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Arsenite and arsenate sorption by hydrous ferric oxide/polymeric material

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Abstract

The occurrence of arsenic in natural ground waters is due to geological composition of soil. There are several methods for removal of arsenic from drinking water, such as coagulation followed by filtration, membrane processes, ion exchange and adsorption. Adsorption methods proved to be effective, economic, easy to perform and construct. The objective of this study was to investigate the removal of arsenic from drinking water using adsorbents prepared by coating the surface of the following polymeric materials: natural alum silicate exchanger zeolite clinoptilolite and ionic exchanger Dowex Marathon C with hydrous ferric oxide. Modified adsorbents were saturated with Fe^{3+} ions from the FeCl_3 solution in acetate buffer solution (pH 3.6) and then converted to hydrous ferric oxide by thermo chemical procedure (NaOH , NaCl , 50°C). Adsorption kinetics of arsenic was investigated as a function of initial arsenite and arsenate concentrations (ranging from 100 to 500 $\mu\text{g/L}$), contact time (from 15 to 360 min) and pH (6.4, 6.9, 7.4, 7.9). The results and sorption characteristics of the prepared hydrous ferric oxide/polymeric material adsorbents were determined using Freundlich and Langmuir adsorption isotherms.

Keywords: Arsenic removal; Adsorption; Ionic exchanger; Zeolite; Hydrous ferric oxides

1. Introduction

Arsenic is a chemical element present in the atmosphere, soil, rocks, natural waters and organisms. Arsenic in drinking water has the greatest impact on the general population and human health. The occurrence of arsenic in natural ground waters is due to geological composition of soil.

High concentrations of arsenic in water are the result of dissolution or desorption of ferric oxides and oxidation of mineral arsenopyrites [1,2] or anthropogenic activities, such as agriculture (the extensive use of herbicides and insecticides) and irregular disposal of hazardous waste from heavy industry [3].

In natural waters arsenic can be found in inorganic forms as oxidized trivalent arsenite ($\text{As}(\text{III})$)

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or pentavalent arsenate (As (V)), mostly as H_2AsO_4^- , HAsO_4^{2-} , H_3AsO_3 and H_2AsO_3^- [4]. Redox potential and pH are the main factors determining the form of arsenic in the water. At lower pH (<6.9) H_2AsO_4^- is a dominant form, while at higher pH the dominant form is HAsO_4^{2-} [5] (Figs. 1 and 2.). The trivalent arsenite species are predominant in moderately reducing anaerobic environments such as groundwater and As(III) is more toxic to the biological systems than As(V) [6–9].

Elevated concentrations of arsenic in ground waters of Eastern Croatia are the result of geological composition of soil. In the Eastern Croatia region, ground water is bailed from several wells and 200,000 people are being supplied by potable

water. The well depths range from 40 to 170 m. Arsenic concentrations in these well waters are 50 to 600 $\mu\text{g/L}$ respectively [10,11].

In 1993 The World Health Organisation set a maximum permissible concentration for arsenic in drinking water at 10 $\mu\text{g/L}$ [12]. Current maximum permissible concentration for arsenic in drinking water in Croatia is also 10 $\mu\text{g/L}$ [13]. However, long term exposure through drinking water to even low concentrations of arsenic ($\leq 50 \mu\text{g/L}$) can cause carcinogenic diseases of skin, lungs, blood and kidneys; as well as hyperkeratosis and hyper pigmentation of skin [14–16].

There are several technologies for arsenic removal from water and their efficiency is dependent on the valence of arsenic. Arsenic is most effectively removed or stabilized when it is present in the pentavalent arsenate form. Most of the technologies include the following processes: precipitation/coagulation, membrane separation, ion exchange and adsorption [17–22].

Adsorption technologies represent innovative, attractive and economic approach to arsenic removal problem. They are characterized by the use of natural and synthetic exchangers whose polymeric structures are saturated by various adsorbents, in order to increase efficiency. Water treatment by adsorption technologies includes simultaneous processes of adsorption and filtration [23–26]. Granular ferric hydroxide; as well as several iron (III) oxides; such as amorphous hydrous ferric oxide, goethite and poorly crystalline hydrous ferric oxide, proved to be promising adsorptive materials for the removal of As(III) and As(V) from aqueous solutions [27–30]. The abovementioned adsorbents are highly efficient, but they are available only as fine powders or are generated in situ as gels, which cause difficulties when it comes to their separation in water treatment process [31]. Thus, finding the optimal carrier that will enable the arsenic removal by column adsorption is an objective of many investigations.

The purpose of this study was to develop a method for preparation of filtration adsorbent for

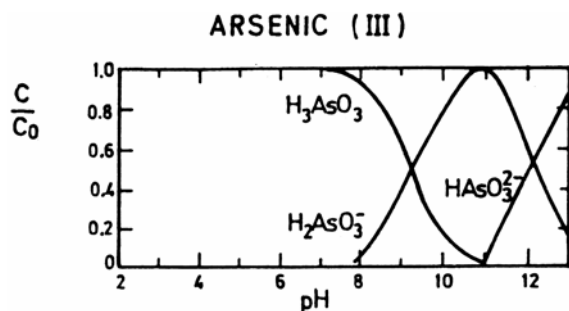


Fig. 1. The stability and predomination of As(III) in the water as a function of pH [4].

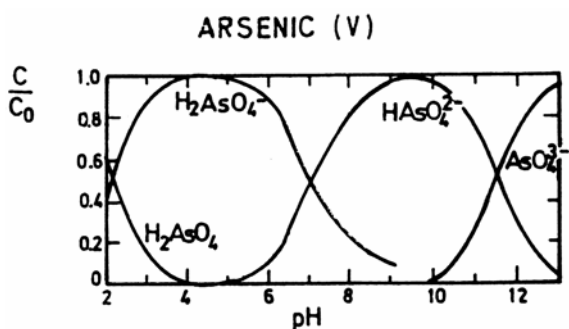


Fig. 2. The stability and predomination of As(V) in the water as a function of pH [4].

arsenic removal from drinking water by coating the surface of the polymeric materials natural alum silicate exchanger zeolite clinoptilolite and ionic exchanger Dowex Marathon C with hydrous ferric oxide.

Adsorption kinetics of arsenic was investigated as a function of initial arsenite and arsenate concentrations, contact time and pH. The results and sorption characteristics of the prepared hydrous ferric oxide/polymeric material adsorbents were determined using Freundlich and Langmuir adsorption isotherms.

2. Materials and methods

2.1. Samples, natural zeolite treatment and preparation of hydrous ferric oxide/zeolite

The investigated sample, natural zeolite clinoptilolite, originates from the mine Donje Jesenje, Croatia. Prior to chemical treatment, natural zeolite sample was grinded in a mortar and then separated using 0.5–0.63 mm sieves. 100 g of zeolite was treated with 500 mL 0.1 M HCl during 24 h. The sample was then rinsed with distilled water, dried and saturated with 500 mL of 0.1 M FeCl_3 in the acetate buffer pH 3.6, during 1 h on a magnetic stirrer. Saturated sample was treated with 4% NaOH solution (450 mL), stirred for an hour and then treated with 4% NaCl solution (250 mL) and stirred for another hour at 50°C. The mixture was transferred to the column, rinsed with distilled water and after that transferred to a glass with 250 mL 50 vol% ethanol and stirred for an hour on a magnetic stirrer at 50°C. The precipitate was filtered, air dried for 24 h and then kept in a desiccator.

2.2. Preparation of hydrous ferric oxide/ionic exchanger Dowex Marathon C

Hydrous ferric oxide/ionic exchanger was prepared according to the following method: 50 g of cationic resin Dowex Marathon C was saturated

with 500 mL of 0.1 M FeCl_3 in the acetate buffer pH 3.6, during 1 h on a magnetic stirrer. Saturated sample was treated with 4% NaOH solution (250 mL) and stirred for an hour. 4% NaCl solution (250 mL) was added to the mixture and stirred for another hour at 50°C. The mixture was transferred to the column, rinsed with distilled water and after that transferred to a glass with 250 mL 50 vol% ethanol and stirred for an hour on a magnetic stirrer at 50°C. The precipitate was filtered, air dried for 24 h and then kept in a desiccator.

2.3. Preparation of arsenite and arsenate standard solutions

Standard solutions of trivalent and pentavalent arsenic were prepared with distilled water. The arsenite stock solution was prepared from 0.01734 g of sodium arsenite NaAsO_2 (Merck, purity >99%) dissolved in distilled water to obtain concentration of 100 $\mu\text{g As}^{3+}/\text{mL}$. The arsenate stock solution was prepared from 0.416 g sodium heptahydrate salt $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Carlo Erba, purity >99%) dissolved in distilled water to obtain concentration of 100 $\mu\text{g As}^{5+}/\text{mL}$.

2.4. Arsenite and arsenate adsorption on hydrous ferric oxide/polymeric material

Adsorption process was conducted within a temperature controlled shaker (Kottermann Labortechnik). The temperature was controlled at 25°C and shaker speed was 120 rpm. Arsenite and arsenate working solutions were prepared by diluting stock solutions with distilled water, concentrations varied from 100 to 600 $\mu\text{g/L}$. Adsorption tests were performed in 100 mL Erlenmeyer flasks: 0.25 g of adsorbent was placed in a flask and 100 ml of prepared arsenite or arsenate solution was added. pH in the Erlenmeyer flasks was adjusted to 7.4 using HCl and NaOH.

The effect of contact time on the adsorption of arsenite and arsenate was investigated for the initial concentration of 200 $\mu\text{g/L}$, for both arsenite

and arsenate solutions, and contact times of 15, 30, 60, 120 and 360 min.

The effect of pH on the adsorption of arsenite and arsenate was investigated for the initial concentrations of 200 $\mu\text{g/L}$ and pH 6.4, 6.9, 7.4 and 7.9. HCl and NaOH were used for pH adjustment.

After the adsorption the samples were filtered on glass filters (150 μm). Residual concentrations of arsenic were determined using a Specord 200 spectrophotometer by the standard spectrophotometric method of determining arsenic using Ag-diethyldithiocarbamate (ISO 6595-1982). The detection limit for this method is 1 $\mu\text{g/L}$ of arsenic.

3. Results and discussion

3.1. Effect of contact time

Fig. 3 shows the effect of contact time on the adsorption of As(III) and As(V) by the use of modified adsorbents: zeolite (MZ) and cationic

exchanger resin (MCER). It is clear from the figure that adsorption of As(V) on MZ and MCER, as well as adsorption of As(III) on MCER increase significantly with time and achieve saturation in 360 min for all three cases. Adsorption of As(III) on MZ does not exhibit significant changes of adsorbed arsenic uptake with time.

3.2. Effect of pH

The effect of pH on the adsorbent process is shown in Fig. 4. The experiments were undertaken at initial As(III) and As(V) concentrations of 200 $\mu\text{g/L}$, adsorbent dose 0.25 g/100 mL and temperature of 25°C. Adsorption percentage of As(III) on MCER increased with the increase of pH. However, adsorption percentage of As(V) decreased with the increase of pH on both modified adsorbents: MZ and MCER. The effect of pH on the adsorption of As(III) on MZ was not significant.

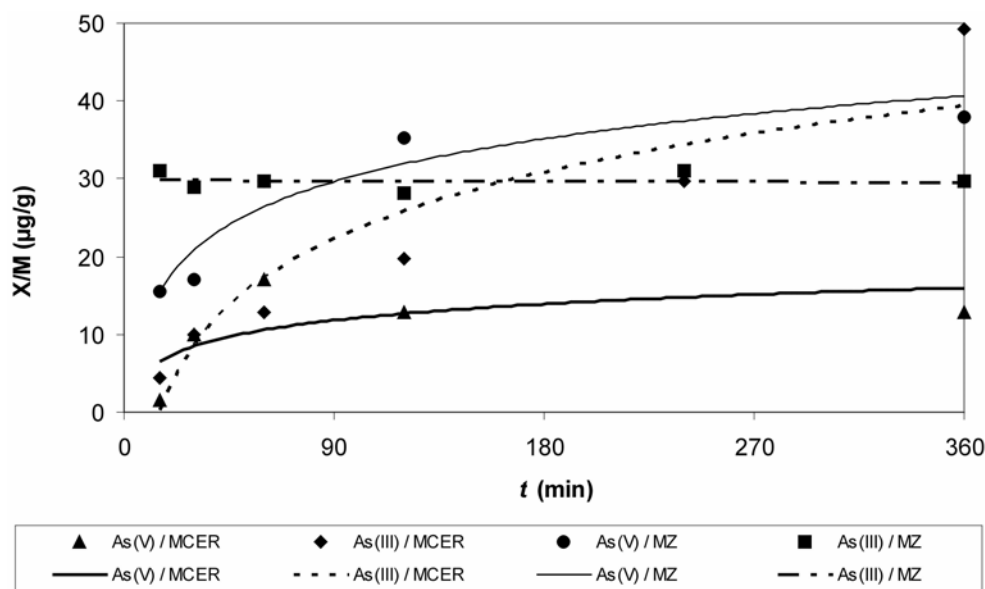


Fig. 3. Effect of contact time on the adsorption of As(III) and As(V) on various carriers coated with hydrous ferric oxide ($c = 200 \mu\text{g/L}$; pH 7.4; $T = 25^\circ\text{C}$; m (adsorbent) = 0.25 g; 120 min^{-1}).

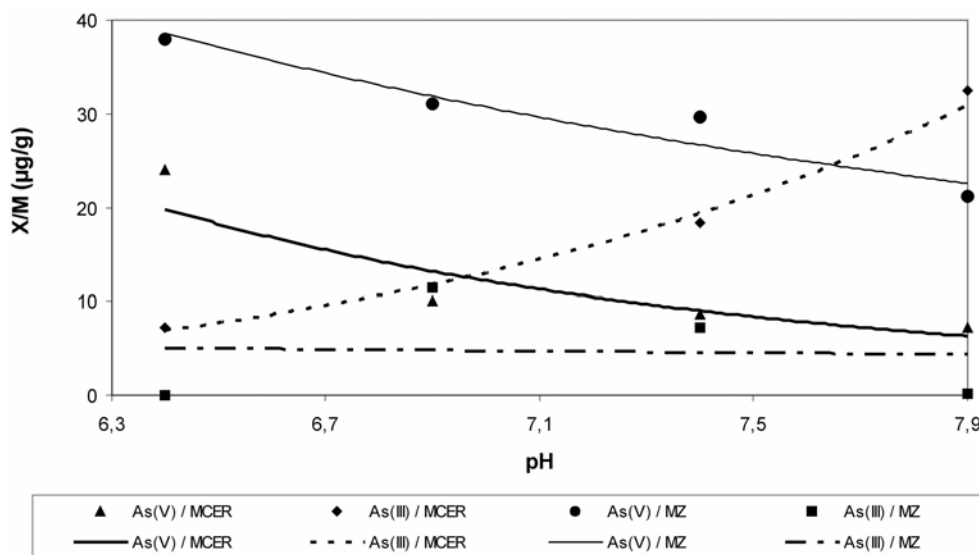


Fig. 4. Effect of pH on the adsorption of As(III) and As(V) on various carriers coated with hydrous ferric oxide ($c = 200 \mu\text{g/L}$; $t = 180 \text{ min}$; $T = 25^\circ\text{C}$; $m(\text{adsorbent}) = 0.25 \text{ g}$; 120 min^{-1}).

3.3. Effect of initial concentration

Fig. 5 shows that adsorption percentage of arsenic decreased with the increase of initial concentration of arsenic for both modified adsorbents MZ and MCER. For the adsorption of As(III) on MZ the effect of initial concentration on the adsorption percentage of arsenic seems to be significant, a little less significant is in the case of As(V) adsorption on MZ and MCER. The effect of initial concentration seems to be insignificant in the case of As(III) adsorption on MCER.

3.4. Adsorption dynamics

Kinetics of adsorption process describes a relationship determined at a constant temperature between the amount of chemical adsorbed and the amount of adsorbent used. To quantify the adsorption capacity of MCER and MZ, for removal of As(III) and As(V) from water, Langmuir and Freundlich adsorption equations were used.

The Freundlich equation is an empirical equation that accurately describes many adsorption

data. The equation is an exponential equation of the form:

Exponential form

$$X/M = K \cdot C_e^{1/n} \quad (1)$$

Linear form

$$\log(X/M) = \log K + 1/n \cdot \log C_e \quad (2)$$

The constant K is related primarily to the capacity of the adsorbent to adsorb arsenic. Larger values of K mean larger capacities of adsorption. The constant $1/n$ is a function of the strength of adsorption. Larger values of $1/n$ mean that the adsorption bond is weak because the value of X/M experiences large changes for small changes in C_e . Smaller values of $1/n$ mean that the adsorption bond is strong.

The results summarized in Table 1 show that K constant is the highest for As(III) adsorption on MCER, while for As(V) adsorption K values are similar for both used adsorbents at pH 7. As(V)

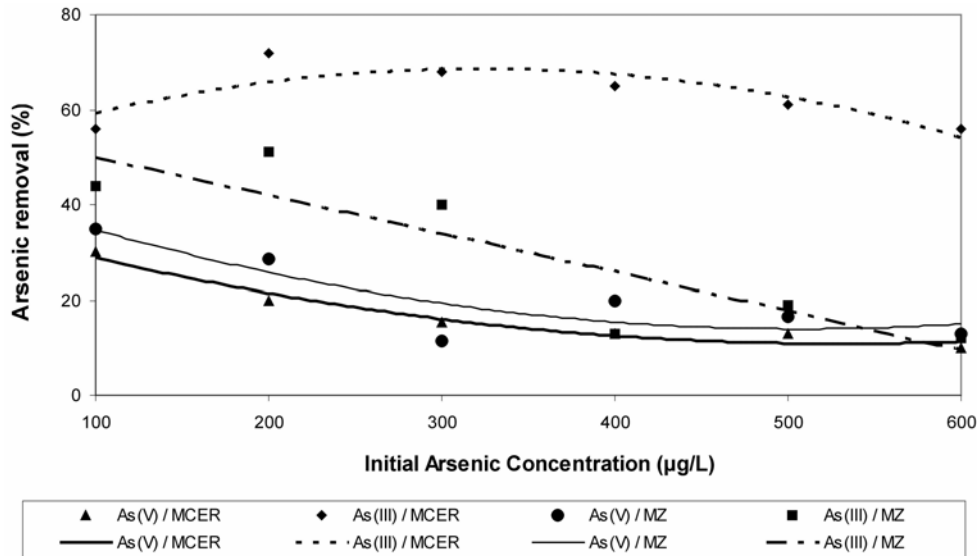


Fig. 5. The effect of initial arsenic concentration on the adsorption of As(III) and As(V) on various carriers coated with hydrous ferric oxide ($c = 200 \mu\text{g/L}$; $t = 180 \text{ min}$; $T = 25^\circ\text{C}$; m (adsorbent) = 0.25 g ; 120 min^{-1}).

Table 1

Freundlich and Langmuir constants for arsenic adsorption on hydrous ferric oxide on various carriers

Adsorbent	Freundlich constants			Langmuir constants			
	K	$1/n$	R^2	x_m	k	$k \cdot x_m$	R^2
As(III)/MCER	6.484	0.5516	0.9839	218.341	0.0065	1.419	0.9950
As(V)/MCER	2.268	0.3856	0.9303	35.625	0.0045	0.1603	0.9836
As(V)/MZ	2.137	0.4621	0.9756	44.385	0.0071	0.3151	0.9989

adsorption on MCER has the highest $1/n$ constant, which means that adsorption bond between the As(V) ion and adsorbent is the strongest.

Correlation coefficient (R^2) for all the isotherms ranged between 0.93 and 0.98, representing an excellent fit of observing data. Fig. 6 shows the Freundlich isotherms for the three sets of data at pH 7.4, where the best removal occurred. The two linearized plots are very close to each other, and one is higher representing the better adsorption of As(III) ions on MCER.

The Langmuir isotherm is derived assuming the following: a limited area available for adsorption, arsenic is adsorbed in a monomolecular layer, adsorption is reversible and equilibrium is achieved. The equation is of the form:

Exponential form

$$X/M = x_m \cdot k \cdot C_e / (1 + k \cdot C_e) \quad (3)$$

Linear form

$$M/X = 1/x_m + (1/x_m \cdot k) \cdot 1/C_e \quad (4)$$

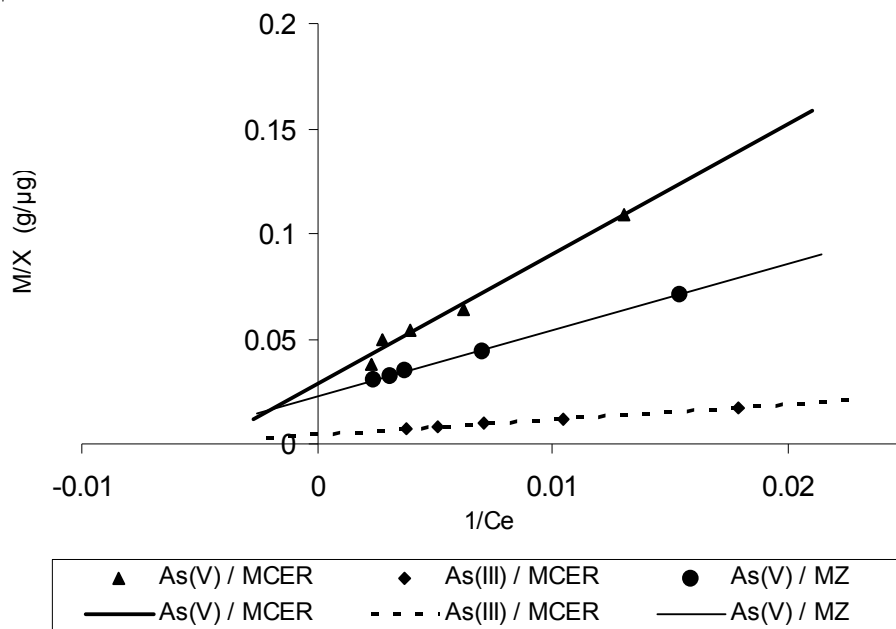


Fig. 6. Freundlich isotherms for arsenic adsorption on various carriers coated with hydrous ferric oxide ($t = 180$ min; pH 7.4; $T = 25^\circ\text{C}$; m (adsorbent) = 0.25 g; 120 min^{-1}).

The linear plots of M/X vs. $1/C_e$ for both MZ and MCER (Fig. 7) indicate applicability of Langmuir adsorption isotherm, consequently suggesting the formation of monolayer coverage of the adsorbate on the surface of the adsorbent in the concentration range studies. Fig. 7 shows Langmuir isotherms calculated for the three sets of data at pH 7.4 where the best removal occurred.

4. Conclusion

This study investigated the removal of arsenite and arsenate compounds from the contaminated water using modified ionic exchanger and modified zeolite as adsorbents. The effect of contact time, pH and initial concentration on adsorption process was also investigated. Adsorption percentage of As(III) ions increased with the increase of pH and contact time when modified ionic ex-

changer resin was used as adsorbent. Increase of the initial concentration, however, had no significant effect on the As(III) ions adsorption.

Unlike modified ionic exchanger resin, when modified zeolite was used adsorption percentage of As(III) did not increase significantly with the increase of pH and contact time. Increase of the initial concentration resulted in the decrease of the amount of As(III) adsorbed. Both modified adsorbents showed similar characteristics for As(V) adsorption processes: adsorption percentage of As(V) increased with the increase of contact time, while the increase of pH and initial concentration resulted in the decrease of the As(V) adsorbed. Maximum As(III) adsorption was achieved when modified ionic exchanger was used as adsorbent at pH 7.4. Maximum As(V) adsorption was achieved when modified zeolite was used at pH 6.4.

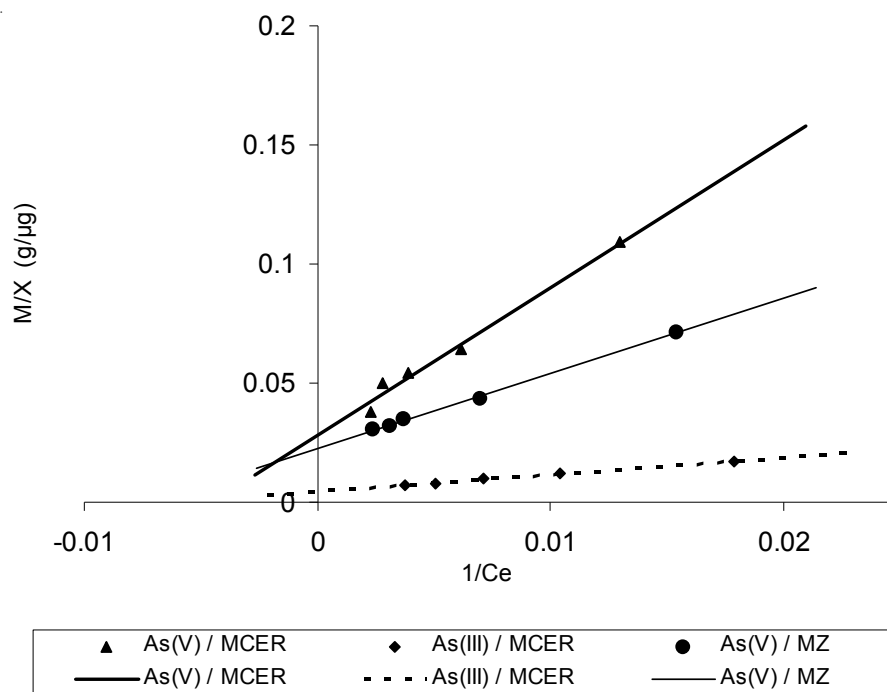


Fig. 7. Langmuir isotherms for arsenic adsorption on various carriers coated with hydrous ferric oxide ($t = 180$ min; pH 7.4; $T = 25^\circ\text{C}$; m (adsorbent) = 0.25 g; 120 min^{-1}).

Symbols

- X — Mass of absorbed arsenic, $\mu\text{g}/100 \text{ mL}$
 M — Mass of adsorbent, g
 C_e — Equilibrium concentration of arsenic in solution after adsorption, $\mu\text{g}/\text{L}$
 K — Constant, $\mu\text{g}/\text{g}$
 n — Constant
 x_m — The limiting value for x (monolayer capacity), g/mg
 k — Constant relating to the energy of sorption

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