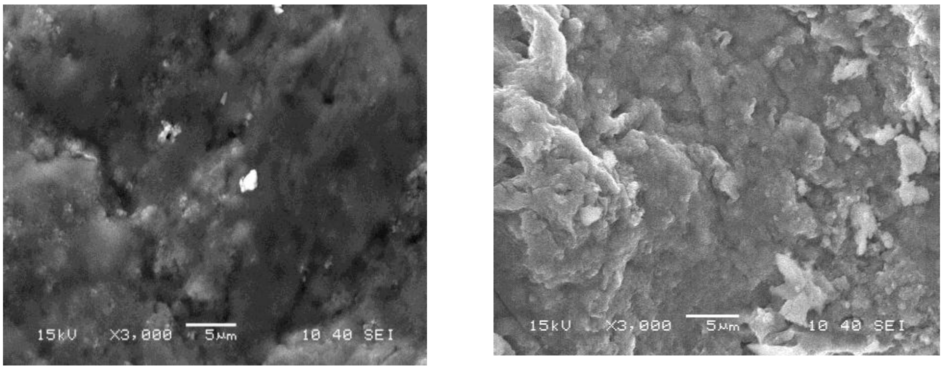
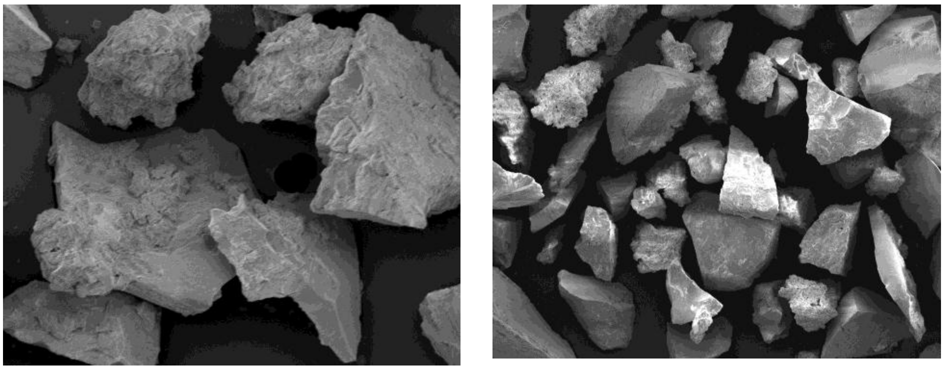


Figure 2: Differential Thermal Analysis and Thermogravimetric analysis of ZrO-EA hybrid material up to 650 ^{o}C



(a) Before Adsorption



(b) After Adsorption

Figure 3: SEM micrographs of Zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material (a) Before Adsorption (b) After Adsorption

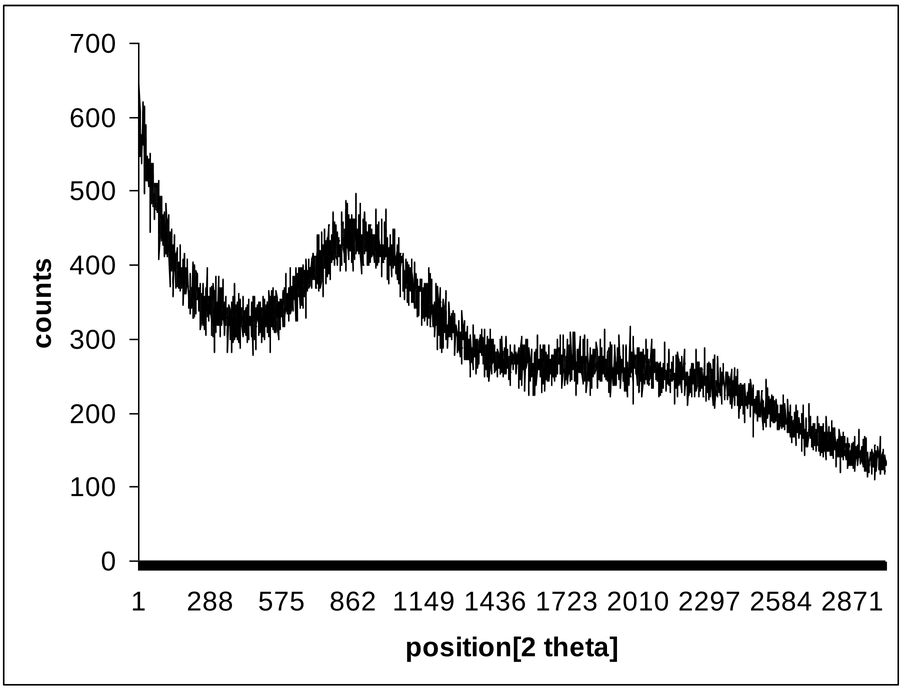


Figure 4: XRD pattern of Zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material

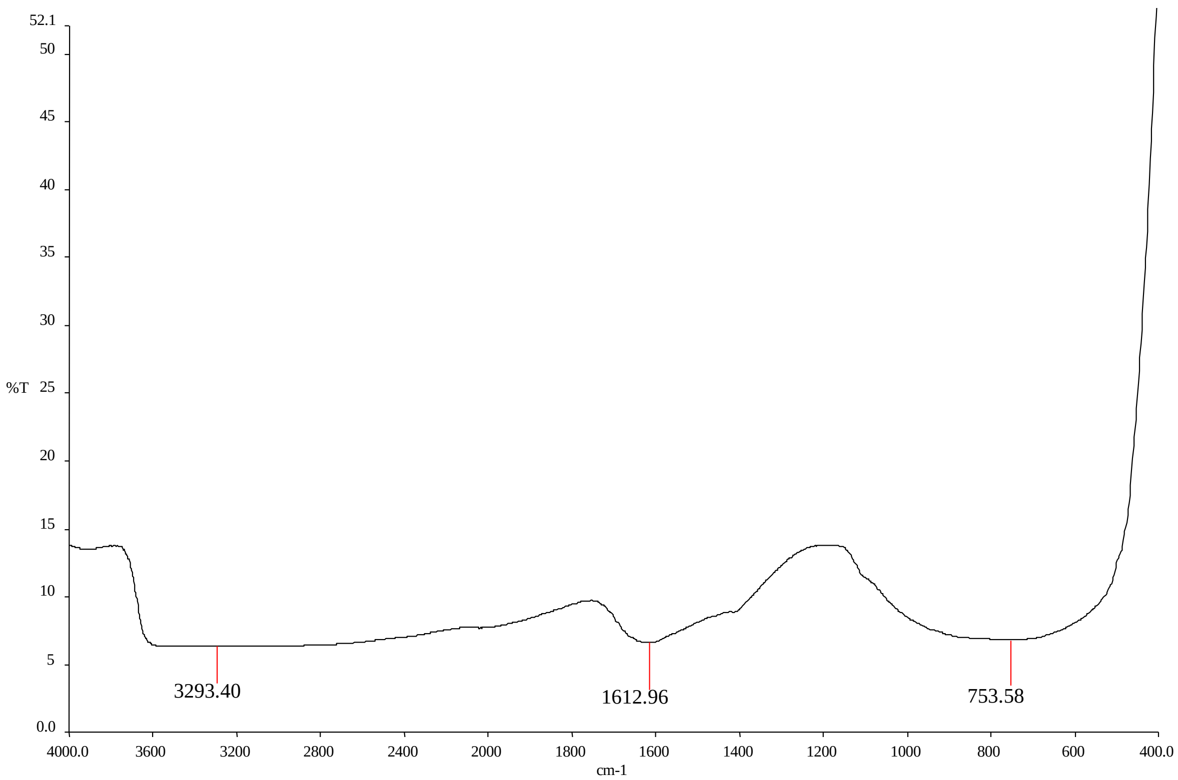


Figure 5: FTIR Spectrum of Zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material

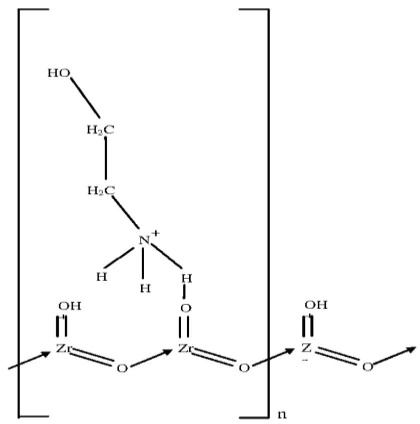


Figure 6: Structure of Zirconium (IV) oxide-ethanolamine (ZrO-EA), hybrid material

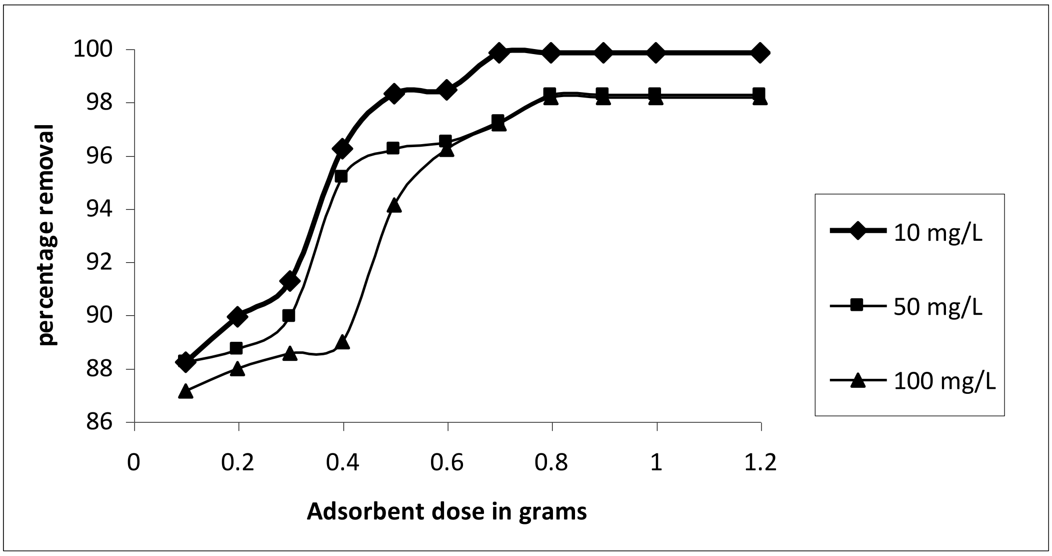


Figure 7: Adsorbent dose versus percentage removal of arsenic (III) with initial concentration of 10 mg/L, 50 mg/L and 100 mg/L.

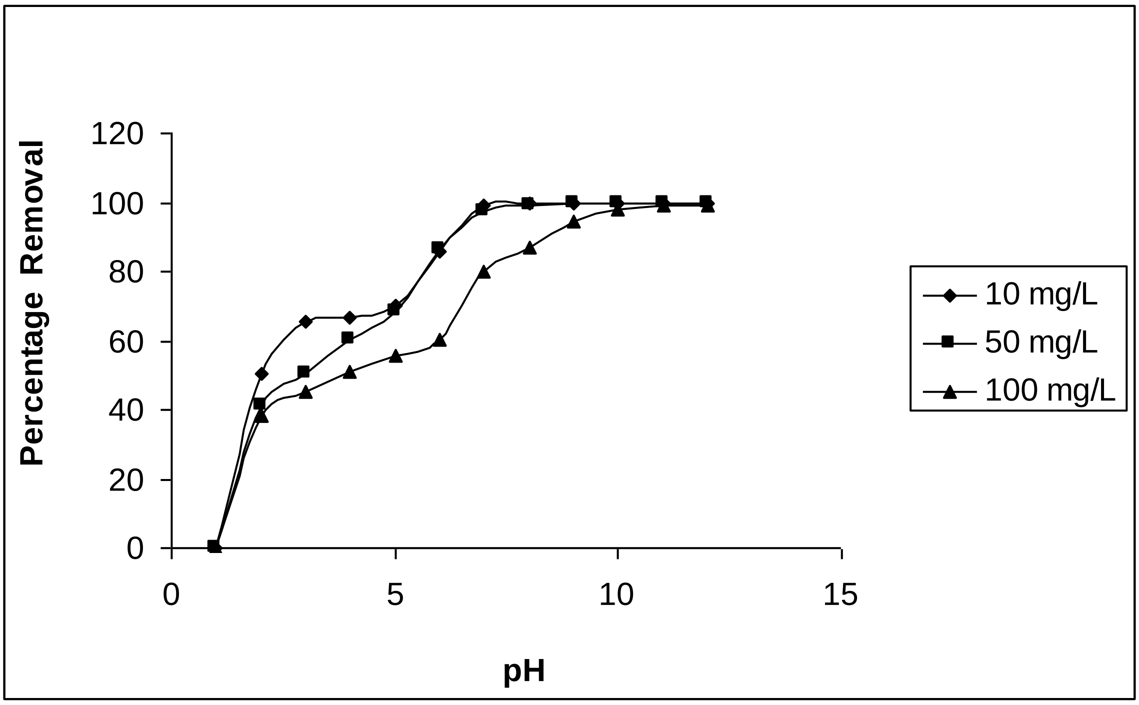


Figure 8: Percentage removal of arsenic (III) of initial concentration of 10 mg/L, 50 mg/L and 100 mg/L versus pH of the synthetic solution

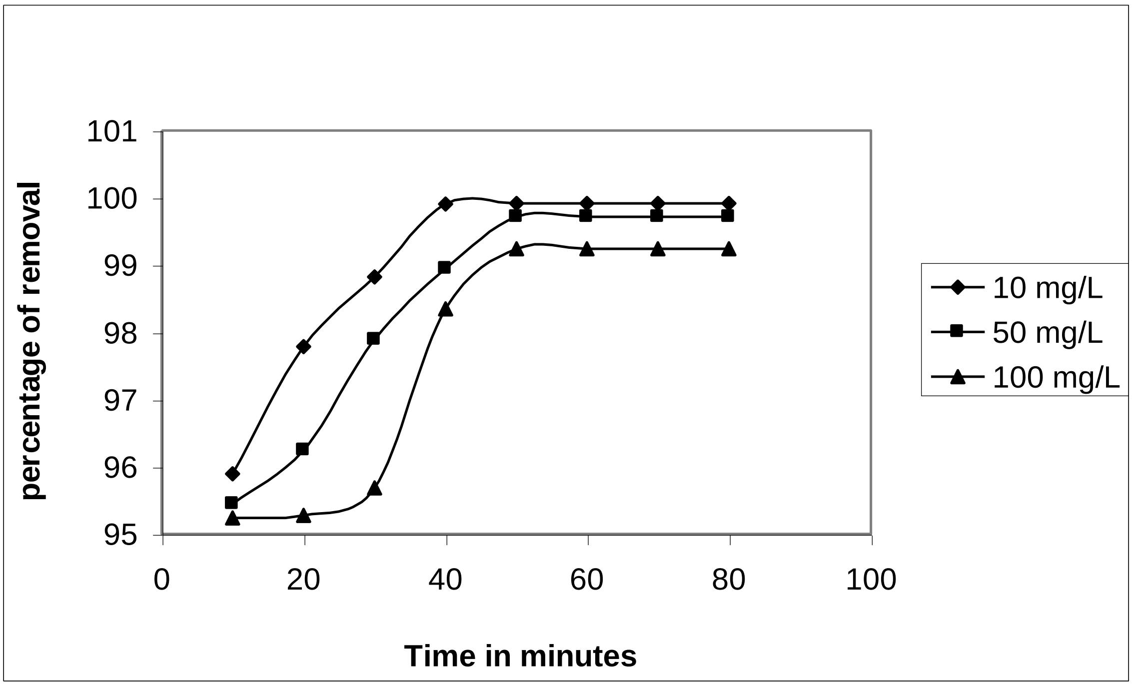


Figure 9: Time versus percentage removal of arsenic (III) with initial concentration of 10 mg/L, 50 mg/L and 100 mg/L.

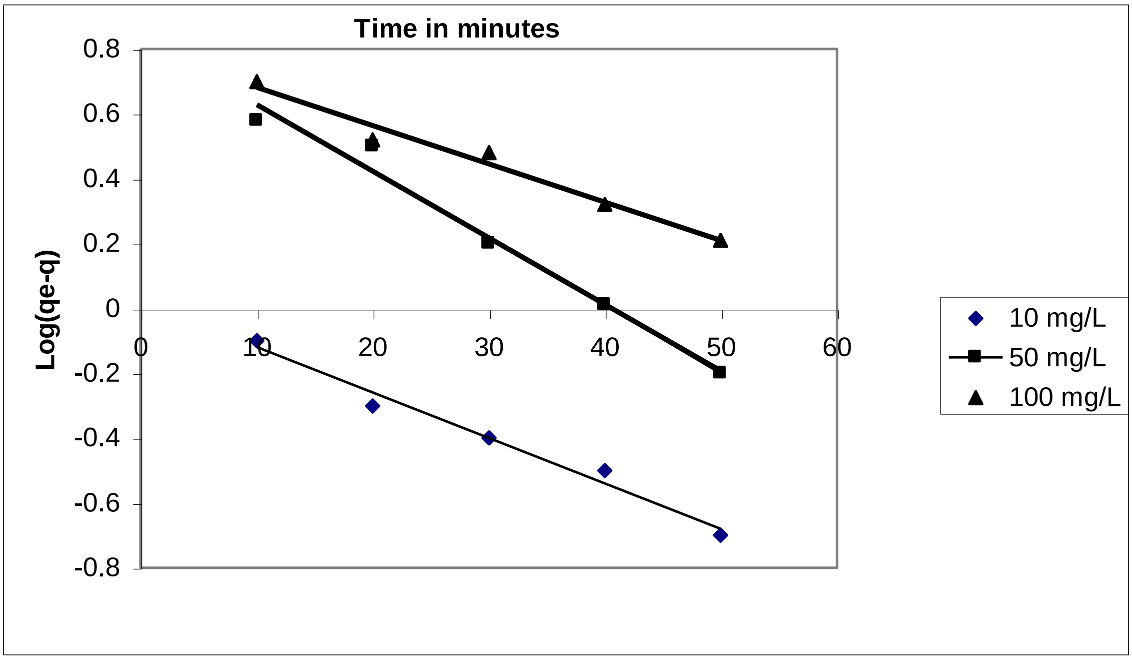


Figure 10: Adsorption kinetics, time versus log (q_e – q) with initial arsenic (III) concentration of 10 mg/L, 50 mg/L and 100 mg/L

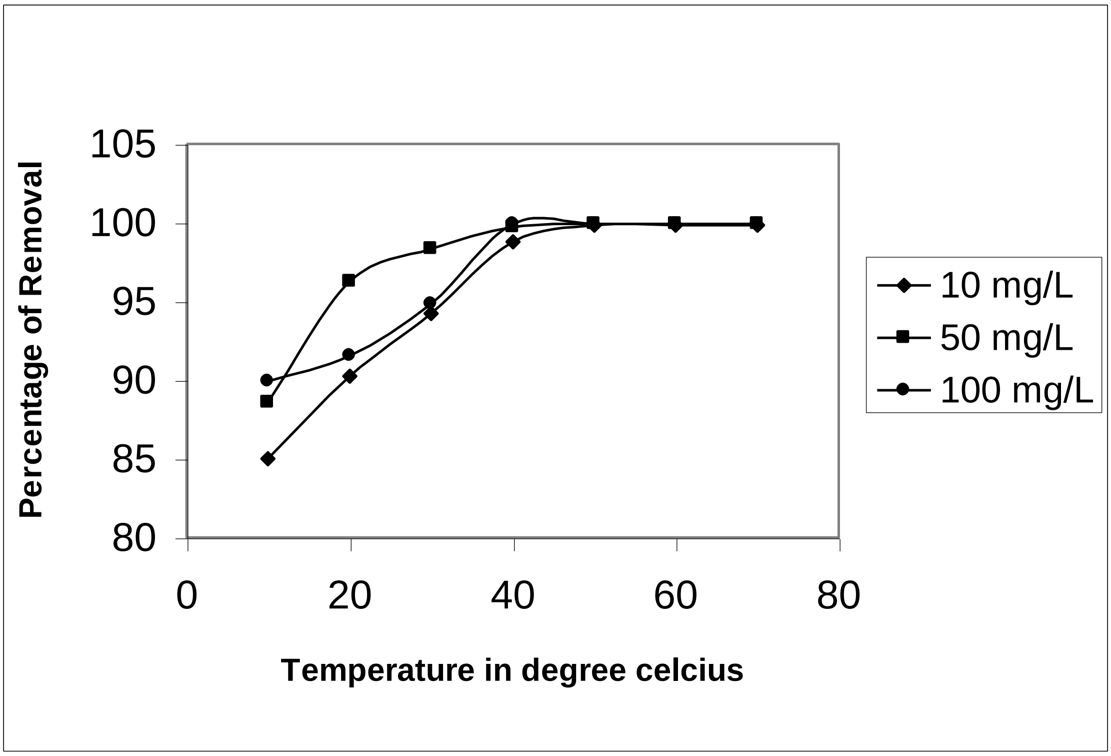


Figure 11: Temperature versus percentage removal of arsenic (III) with initial concentration of 10 mg/L, 50 mg/L and 100 mg/L.

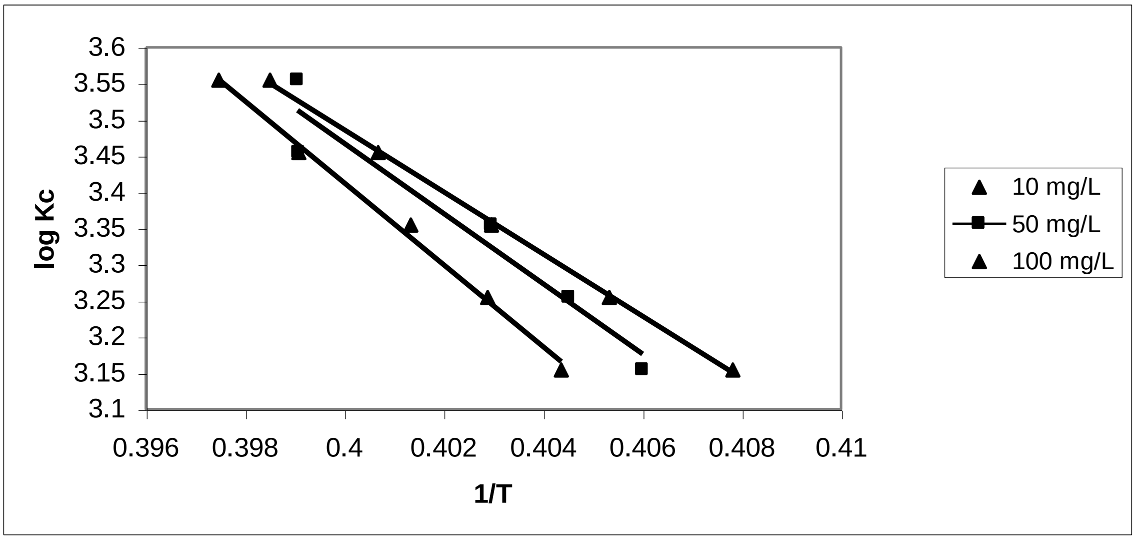


Figure 12: Van’t Hoff plots, log Kc versus 1/T.

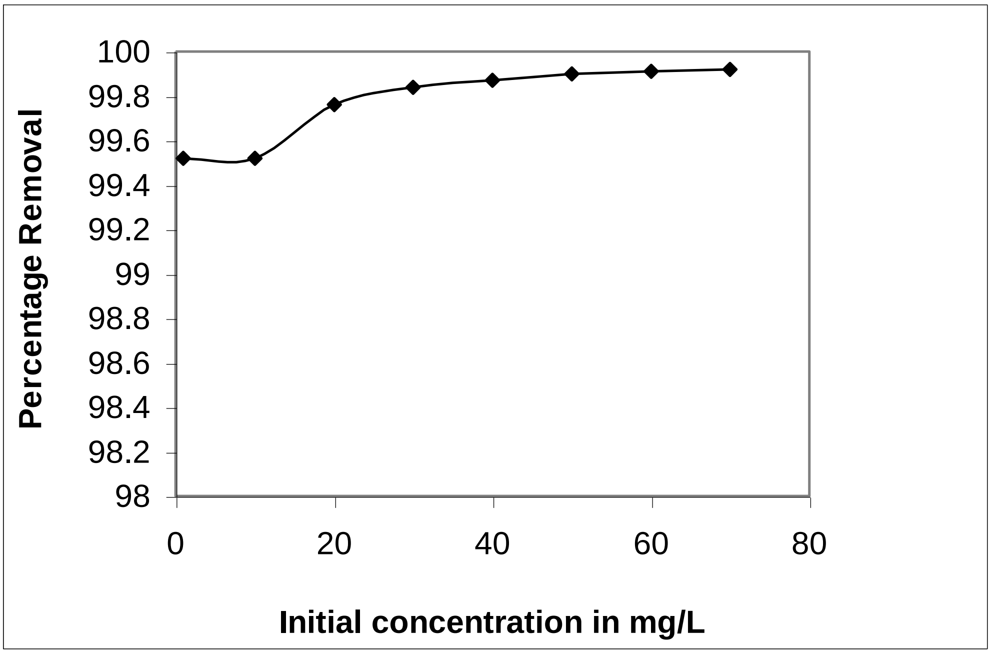


Figure 13: Initial arsenic concentration versus percentage removal

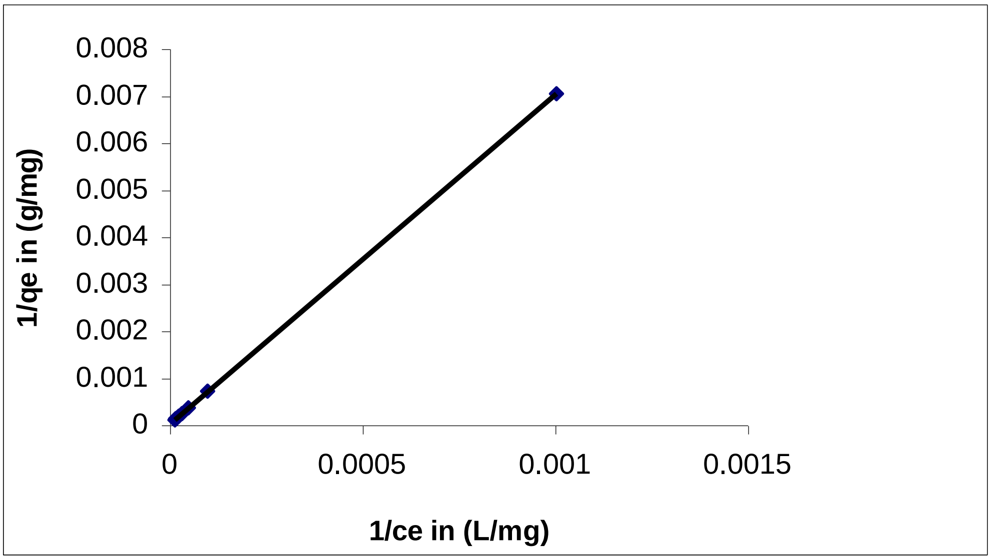


Figure 14: Langmuir adsorption isotherm, $1/C_e$ versus $1/q_e$

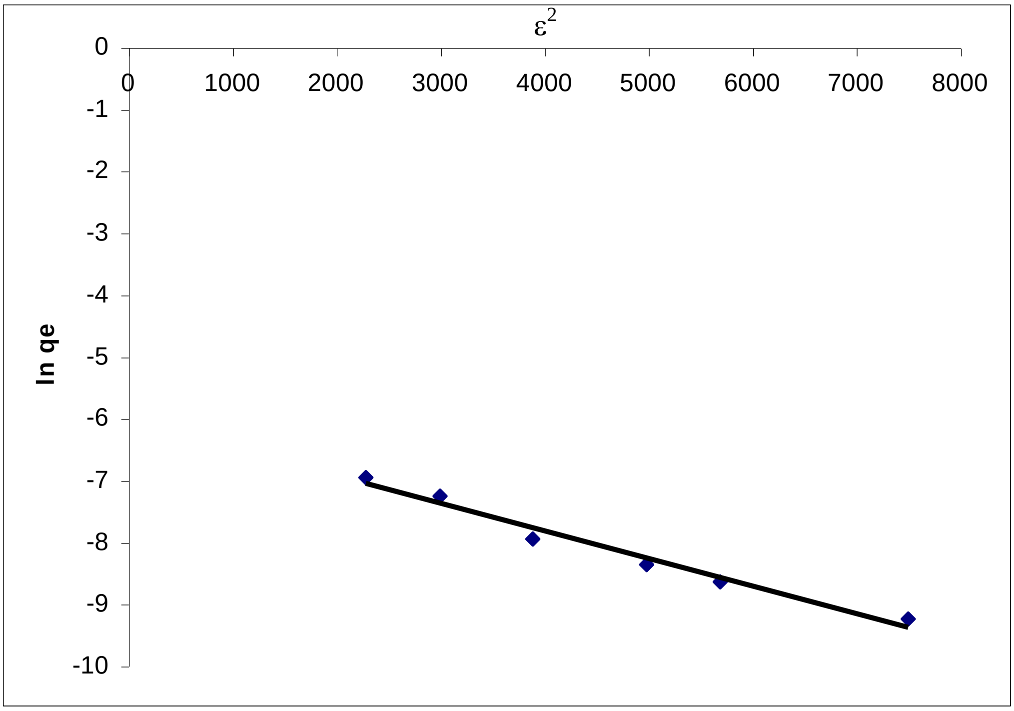


Figure 15: D-R adsorption isotherm, ln qe versus ε^2

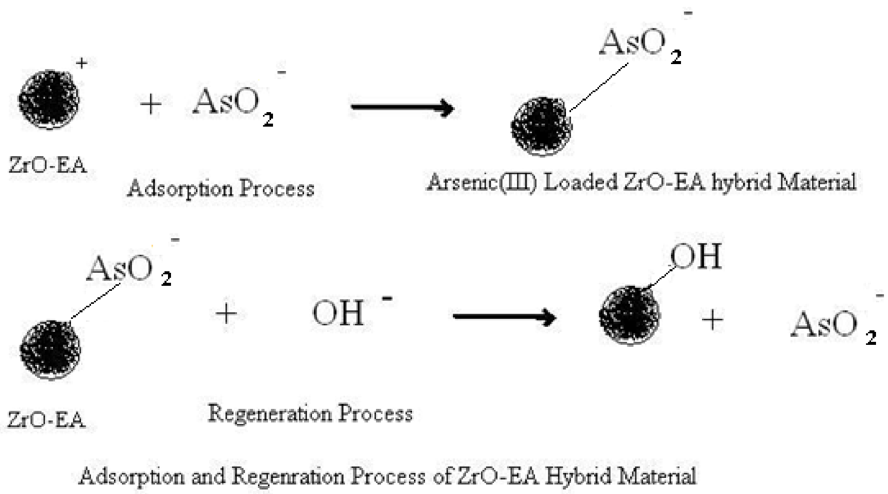


Figure 16: Adsorption and Regeneration mechanism

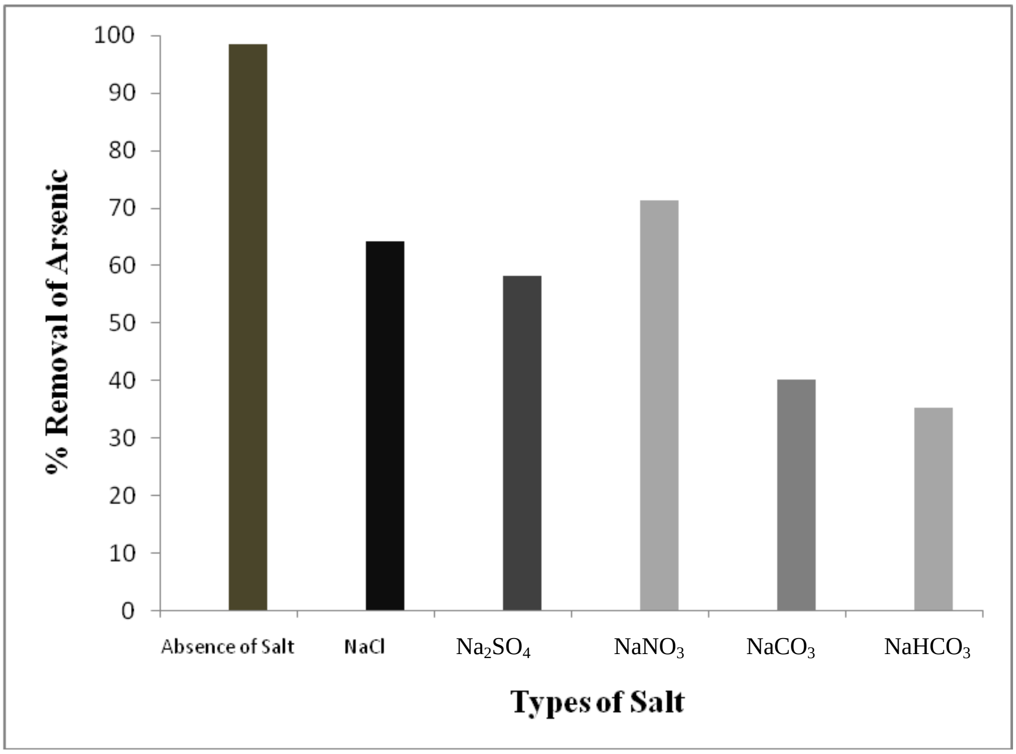


Figure 17: Effect of the presence of anions on removal of Arsenic (initial concentration =10 mg L^{-1}; optimum dose= 0.7 mg L^{-1}; Contact time= 24h). (■) Adsorption of Arsenic in the absence of salt; (■) Adsorption of arsenic in the presence of 0.1 M sodium Chloride (NaCl); (■) Adsorption of arsenic in the presence of 0.1 M Sodium Sulfate (Na_2SO_4); (■) Adsorption of arsenic in the presence of 0.1 M Sodium Nitrate ($NaNO_3$); (■) Adsorption of arsenic in the presence of 0.1 M sodium Carbonate ($NaCO_3$); (■) Adsorption of arsenic in the presence of 0.1 M sodium Bicarbonate ($NaHCO_3$).

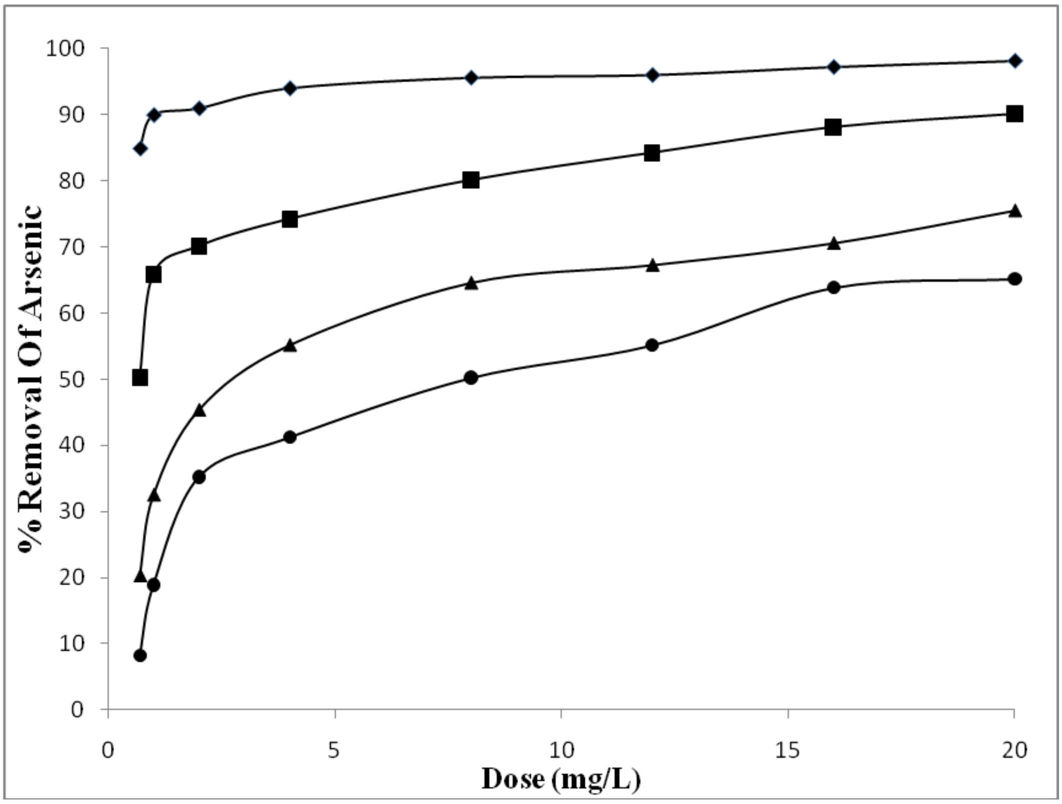


Figure 18: Reusability of adsorbent for removal of arsenic (III). (◆) Fresh Adsorbent; (■) 1st reuse; (▲) 2nd reuse; (●) 3rd reuse