The utilization of okra leaves as an agricultural waste for the removal of As(III) and As(V)

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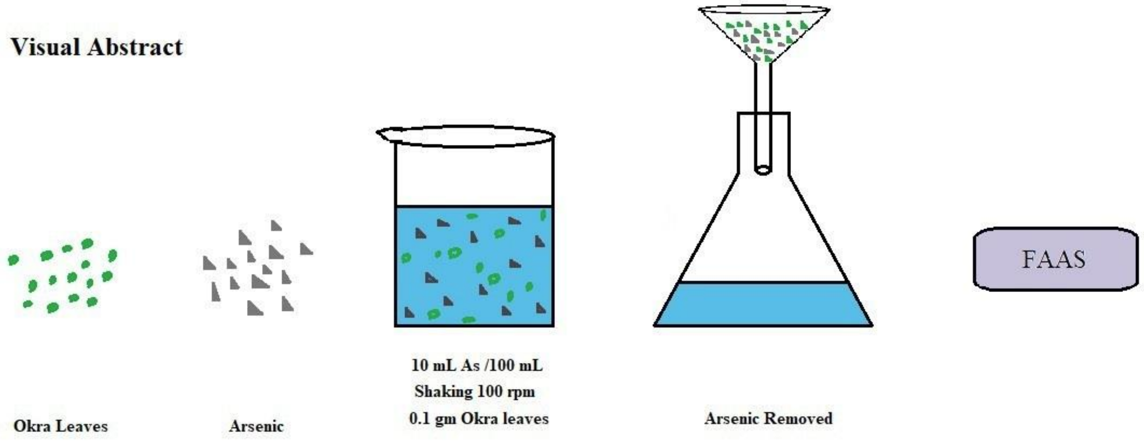
Abstract

In the present study the sorption efficiency of okra leave sorbent for As(III) and As(V) is demonstrated. Sorption reaction is pH and time dependent. The sorbent shows maximum removal of As(III) and As(V) at pH 7 and pH 6 respectively and equilibrium was achieved at 180 minutes. In isotherm study experimental data were explained by Freundlich and Flory-Huggins models. Maximum sorption capacities calculated by Freundlich Isotherm were 5672.0 µg g^{-1} and 13160 µg g^{-1} for As(III) and As(V) respectively. Psuedo-second order rate equation and Morris-Weber equation explained the kinetics of sorption reaction. Due to the presence of heterogeneous active sites on the sorbent, surface sorption as well as intra-particle diffusion occurred. Thermodynamically, sorption reaction was endothermic in nature and proceeded spontaneously. Desorption study revealed that 89.82% of As(III) and 97.11% of As(V) were removed with 1M HCl.

Keywords: Okra, Sorption, Arsenic, Equilibrium, Thermodynamics



1 Introduction

Arsenic, a metalloid, is present in air, soil, water, minerals, rocks and biota with various concentrations (Chowdhury and Mulugan, 2011). Arsenic is the 20th most abundant element in the earth's crust, 14th in sea water and 12th in the human body (Shafique et al., 2012). Since its discovery in 1250 A.D, arsenic has been used in medicines, agriculture, metallurgy and electronics. It is estimated that nearly 22% of arsenic production is used in agricultural chemicals (Chen et al., 2010). The solubility of arsenic depends upon pH, redox condition, temperature and solution composition (Giri et al., 2011). It is non-biodegradable and detrimental to the flora and fauna. More than 300 species of arsenic bearing minerals exist in nature (Lorenzen et al., 1995). Mostly natural processes (e.g., geochemical reactions and volcanic emissions) and anthropogenic activities (e.g., mining, industrial, chemical waste and arsenical pesticides) are the major causes of arsenic pollution (Haron et al., 1999; Huang and Fu,1984; Maheshwari and Murugesan, 2011).

The existence of arsenate, arsenite, monomethyl (MMA) arsenic acid and dimethyl (DMA) arsenic acid depends upon the environment (i.e., pH, Eh) and microbial activity (Jing et al., 2009). Generally, stable inorganic species of arsenic are found with oxidation states like -3 (arsine gas AsH_3), 0 (crystalline / metallic arsenic), +3 (arsenite), and +5 (arsenate). A crystalline form of arsenic is very rarely found. The favorable conditions for arsine gas, arsenite (ground water) and arsenate (surface water) are extreme reducing, mild reducing and oxygenated environments respectively. Generally inorganic arsenic compounds have higher toxicities than organic arsenicals (Chen et al., 1994; Li et al., 1995). As(III) compounds are (25-60 times) more toxic than As(V) compounds (Aryal et al., 2010). As(III) which is more mobile is difficult to remove as compared to As(V), which exists predominantly as deprotonated oxyanions ($H_2AsO_4^{1-}$ or $HAsO_4^{2-}$). Very minute quantity of arsenic is required for the human healthy growth. Above the recommended concentration, arsenic disturbs the regular metabolic activity of living organisms. The accumulation of arsenic compounds in food, even at very low concentration causes different diseases in plant, animal and human life (Pokhrel et al., 2008). It has mutagenic and tetratogenic capacity for human health (ATSDR 1990) severe arsenic poisoning causes even to death. In mammals, arsenic diseases are due to the reaction with sulfhydryl groups of enzymes(Korte et al., 1991). Arsenic poisoning causes heart disease, keratosis, hyperpigmentation, burning sensation of eyes, anaemia, liver fibrosis, neuropathy, solid swelling of legs, gangrene of toes, lung cancer, skin cancer, liver cancer, bladder cancer, kidney cancer and prostate

(National Research Council, Report: 1999; Sari et al., 2011; Smith et al., 2004; Tuzen et al., 2009).

To handle water pollution by arsenic, various conventional processes such as precipitation, coagulation, solvent extraction, ion-exchange and reverse osmosis etc. have been employed (Khaskheli et al., 2011). Considering the advantages and disadvantages of other metal removal methods, sorption has been emerged as an alternative. In the past 20 years sorption has gotten much importance because in this technique, various types of sorbents are frequently used (Biswas et al., 2008). Sorption has many different advantages such as high metal binding efficiency, short operating time, reusability of biomass, improved selectivity for specific metals of interest, no production of secondary toxic compounds (Kamala et al., 2005; Rahman et al., 2008). Further, it has practical applicability for small scale industries.

The present work demonstrates the uptake efficiency of okra (*Abelmoschus esculentus)* leaves for the removal of arsenic(III) and arsenic(V) from aqueous solution. Different parameters like pH, contact time and sorbate amount were optimized. Freundlich and Florry-Huggins models were used to describe equilibrium isotherms. For understanding the sorption mechanism of arsenic species on okra leaves, the observed experimental data were kinetically and thermodynamically analyzed.

2 Eperimental Procedure

2.1 Reagents and Equipments

In the experiments all reagents used were of analytical grade or equivalent. Stock solutions (1000 mg L^{-1}) of As(III) and As(V) were prepared by dissolving calculated amounts of As_2O_3 (Poole, England) and Na_3AsO_4 (Merck, Germany) in de-ionized water respectively. Working solutions for experiments were freshly prepared from the stock solutions. For adjusting the pH, buffers of acetic acid (CH_3COOH), sodium acetate (CH_3COONa), potassium chloride (KCl), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used. Reducing agent for arsenic was prepared by mixing the 0.2% w/v sodium borohydride ($NaBH_4$) (Darmstadt company, Merck, Germany) in 0.05 % w/v NaOH (Fisher scientific UK).

During sorption experiments pH of all solutions was measured by Thermo Scientific Orion 5 Star (8102BNUWP; made in USA) pH meter. To facilitate the reaction between sorbent and sorbate shaking incubator model 1-40000 Irmeco GmbH (made in Germany) was used. Arsenic concentration was analyzed by Atomic Absorption Spectrometer

(Analyst 800 Perkin Elmer, USA) connected with a Flow Injection System for hydride generation (FIAS 100 Perkin Elmer, USA). Atomic Absorption Spectrometer equipped with a hallow cathode lamp having current mA 18, wavelength nm 193.7, energy 40, band width 0.7 nm (made in Singapore) and Quartz Tube Atomizer (Universal QAT, part number B300 - 0350, USA) were used.

2.2 Collection and Preparation of Biomass

The green okra leaves (sorbent material) obtained from the agricultural farm located in Kingri, District Khairpur Mirs, Sindh, Pakistan. In order to remove dust and extraneous particles, okra leaves were washed with tap and deionized water. Then the leaves were put in oven for drying at 60 °C for 24 h. The dried sorbent material was ground and sieved in range of 0.125 - 0.42 mm particle size. After the selection of particle size (0.125 mm) 1 g of the desired particle size of the sorbent was treated with 25 mL of 1M NaOH at 30 °C, agitation at 250 rpm for 15 minutes. Then base treated sorbent material was washed with de-ionized water till filtrate became colorless. In the last, again washed material was dried in oven at 80 °C for 10 h.

2.3 Batch Sorption Procedure

The metal sorption behavior of okra sorbent was investigated using batch equilibrium experiments. The calculated amount of okra sorbent was added to 10 mL of arsenic solution in 100 mL stopper conical flask and agitated in an electric thermostatic reciprocating shaker at 100 rpm for desired contact time. The sorption reactions were carried out at 30, 35, 40 and 45 °C. The equilibrium time was determined by taking out the samples from electrical thermostatic shaker at different times. After filtering the samples, the arsenic concentration in the filtrate was analyzed by Absorption Spectrometer connected to FIAS system. The stated experimental procedure was repeated for the optimization of different parameters- biomass dosage (0.05 - 0.3 g), sorbent particle size (0.125 - 0.42 mm) contact time (0 - 1440 min), agitation speed (50 - 250 rpm), volume of test solution (10 - 50 mL), metal concentration (0.01 - 50 mg L^{-1}) and pH (1 - 10).

3. Results and Discussion

3.1 Sorbent Characterization

3.1.1 EDX Analysis

To carry out further experiments for the method development, it is very necessary to characterize the sorbent nature before and after the sorption of arsenic ions. For Energy Dispersive X-ray (EDX) analysis, BRUKER X-FLASH 4010 133ev (made in Germany) was used. In Fig.1a and 1b elements are shown on the surface of untreated and arsenic treated sorbent respectively. Fig. 1a contains oxygen, calcium and carbon. In Fig. 1b the presence of small peak of arsenic confirms the sorption of arsenic.

(Figure 1)

3.1.2 Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

The FT-IR study demonstrates the changes in vibrational frequencies of functional groups present in the okra sorbent before and after the sorption of arsenic ions. In the Fig. 2 the spectra of untreated and arsenic treated sorbent are taken. The frequency of spectra was maintained in the range of 500 - 4000 cm^{-1}. The recorded changes in the frequencies are shown in Table 1. The peaks at 3301 cm^{-1} and 2847 - 2908 cm^{-1} attributed to the stretching of O-H hydrogen bonding (alcohol or phenol) showed a shift for both As(III) and As(V) loaded sorbent. The appearance of new peaks at 1728 cm^{-1} and 1221 cm^{-1} and disappearance of peak at 1413 cm^{-1} in As(V) loaded sorbent indicates the involvement of C=O, C-O (ether or ester) and C-H respectively for As(V) ions retention. The change in the vibrational frequencies at 1000 cm^{-1} and 1147 cm^{-1} for As(III) and As(V) loaded okra sorbent demonstrate the role of C-O (alcohol) and C-O (ether or ester) respectively in the sorption process.

(Figure 2)

(Table 1)

3.2 Effect of pH

During the pH study, pH range of 1–10 was maintained. The effect of pH on the sorption of As(III) and As(V) on okra sorbent is shown in Fig. 3. It was observed that maximum sorption of both arsenic species was seen in the range of pH 6.0 - 7.0. Such type of sorption trend is also reported in the literature (Aniruthan et al., 2007; Ghimiri et al., 2002).

In case of As(III) at the mentioned pH mono-anionic ($H_2AsO_3^-$) specie is considered as responsible for the sorption and substitute hydroxyl ions or water molecules. H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} are the dominant As(V) species in pH ranges of <2.26, 2.26 - 6.76, 6.76 - 11.29 and >11.29 respectively (Su et al., 2010). A small decrease in sorption in alkaline pH can be attributed to the repulsion created between the anionic species of arsenic and negatively charged sorbent.

(Figure 3)

3.3 Effect of Biomass Concentration

Amount of sorbent has key role in the sorption process. It affects the % sorption of metal ions. By maintaining all other parameters, the amount of okra leave was varied in the range of 0.1- 0.6 g. Fig. 4 shows that there is a slight increase in % sorption as amount of biomass increased from 0.1g to 0.6 g for both arsenic species. Thus, for making method economical 0.1 g of amount was taken for further study.

(Figure 4)

3.4 Effect of Contact Time

The effect of reaction time was studied by maintaining the volume of arsenic ions 10 ml, arsenic ion concentration 5 mg L^{-1}, shaking speed 250 rpm, the amount of biomass 0.1 g, temperature 30 °C and pH 7.0 for As(III) and pH 6 for As(V). Results in Fig. 5 indicated that up to 180 minutes sorption was continuously increased and then slowly decrease was registered. This trend of decrease in sorption may be due to auto desorption of metal ions.

(Figure 5)

3.5 Sorption Isotherm Study

Isotherms deal surface properties of a sorbent and its binding forces for metal ions at optimum pressure and temperature. The recorded experimental data were analyzed by the following isotherm models.

3.5.1 Freundlich Adsorption Isotherm Model

Freundlich equation is one of the most commonly used isotherm equations. This equation analyzes the experimental data related to the sorption of inorganic and organic compounds on natural as well as synthetic adsorbents. It also explains the nature of sorbents. The following linear form of the Freundlich equation was used (Khaskheli et al., 2017).

$$logq_e = logK_F + \frac{1}{n_F}\log C_e$$

Where C_e is amount of metal ions in the liquid phase at equilibrium, q_e amount of metal ions sorbed, K_f (Freundlich Constant) relative sorption capacity and n is sorption intensity. 1/n >1 concave isotherm while 1/n <1 suggest the presence of convex isotherm $Logq_e$ is plotted against $logC_e$. Agreement of the experimental data to the equation indicates that sorbent contains non-equivalent sites (heterogeneous surface). The values of n and K_f are determined from the slope and intercept. The calculated values of n are less, but near to 1 (1/n > 1) and supports the concave nature of isotherm (Febrianto et al., 2009). Table 2 shows that K_F increases with the increase of temperature.

(Table 2)

3.5.2 Flory-Huggins Adsorption Isotherm Model

Flory-Huggins isotherm is used to measure the degree of surface coverage of metal ions on sorbent and change occurred in Gibbs free energy of sorbent (Jnr et al., 2005). Following linear form of the equation is employed for the analysis of the data (Vijayaraghavan et al., 2006).

$$log\frac{\theta}{C_i} = logK_{FH} + n_{FH}\log(1-\theta)$$

$$\theta = 1 - \frac{C_e}{C_i}$$

Where C_e is equilibrium metal ion concentration, θ is degree of surface coverage, K_{FH} is the Flory-Huggins model equilibrium constant and n_{FH} is the Flory-Huggins model exponent represents the number of metal ions of solute occupy active sites of sorbent. The plot of $\log\theta/C_i$ versus $\log(1-\theta)$ yields a straight line with high regression values and confirms that experimental data follow the Flory-Huggins model. The values of n_{FH} and K_{FH} are calculated from the intercept and slope of the plot respectively. Table 2 indicates that with the increase of temperature, the number of occupying sorption sites of okra sorbent increases for As(III) and decreases for As(V). Flory-Huggins constant K_{FH} is used to calculate the Gibbs free energy of spontaneity ($\Delta G°$) by following relationship.

$$\Delta G° = -RTlnK_{FH}$$

Negative values of Gibbs free energy show that process is feasible and spontaneous in nature (Kiran et al., 2008).

3.6 Kinetic study

Kinetic study determines the mechanism of sorption time to establish equilibrium. Physical and chemical compositions of okra sorbent have an important role in describing the kinetics of the reaction

3.6.1 Pseudo Second Order rate Equation

Ho and McKay (Ho et al., 1998) consider pseudo-second-order model is best for understanding the kinetics of sorption system. According to this equation rate of sorption reaction depends on the chemical bonding between sorbent and metal ions (Nadeem et al., 2008). Pseudo-second-order rate equation may be written as:

$$\frac{dq_t}{d_t} = k(q_e - q_t)^2$$

After putting boundary condition values, integrating and rearranging, the following linear equation is obtained.

$t = 0$, $q_t = 0$; $t = t$ $q_t = q_t$;

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$$

$$h = kq_e^2$$

Where

k = equilibrium rate constant

h = initial adsorption rate

Where k is the equilibrium rate constant which is calculated from slope of the plot t/q_t against t. Straight lines of the graph of the both arsenic species along with high values of correlation coefficient (0.99-1) as indicated in Table 3 show that experimental data are well fitted to the equation. From this, it may be deduced that monolayer (chemisorption) of the sorbate is formed by involving valence forces through sharing (covalent bond) or exchange (ionic bond) of electrons or complex compounds may be formed between arsenic ions and okra sorbent. Further, this equation also supports that okra sorbent contains heterogeneous energetic, active sites on the surface.

(Table 3)

3.6.2 Intra-particle Diffusion (Morris-Weber Equation)

Intra-particle diffusion (Morris-Weber) model (Morris et al., 1963) is used to study the mass transfer resistance on the binding of metal ion to the sorbent.

$$qt = Rdr\sqrt{t} + C$$

Where qt is sorption capacity of metal ions on sorbent at time t (mg/g), Rdr intra-particle diffusion rate constant ($mg/g.min^{0.5}$) and C intercept which gives the idea of the thickness of the boundary layer. The graph was plotted between qt versus $t^{1/2}$. According to Table 3, experimental data of As(III) and As(V) followed equation up to 180 minutes with k_{id} values of 1.01 $mg/g.min^{0.5}$ and 2.27 $mg/g.min^{0.5}$ respectively. A linear portion of the plot which is not passing through origin reveals that intra-particle diffusion cannot only be attributed the rate limiting step (Chen et al., 2010). It may be explained that mechanism of sorption is complex; Intra-particle diffusion as well as surface adsorption occurs. Similar mechanism of sorption was noticed for the sorption of arsenic on bone char (Chen et al., 2008).

3.7 Thermodynamic Study

Thermodynamic study helps in estimating the nature and feasibility of the sorption reaction (Iftikhar et al., 2009; Khaskheli et al., 2016; Ladeira et al., 2004). Thermodynamic parameters (enthalpy change, entropy change and Gibbs free energy) were calculated by using the following equation.

$$\Delta G = \Delta H - T\Delta S$$

Entropy change (ΔS) and enthalpy change (ΔH) were calculated by plotting ΔG versus temperature (T). Table 4 shows that negative values of Gibbs free energy (ΔG) for both As(III) and As(V) show the spontaneous (i.e strong forces of sorption control the potential barrier between arsenic and sorbent) nature of sorption. An increase in the negative value of ΔG with the rise of temperature favors the sorption process. Positive values of ΔS for As(III) and As(V) demonstrated the increasing randomness at solid / solution interface during the sorption. Positive values of enthalpy change ΔH for both species of arsenic indicated the endothermic nature of the sorption process.

(Table 4)

3.8 Desorption / Regeneration Study

To make method efficient and more economical, it is very important to recover sorbent and sorbate. Desorption process yields metals in concerted form, facilitate their disposal and restore the sorbent for effective reuse [39]. With 1M HCl maximum recoveries of As(III) and As(V) were 89.82% and 97.11% respectively.

3.9 Interference Study

Contaminated real water samples have various electrolytes with different concentrations which affect the sorption process. Thus the study of electrolytic effect is necessary. The effect of some common electrolytes in the ratios of 1:10 and 1:100 were examined on the removal efficiency of As(III) and As(V) with okra leaves. According to histogram Fig. 6a As(III) in the presence of iron(III) with 1:10 and sodium ions with 1:100 showed more than 90% removal. While ~ 90% removal capacity of As(V) (Fig. 6b) was observed with Fe(III) and Al ions in 1: 100 ratio.

(Figure 6)

4 Application

The applicability of the developed method was analyzed by the removal of arsenic ions from real water samples. The real water samples were taken from (sample S1) Karachi Wah at the draining point of Industrial effluents of the Kotri Site area, District Jamshoro, Pakistan and (sample S2) tube well water near United Ethanol Industry Sadiqabad, District

Rahimyar Khan, Pakistan. The Table 5 shows that method was successfully applied in real systems and up to 81.98% of arsenic was removed.

(Table 5)

5 Conclusion

Okra leaves sorbent proved to be an efficient for the removal of As(III) and As(V) from aqueous medium. Sorption reaction of both arsenic species depended on pH and time. At pH 7.0 and pH 6.0 the maximum uptake of As(III) 5672 µg g^{-1} and As(V) 13160 µg g^{-1} respectively was observed. Equilibrium was achieved in 180 minutes. Freundlich and Flory-Huggins models were employed for the isotherm study. Psuedo second order rate equation and Morris-Weber equation explained the kinetics of sorption reaction. Thermodynamic parameters indicated that sorption reaction was endothermic in nature and proceeded spontaneously. Desorption study revealed that 89.82% of As(III) and 97.11% of As(V) were removed with 1M HCl.

References

Aniruthan T.S. and Unnithan M.R. (2007), Arsenic(V) from aqueous solutions using an anion exchanger derived from coconut coir pith and its recovery, Chemosphere, **66**, 60-66.

Aryal M., Ziagova M. and Kyriakides M.L. (2010), Study on arsenic biosorption using Fe(III)-treated biomass of *Staphlococcus xylosus*, Chemical Engineering Journal, **162**, 178-185.

ATSDR, (1990), *Agency for Toxic Substances and Disease Registry: Case studies in Environmental Medicine*, *Arsenic Toxicity*. U.S. Public Health Services, Atlanta USA, June.

Biswas B.K., Jun-ichi Inoue K., Ghimire K.N., Harada H., Ohto K. and Kawakita H. (2008), Adsorptive removal of As(V) and As(III) from water by a Zr(IV)-loaded orange waste gel, Journal of Hazardous Materials, **154**, 1066-1074.

Chen S., Yue Q., Gao B. and Xu X. (2010), Equilibrium and kinetic adsorption study of the adsorptive removal of Cr(VI) using modified wheat residue, Journal of Colloid and Interface Science, **349**, 256-264.

Chen R., Zhang Z., Feng C., Hu K., Li M., Shunizu K., Chen N. and Sugiura N. (2010), Application of simplex-centroid mixture design in developing and optimizing ceramic adsorpbent for As(V) removal from water solution, Microporous and Mesoporous Materials, **131**, 115-121.

Chen Y.N., Chai L.Y. and Shu, Y.D. (2008), Study of arsenic(V) adsorption on bone char from aqueous solution, Journal of Hazardous Materials, **160**, 168-172.

Chen S., Dzeng S.R., Yang M., Chiu K., Shieh G. and Wai C.M. (1994), Arsenic species in ground waters of the Black foot disease area, Taiwan. Environ. Sci. Technol, **28**, 877-881.

Chowdhury M.R.I. and Mulugan C.N.J. (2011), Biosorption of arsenic from contaminated water by anaerobic biomass, Journal of Hazardous Materials, **190**, 486-492.

Febrianto J., Kosasih A.N., Sunarso J., Ju Y.H., Indraswati N. and Ismadji S. (2009), Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies, Journal of Hazardous Materials, **162**, 616-645.

Ghimiri K.N., Inoue K., Makino K. and Miyajima T. (2002), Adsorption removal of arsenic using orange juice residue, Separation Science and Technology, **37**, 2785-2799.

Giri A.K., Patel R.K. and Mahaptra S.S. (2011), Artificial neutral network approach for modeling of As(III) biosorption from aqueous solution by living cells of Bacillius cereus biomass, Chemical Engineering Journal, **178**, 15-25.

Haron M.J., Yunus W.M.Z.W., Yong N.L. and Tokunaga S. (1999), Sorption of arsenate and arsenite anions by iron(III)-poly (hydroxamic acid) complex, Chemosphere, **39**, 2459-2466.

Ho Y.S. and McKay G. (1998), Kinetic model for lead(II) sorption onto peat, Adsorption Science and Technology, **16**, 243-255.

Huang C.P. and Fu P.L.K.J. (1984), Treatment of arsenic(V)- containing water by the activated carbon process, Water Pollution and Control Federation, **56,** 233-242.

Iftikhar A.R., Bhatti H.N., Hanif M.A. and Nadeem R. (2009), Kinetic and thermodynamic aspects of Cu(II) and Cr(III) removal from aqueous solutions using rose waste biomass, Journal of Hazardous Material, **161**, 941-947.

Jing C., Mang X., Calvache E. and Jiang G. (2009), Remediation of organic and inorganic arsenic contaminated ground water using a nanocrystalline TiO_2-based adsorbent, Environmental Pollution, **157**, 2514-2519.

Jnr M.H. and Spiff A.I. (2005), Equilibrium sorption study of Al^{3+}, Co^{2+} and Ag^{2+} in aqueous solutions by fluted pumpkin (*Telfairia accidentalis HOOK f)* waste biomass, Acta Chimica Slovenica, **52**, 174-181.

Kamala C.T., Chu K.H., Chary N.S., Pandey P.K., Ramesh S.L., Sastry A.R.K. and Sekhar K.C. (2005), Removal of arsenic(III) from aqueous solution using fresh and immobilized plant biomass, Water Research, **39**, 2815-2826.

Khaskheli M.I., Memon S.Q., Wahid B.J., Chandio Z.A., Shar G.K., Malik A. and Shaista K. (2017), Competitive sorption of nickel, copper, lead and cadmium on okra leaves (Abelmoschus esculentus), Global Nest Journal, 19, 278-288.

Khaskheli M.I., Memon S.Q., Chandio Z.A., Jatoi W.B., Mahar M.T. and Khokhar F.M. (2016), Okra leaves-Agricultural wasate for the removal of Cr(III) and Cr(VI) from contaminated water, American Journal of Analytical Chemistry, **7**, 395.

Khaskheli M.I., Memon S.Q., Siyal A.N. and Khuhawar M.Y. (2011), Usage of orange peel waste for Arsenic remediation of drinking water, Waste Biomass Valorization, 2, 423-433.

Kiran B. and Kaushik A. (2008), Chromium binding capacity of *Lyngbya putealis* exopolysaccharides, Biochemical Engineering Journal, **38**, 47-54

Korte N.E. and Fernando Q. (1991), A review of arsenic(III) in ground water, Critical Reviews in Environmental Control, **21**, 1-39.

Ladeira A.C.Q. and Ciminelli V.S.T. (2004), Adsorption and desorption of arsenic on an oxisol and its constituents, Water Research, **38**, 2087-2094.

Li Z., Mou S., Ni Z. and Riviello J.M. (1995), Sequential dertermination of arsenite and arsenate by ion chromatography, Analytica Chimica Acta, **307**, 79-87.

Lorenzen L., Deventer J.S.J.V. and Landi W.M. (1995), Factors affecting the mechanism of the adsorption of arsenic species on activated carbon, Minerals Engineering, **8**, 557-569.

Maheshwari S. and Murugesan A.G. (2011), Removal of arsenic(III) ions from aqueous solution using *Aspergillius flavus* isolated from arsenic contaminated site, Indian Journal of Chemical Technology, **18**, 45-52.

Morris W.J. and Weber C. (1963), Kinetics of adsorption on carbon from solution, Journal of the Sanitary Engineering Division, **89**, 31-59.

Nadeem R., Ansari T.M. and Khalid A.M. (2008), Fourier transform infrared spectroscopic characterization and optimization of Pb(II) by fish (Labeo rohita) scales, Journal of Hazardous Materials, **156**, 64-73.

National Research Council, Report: (1999), *Arsenic in drinking water*. National Academy of Sciences, Washington DC.

Pokhrel D. and Viraraghavan T. (2008), Arsenic removal from an aqueous solution by modified *A. niger* biomass: Batch kinetic and isotherm studies, Journal of Hazardous Materials, **150**, 818-825.

Rahman M. S., Basu A. and Islam M.R. (2008), The removal of As(III) and As(V) from aqueous solutions by waste materials, Bioresour Technol, **99**, 2815-2823.

Sari A., Uluozlu O.D. and Tuzen M. (2011), Equilibrium, thermodynamic and kinetic investigations on biosorption of arsenic from aqueous solutions algae (*Maugeotia genuflexa*) biomass, Chemical Engineering Journal, **167**, 155-161.

Shafique U., Ijaz A., Salman M., Zaman W., Jamil N., Rehman R. and Javaid A. (2012), Removal of arsenic from water using pine leaves, Journal of Taiwan Institute of Chemical Engineers, **43**, 256-263.

Smith A.H. and Smith M.M.H. (2004), Arsenic drinking water regulations in developing countries with extensive exposure, Toxicology, **198**, 39-44.

Su T., Guanc B.X., Tanga Y.B., Gub G. and Wanga J. (2010), Predicting competitive adsorption behavior of major toxic anionic elements onto activated alumina: A speciation-based approach, Journal of Hazardous Materials, **176**, 466-472.

Tuzen M., Sari A., Mendil D., Uluozlu O.D., Soylak M. and Dogan M. (2009), Characterization of biosorption process of As(III) on green algae, Journal of Hazardous Materials, **165**, 566-572.

Vijayaraghavan K., Padmesh T.V.N., Palanivelu K. and Velan M. (2006), Biosorption of nickel(II) ions onto *Sargassum wightii:* application of two-parameter and three-parameter isotherm models, Journal of Hazardous Materials, **B133**: 304-308.

Table 1. FT-IR absorption bands and assignments for okra leaves and arsenic loaded okra leaves

IR peak frequency (cm^{-1})			
Okra leaves	**Okra leaves loaded with As(III)**	**Okra leaves loaded with As(V)**	**Assignment**
3301.25	3280.82	3305.33	Hydrogen bond O-H stretching (phenols or alcohols)
2908.97	2917.14	2913.05	C-H stretching (alkane)
2847.67	2843.59	2851.76	
-	-	1728.04	C=O stretching
1593.19	1593.19	1634.05	C=C bending (aromatic)
1413.39	1417.00	-	O-H bending (carboxylic acid)
-	-	1221.34	C-O stretching (ether or ester)
1147.79	1143.70	1139.61	
1000.68	1012.94	1008.85	C-O stretching (alcohol)

Table 2. Regression parameters for the Fruendlich and Florry-Huggins isotherms by using okra leaves as sorbent at different temperatures

Metals	**As(III)**				**As(V)**			
Temperature (ºC)	30	35	40	45	30	35	40	45
Freundlich								
K_F(µg g^{-1})	4070.0	5020.0	5027.0	5672.0	3040.0	7928.0	10660	13160
n	0.880	0.954	0.945	1.094	0.798	0.753	0.746	0.737
r	0.9962	0.9958	0.9932	0.9865	0.9992	0.9933	0.9965	0.9959
Flory-Huggins								
n_{FH}	5.38	5.44	5.66	5.67	6.02	4.18	3.91	3.71
K_{FH} 10^8	4.71	51.5	57.2	67.6	0.80	0.89	1.16	1.24
ΔG(kJ mol^{-1})	-50.31	-57.26	-58.46	-59.84	-45.85	-46.88	-48.32	-49.27
r	0.9539	0.9746	0.9985	0.9274	0.9715	0.9664	0.9623	0.9616

K_F = Freundlich Constant
n = sorption intensity
K_{FH} = Flory-Huggins model equilibrium constant
ΔG = Gibbs free energy of spontaneity
n_{FH} = Flory-Huggins model exponent represents the number of metal ions of solute occupy active sites of sorbent

Table 3. Kinetics parameters for the adsorption of As(III) and As(V) on okra leaves at various temperatures

Metals	**Second order rate equation**				**Intra-particle Diffusion**		
	K (g /mg.·min.)	q_e (mg/g)	h (m/g. min.)	r	k_{id} (µmol/g. $min^{0.5}$)	C (intercept)	R
As(III)	0.0975	4.14	1.673	0.9996	1.01	42.17	0.9762
As(V)	0.0487	4.62	1.040	0.9998	2.27	39.40	0.9668

K = equilibrium rate constant
q_e = sorption capacity of sorbent at equilibrium
h = initial adsorption rate
r = correlation coefficient
k_{id} = intra-particle diffusion rate constant

Table 4. Thermodynamic constants for the sorption of As(III) and As(V) on the Okra leaves at different temperatures

Metals	**Temp. (K)**	**ΔG (kJ mol^{-1})**	**ΔH (kJ mol^{-1})**	**ΔS (J mol·K^{-1})**
As(III)	303	-50.31		
	308	-57.26		
	313	-58.46		
	318	-59.84	128.5	0.596
As(V)	303	-45.85		
	308	-46.86		
	313	-48.32		
	318	-49.27	25.07	0.234

Table 5. Removal of arsenic from real water samples

Samples	Original arsenic conc. in sample (µg L^{-1})	Amount of arsenic added (µg L^{-1})	% Recovery	Residual amount (µg L^{-1})
1	40.0	-	76.5	09.40
2	40.0	50	89.44	09.50
3	0.68	50	71.98	09.10

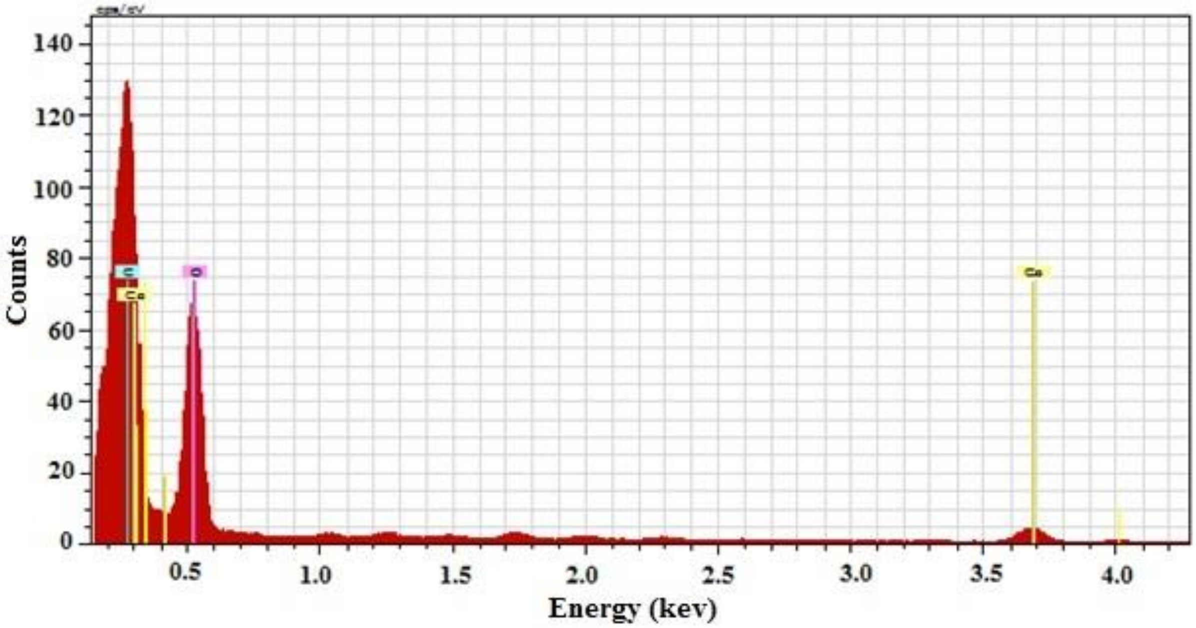


Figure 1a. EDX of okra leaves before arsenic retention.

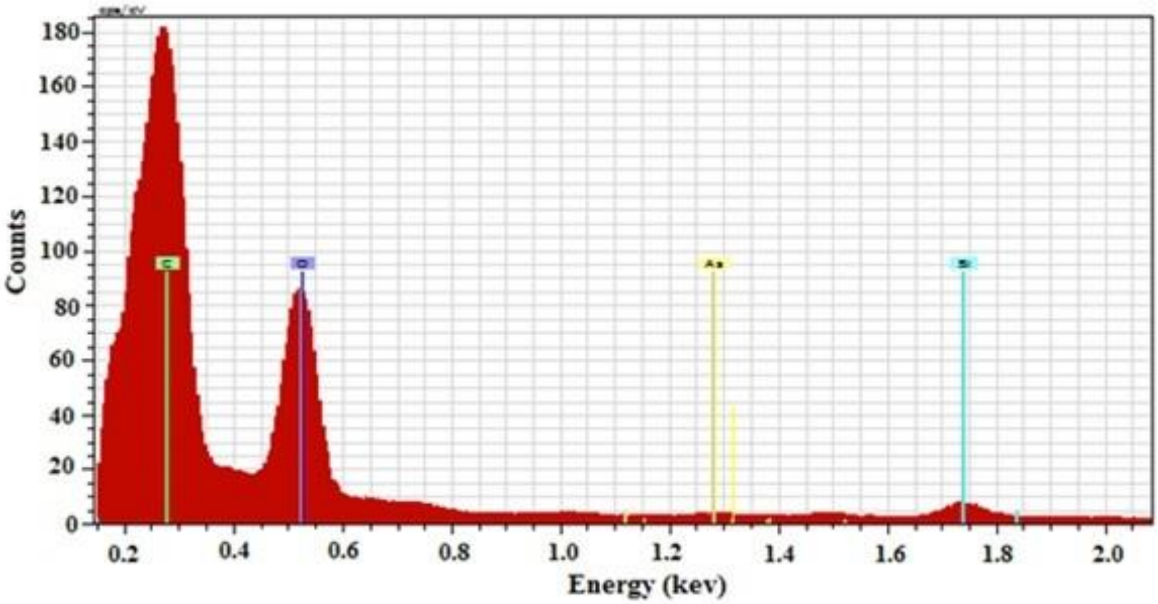


Figure 1b. EDX of okra leaves after arsenic retention.

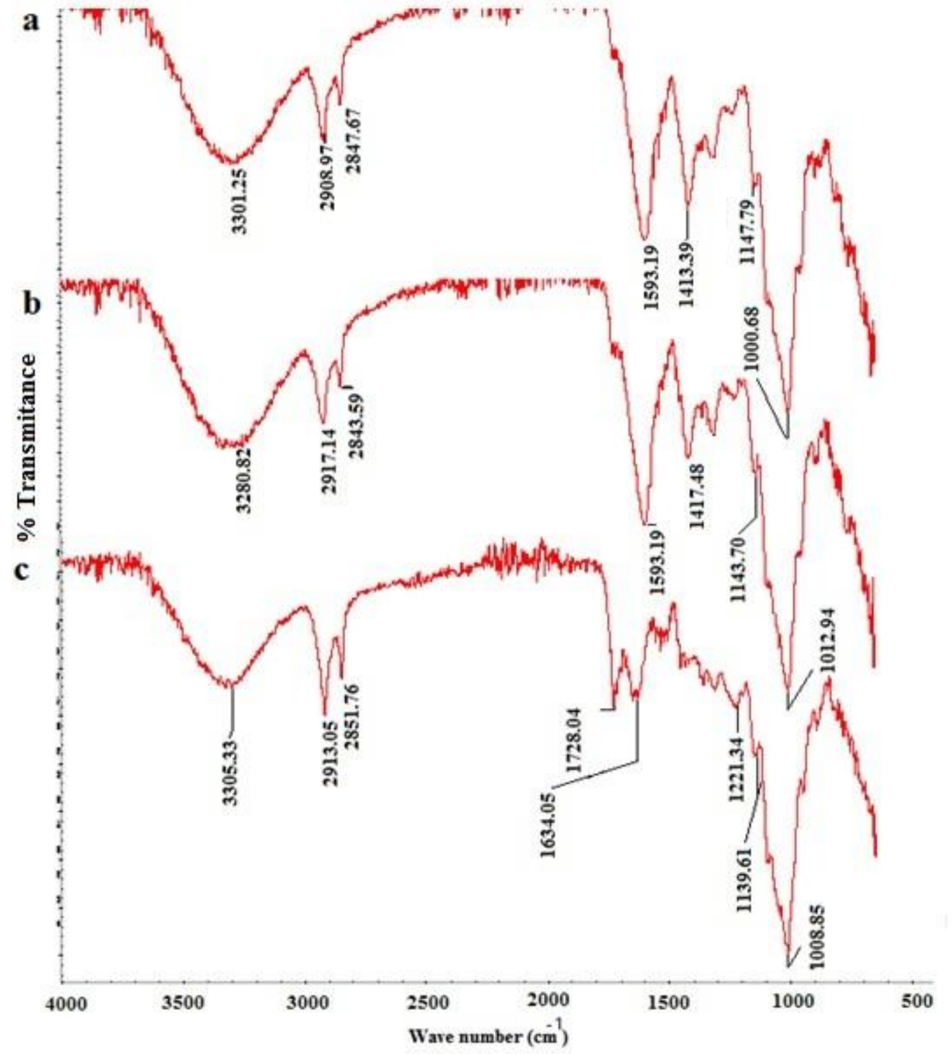


Figure 2.FT-IR spectra of (a)-okra leaves (b)-As(III)-loaded okra leaves (c)-As(V) loaded okra leaves.

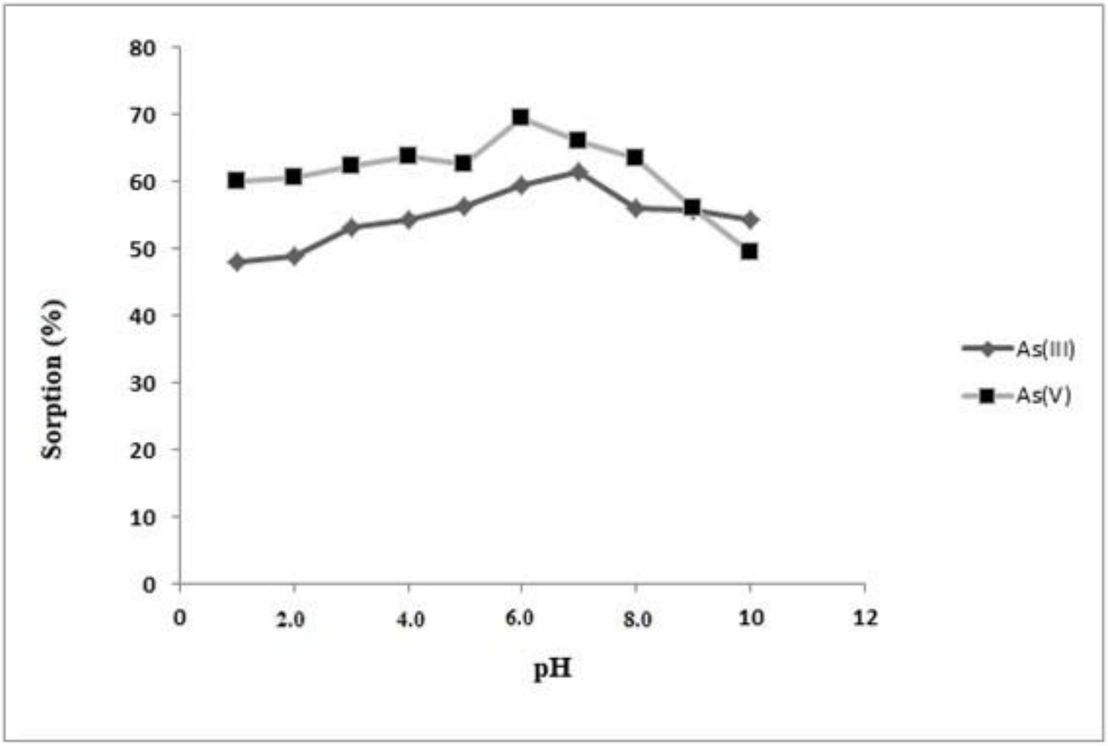


Figure 3. Effect of pH on the sorption of As(III) and As(V).

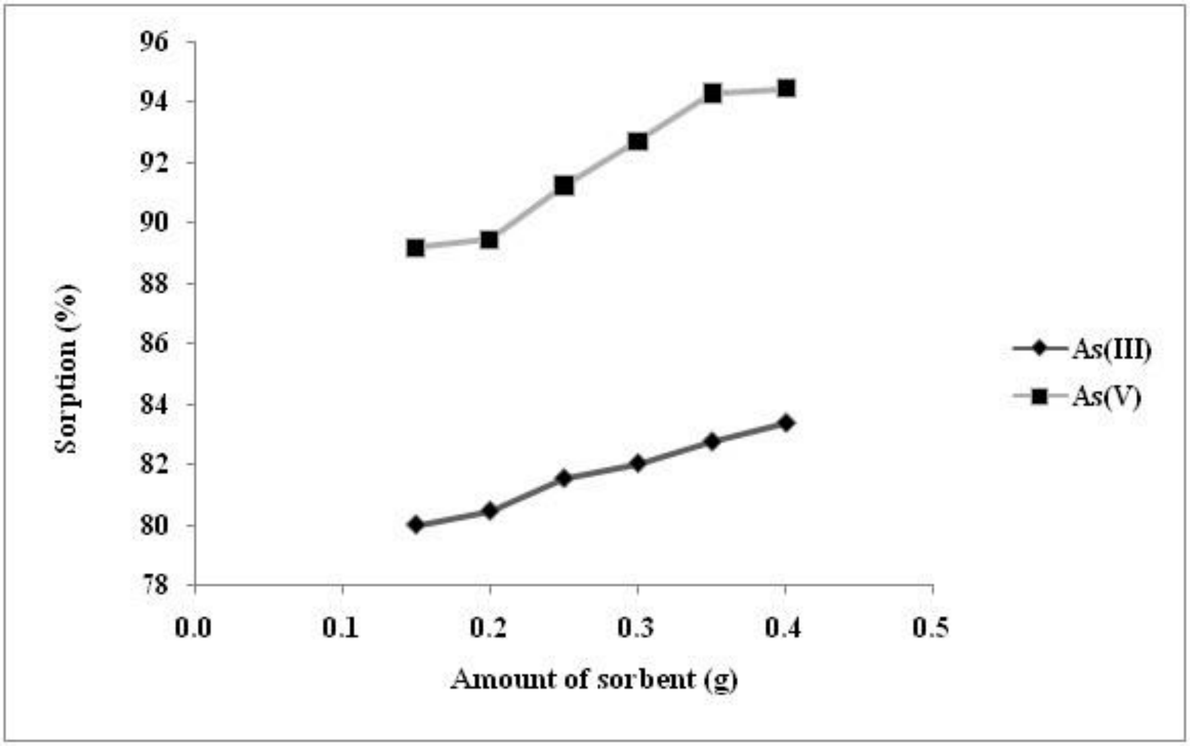


Figure 4. Effect of biomass on the sorption of As(III) and As(V).

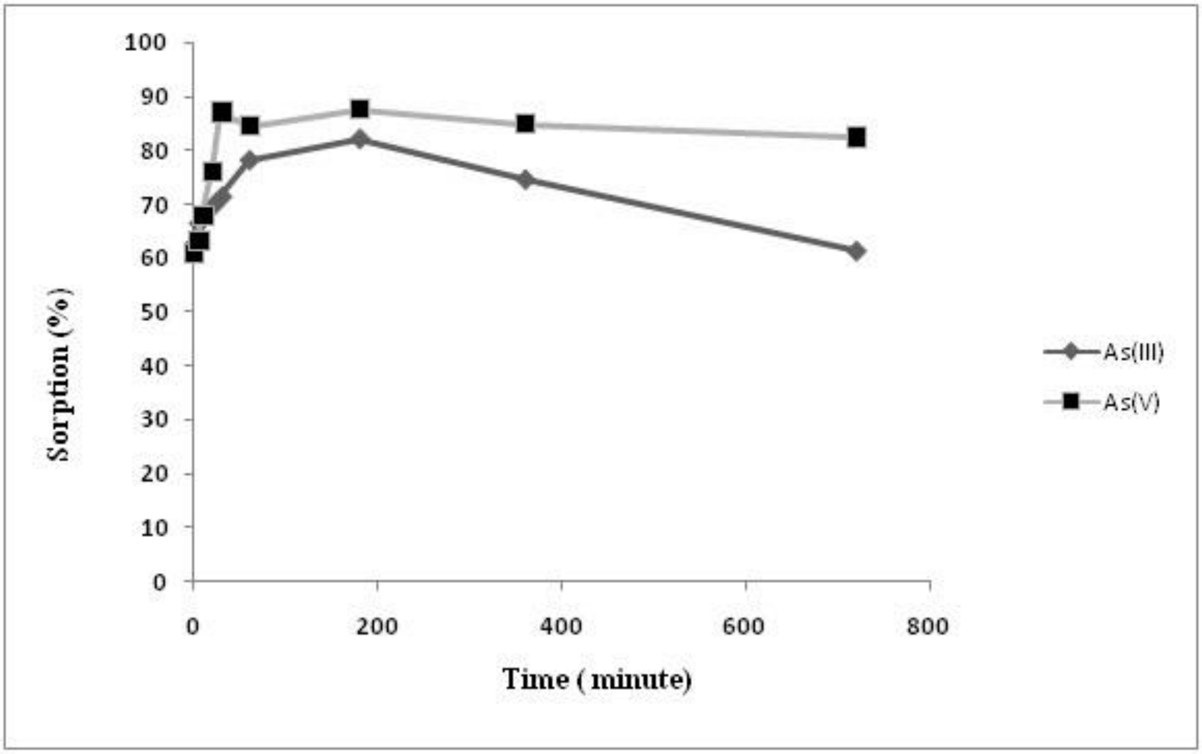


Figure 5. Effect of contact time on the sorption of As(III) and As(V).

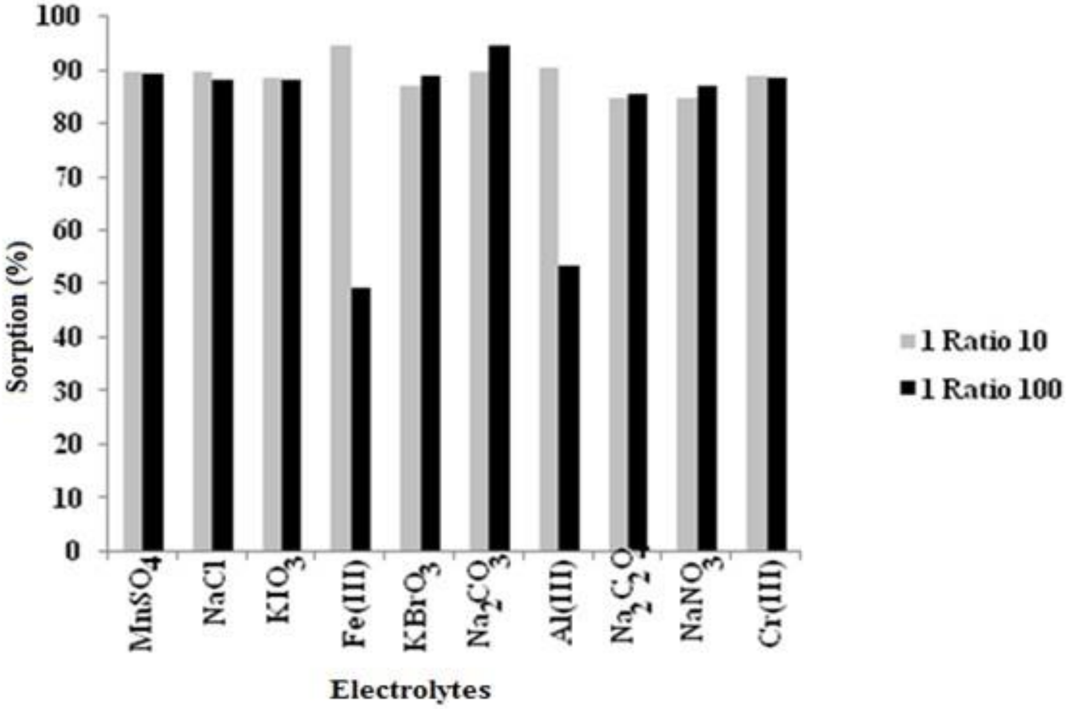


Figure 6a.Electrolytic effect on the sorption of As(III) ions on okra leaves.

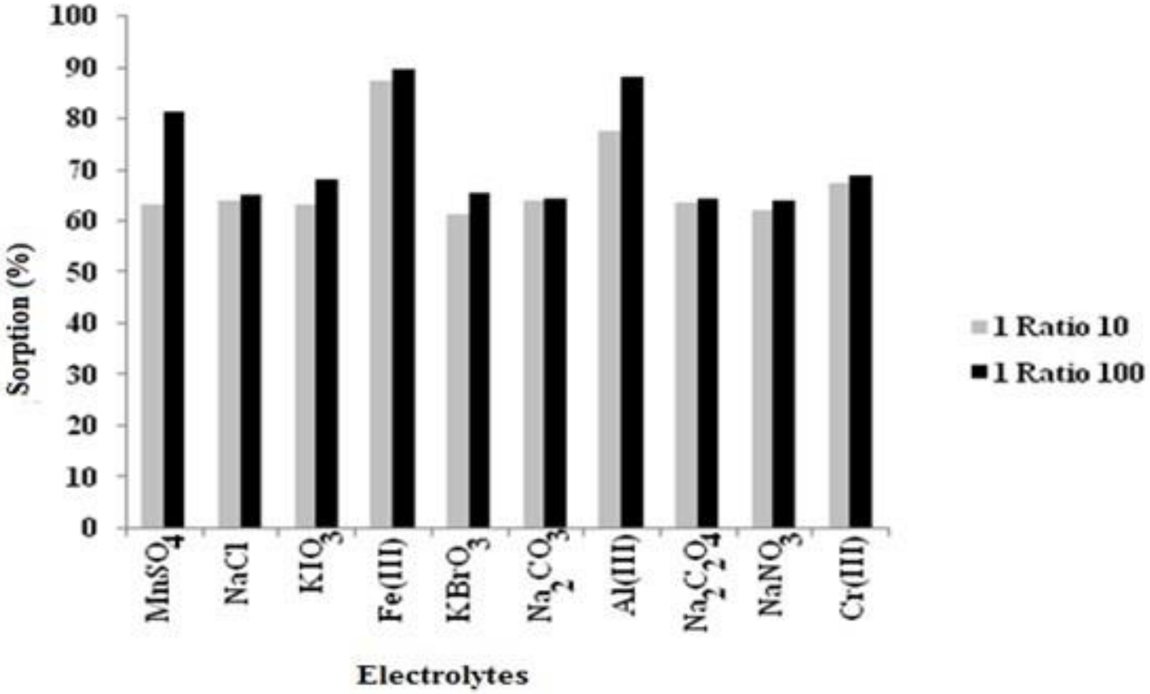


Figure 6b.Electrolytic effect on the sorption of As(V) ions on okra leaves.