

# Adsorption characteristics of As(III) from aqueous solution on iron oxide coated cement (IOCC)

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## Abstract

Contamination of potable groundwater with arsenic is a serious health hazard, which calls for proper treatment before its use as drinking water. The objective of the present study is to assess the effectiveness of iron oxide coated cement (IOCC) for As(III) adsorption from aqueous solution. Batch studies were conducted to study As(III) adsorption onto IOCC at ambient temperature as a function of adsorbent dose, pH, contact time, initial arsenic concentration and temperature. Kinetics reveal that the uptake of As(III) ion is very rapid and most of fixation occurs within the first 20 min of contact. The pseudo-second order rate equation successfully described the adsorption kinetics. Langmuir, Freundlich, Redlich–Peterson (R–P), and Dubinin–Radushkevich (D–R) models were used to describe the adsorption isotherms at different initial As(III) concentrations and at 30 g l<sup>-1</sup> fixed adsorbent dose. The maximum adsorption capacity of IOCC for As(III) determined from the Langmuir isotherm was 0.69 mg g<sup>-1</sup>. The mean free energy of adsorption (*E*) calculated from the D–R isotherm was found to be 2.86 kJ mol<sup>-1</sup> which suggests physisorption. Thermodynamic parameters indicate an exothermic nature of adsorption and a spontaneous and favourable process. The results suggest that IOCC can be suitably used for As(III) removal from aqueous solutions.

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**Keywords:** As(III); Iron oxide coated cement; Adsorption; Isotherms; Thermodynamics

## 1. Introduction

Groundwater is generally considered a safe source of drinking water, which is usually free from microbiological contaminants and may be supplied without much treatment. However, in recent years, contamination of potable groundwater with arsenic has become a global concern (elevated arsenic concentrations have been found in many regions in different parts of the world [1]) and probably poses the greatest threat to human health. Hence, there is an urgent need for processes to selectively remove arsenic from potable water. Following various epidemiological evidences on arsenic carcinogenicity and other deleterious effects on humans [2,3], the WHO drinking water guideline for arsenic was lowered from 0.05 to 0.01 mg l<sup>-1</sup> in 1993 [4], and countries have since adopted the new value as a drinking water standard. In January 2001, the USEPA lowered the USA drinking water limit from 0.05 to 0.01 mg l<sup>-1</sup> [5].

Arsenic can exist in the environment in both organic and inorganic forms and in several oxidation states (-3, 0, +3, and +5), but in natural waters it is mostly found in inorganic form as oxyanions of trivalent [As(III)] or pentavalent arsenic [As(V)] as organic arsenic undergoes biotransformation and detoxifies through methylation. Arsenate species (pentavalent state) are stable in oxygenated waters. Under anoxic and reducing conditions, arsenites (trivalent state) predominate [1]. The toxicity of arsenic firmly depends on its oxidation state, and trivalent arsenic has been reported to be more toxic than pentavalent and organic arsenicals [6]. Thus, there is an immediate need to develop technologies that are effective for arsenic removal especially As(III) as well as cater to the needs of people living in small communities in developing countries. Numerous treatment technologies like adsorption, ion-exchange, precipitation, coagulation and filtration, reverse osmosis, electro-dialysis, modified lime softening and oxidation/filtration [1,7] have been developed for the removal of arsenic from water. Recently, bioremediation of arsenic is also gaining increasing attention and application due to the existence of certain advantages, besides being economical, over the conventional physicochemical treatment methods [8,9]. However, adsorption still remains an attractive and promising

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technology because of its simplicity, ease of operation and handling, sludge free operation, and regeneration capacity. Various attempts are being made by researchers to develop a suitable adsorbent for the removal of As(III) from water. Removal of As(III) from water by adsorption on coconut husk carbon [10], MnO<sub>2</sub> coated sand [11], basic yttrium carbonate [12], activated alumina [13], carbon from fly ash [14], granular titanium dioxide [15], and hybrid polymeric sorbent [16] were investigated. Considering the affinity of arsenic toward iron, various types of iron ores, iron oxides, iron oxide coated materials and also zerovalent iron [17–19] have been effectively used as adsorbents for the removal of both As(III) and As(V) from the aqueous environment. However, the occurrence of iron oxides in fine powdery forms limits their use in column operations. Adsorption of As(III) by amorphous iron hydroxide [20], hematite [21], iron(III) hydroxide loaded coral lime stone (Fe-coral) [22], iron oxide coated sand [23,24], iron oxide-impregnated alumina [25], iron oxide coated granulated activated carbon [26], and red mud [27] has been reported in literature. However, in most of the cases difficulty in regeneration, low adsorption capacities of the sorbents, high pressure loss during column runs, lack of extensive studies are some of the disadvantages that limit their use. Iron oxide coated cement (IOCC), the adsorbent used in the present study, has been found to be very effective in the removal of As(V) [1] and also arsenic from real life groundwater samples.

The aim of the present study is to investigate the sorption characteristics of As(III) onto IOCC from aqueous environment under various kinetic, equilibrium, and thermodynamic conditions with a view to achieve a feasible solution to the arsenic contaminated potable water problem in small community systems. Batch experiments were carried out to study the ability of IOCC to adsorb As(III) from solution as a function of some experimental parameters. The values of well-known thermodynamic functions have been determined and isotherm studies at room temperature ( $27 \pm 2^\circ\text{C}$ ) have been performed to elucidate the equilibrium of the removal of As(III).

## 2. Materials and methods

### 2.1. Materials

All the chemicals used in the study were of analytical grade. Double distilled water was used in preparation of all the solutions. For all the batch adsorption experiments, stock solutions containing  $1000\text{ mg l}^{-1}$  of As(III) were prepared by dissolving NaAsO<sub>2</sub> (LOBA Chemie) in the double distilled water. Working solutions, as per the experimental requirements, were freshly prepared from the stock solution for each experimental run. Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merck) was used for the coating process. 0.1N HCl (Merck) and 0.1N NaOH (Merck) solutions were used for pH adjustment.

### 2.2. Synthesis and characterization of IOCC

The iron oxide coated cement adsorbent used in this study was prepared by mixing 100 g white cement granules (geometric mean size = 212 μm) in a solution of Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O prepared

by dissolving 50 g Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 150 ml water and then heating the mixture at 100 °C for 16 h, with frequent stirring to maintain the homogeneity of the mixture. The detailed procedure for the preparation of IOCC has already been reported [1].

IOCC was characterized by X-ray diffraction (XRD), physical and chemical analyses. Energy dispersive X-ray (EDX) analysis was used to determine the chemical composition of IOCC. The pH of the point of zero charge (pH<sub>PZC</sub>) of IOCC was determined using a method suggested by Noh and Schwarz [28].

The total coated iron on IOCC was determined as per the method described by Kuan et al. [29]. The suspension was filtered using Whatman No. 42 filter paper and the filtrate was analysed for iron.

A quantitative analysis of the loss of iron from the adsorbent, which may occur after the adsorption experiment, was undertaken by conducting a leachability test. One gram of IOCC was agitated with 50 ml of distilled water on a rotary shaker for 24 h. The adsorbent was filtered by Whatman No. 42 filter paper and the filtrate was analysed for iron.

### 2.3. Analysis

Quantitative determination of arsenic was done with the help of UV–visible spectrophotometer (Thermospectronic, Model No. UV-1, UK) at a wavelength of 535 nm, by the silver dithiodiethylcarbamate method (minimum detectable quantity = 1 μg As), commonly known as the SDDC method [30].

Iron was measured using flame atomic adsorption spectrophotometry (Shimadzu, Model AA-6650) [30]. The pH measurements were done by Cyber Scan 510 pH meter, Oakton Instruments, USA. The adsorption experiments were studied by the batch technique using a temperature controlled BOD incubator shaker (Sambros, India, Model No. TM/34C/10/S).

The IOCC adsorbent was analysed by X-ray diffraction using a Miniflex diffractometer 30 kV, 10 Maq; Rigaku Corp., Tokyo, Japan, with Cu Kα source and a scan rate of  $2^\circ\text{ min}^{-1}$  at room temperature and energy dispersive X-ray (EDX) analysis with an Oxford ISIS-300 model.

### 2.4. Sorption studies

Adsorption tests of As(III) on IOCC were carried out in the batch reactor. The batch sorption experiments were conducted to obtain the data for the equilibrium, kinetic and thermodynamic parameters, using 150 ml capacity polyethylene bottles (Tarson Co. Ltd., India) containing 50 ml of As(III) solution at desired concentrations and pH. The adsorbent was added to the As(III) solution as per the required dose and the test bottles were shaken in the BOD incubator shaker, at a speed of  $180 \pm 10\text{ rpm}$ . The samples were collected at definite time intervals and were filtered using Whatman No. 42 filter paper to remove the adsorbent and the filtrate analysed for residual arsenic after adsorption. The amount of As(III) adsorbed was calculated from the difference between the initial and final solution concentrations.

The equilibrium, kinetic, and thermodynamic results are given as units of adsorbed As(III) quantity per gram of adsorbent at any time and at equilibrium.

Table 1  
Properties of the IOCC medium

Chemical composition of the IOCC media (wt%)		Some other properties of the IOCC media	
		Properties	Quantitative value
MgO	0.58	Geometric mean size (mm)	0.212
Al <sub>2</sub> O <sub>3</sub>	11.06	Bulk density (g cm <sup>-3</sup> )	1.43
Quartz	9.72	Porosity	0.56
CaO	55.11	Specific gravity	2.54
Fe-oxide	23.53	Iron content (mg Fe/g adsorbent)	22.5
		pH of point of zero charge (pH <sub>PZC</sub> )	11.1

The amount of As(III) adsorbed per unit mass at any time ( $q_t$ , mg g<sup>-1</sup>) and at equilibrium ( $q_e$ , mg g<sup>-1</sup>) was calculated as  $q_t = (C_i - C_t)/m$  and  $q_e = (C_i - C_e)/m$ , respectively, where  $C_i$ ,  $C_t$ , and  $C_e$  are the initial, any time ( $t$ ) and equilibrium concentrations of As(III) ions in solution (mg l<sup>-1</sup>), respectively, and  $m$  is the adsorbent dose (g l<sup>-1</sup>).

The adsorption efficiency ( $R\%$ ) of the system determined as the As(III) removal percentage relative to the initial amount, is expressed as

$$R\% = \frac{C_i - C_t}{C_i} \times 100 \quad (1)$$

Experiments to study the effect of adsorbent dose were done by varying the dose from 5 to 40 g l<sup>-1</sup> at a fixed initial pH of 7 with an initial As(III) concentration of 1 mg l<sup>-1</sup> and a contact time of 2 h. The effect of initial pH (3.2–12) on the As(III) removal were conducted with initial As(III) concentration of 1.35 mg l<sup>-1</sup>, an adsorbent dose of 30 g l<sup>-1</sup> and a contact time of 2 h. The kinetic study (5–180 min) was done with an initial As(III) concentration of 1.35 mg l<sup>-1</sup> and an adsorbent dose of 30 g l<sup>-1</sup>. Isotherm studies were performed by varying the initial As(III) concentrations (0.5–10 mg l<sup>-1</sup>) keeping the adsorbent dose fixed at 30 g l<sup>-1</sup>. The thermodynamic studies were done with an initial As(III) concentration of 1.35 mg l<sup>-1</sup> at temperatures of 15, 25, 35, and 45 °C. Equilibrium time for the isotherm and thermodynamic studies was kept as 2 h. No pH adjustments were done for the kinetic, thermodynamic and isotherm studies. Except the thermodynamic studies, all the other experiments were carried out at room temperature (27 ± 2 °C).

Experiments were duplicated to check the reproducibility and the mean values were considered. The limit of experimental error of duplicates was ±5%. The blank experiments showed no detectable As(III) adsorbed on the walls of the flask.

### 3. Results and discussion

#### 3.1. Characterisation of the IOCC

The chemical composition of IOCC determined by the EDX analysis, is presented in Table 1. It emerges that the chief constituents of IOCC are CaO (55.11 wt%) and Fe-oxide (23.53 wt%). The presence of iron oxide at such a higher percentage indicates the effectiveness of the iron oxide coating as white cement alone contains a very meagre quantity of iron in the range of 0.4 wt%. Table 1 also presents some other properties of IOCC.

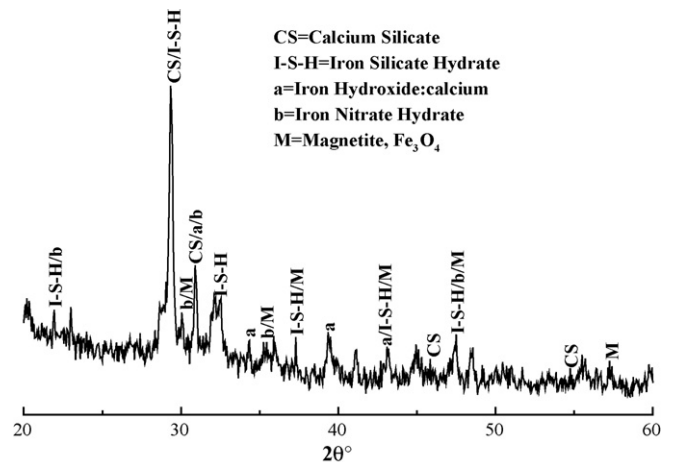


Fig. 1. X-ray diffraction pattern on IOCC.

The diffractograms presented in Fig. 1 showed that in addition to the hydration products of cement (portlandite [Ca(OH)<sub>2</sub>] (20–25%) and amorphous calcium–silica–hydrate [C–S–H] (60–70%) [31]), there is dominance of the magnetite (Fe<sub>3</sub>O<sub>4</sub>) variety of iron oxide. Table 2 shows the observed  $d$ -values (interplanar spacing) for Fe<sub>3</sub>O<sub>4</sub> in comparison with the standard literature values. However, traces of other iron compounds have also been found.

Pure iron oxides, whether they can be identified as having a particular crystal structure or not, typically have PZCs in the range 7–9 [32]. The fact that the measured PZC of IOCC is higher than that of any pure iron oxide may be attributed to the cement matrix. Comparative studies done on the removal of As(III) using IOCC and cement without coating indicated that IOCC removes a markedly higher percentage of As(III) which suggest that the iron oxide dominates IOCC–solution interactions.

Table 2  
X-ray diffraction data of Fe<sub>3</sub>O<sub>4</sub> obtained after iron oxide coating

Observed $d$ -value (nm)	Standard $d$ -value <sup>a</sup> (nm)
2.971	2.967 (2 2 0) <sup>b</sup>
2.546	2.531 (3 1 1)
2.411	2.423 (2 2 2)
2.099	2.098 (4 0 0)
1.914	1.925 (3 3 1)
1.609	1.615 (5 1 1)

<sup>a</sup>  $d = \frac{n\lambda}{2\sin\theta}$ , where  $n = 1$  and  $\lambda = 1.5418 \text{ \AA}$ .

<sup>b</sup> The numbers in brackets indicate Miller indices ( $hkl$ ).

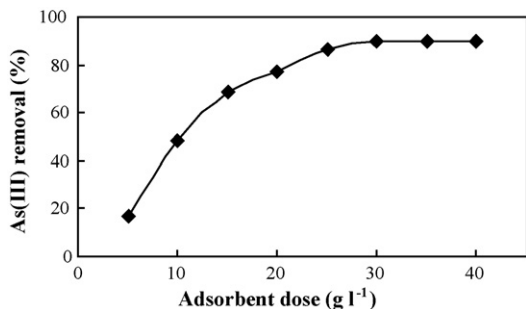


Fig. 2. Effect of adsorbent dose on As(III) uptake by IOCC ( $T: 27 \pm 2^\circ\text{C}$ ;  $C_0: 1.0\text{ mg l}^{-1}$ ;  $t_{\text{eq}}: 2\text{ h}$ ;  $\text{pH } 7$ ).

Iron leaching from the adsorbent obtained from the leachability test was found to be very insignificant in the range of  $0.018\text{--}0.02\text{ mg l}^{-1}$ .

### 3.2. Adsorption study

#### 3.2.1. Effect of adsorbent dose

The effect of adsorbent dose on the removal of As(III) is shown in Fig. 2, which indicates a good amount of increase in the As(III) uptake as the adsorbent dose increases from  $5\text{ to }25\text{ g l}^{-1}$ . This increase may be attributed to the increase in the adsorption surface which in turn accounts for higher As(III) fixation as the dose is increased. Beyond  $30\text{ g l}^{-1}$ , the As(III) removal becomes more or less constant. Therefore, an adsorbent dose of  $30\text{ g l}^{-1}$  of IOCC was selected for all further experiments.

#### 3.2.2. Effect of pH

The uptake of As(III) at various initial pH levels ( $3.2\text{--}12$ ) for an arsenic concentration of  $1.35\text{ mg l}^{-1}$  was studied to determine the optimum pH and is shown in Fig. 3. It is evident from Fig. 2 that at near neutral pH values ( $6 < \text{pH} < 8$ ), As(III) removal was more with maximum removal ( $89.8\%$ ) at  $\text{pH } 6.7$ . This somewhat agrees with the other results obtained on pillared clays and iron oxides [3], carbon-based adsorbents [14] and on zerovalent iron [33]. Perusal of Fig. 3 reveals that the percentage of As(III) removal is not much effected ( $74.6\text{--}89.8\%$ ) over the pH range investigated. However, it is clear that there is a decrease in the As(III) removal efficiency beyond  $\text{pH } 8$  with the lowest removal efficiency at  $\text{pH } 10 < \text{pH} < 12$ . When the pH is above 9, the negatively charged  $\text{H}_3\text{AsO}_3^-$  becomes predominant [33],

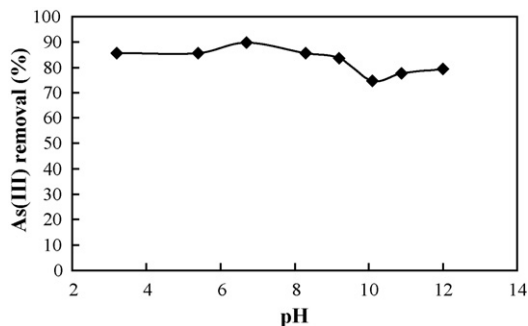


Fig. 3. Effect of pH on As(III) adsorption by IOCC ( $T: 27 \pm 2^\circ\text{C}$ ;  $C_0: 1.35\text{ mg l}^{-1}$ ;  $t_{\text{eq}}: 2\text{ h}$ ; sorbent dose:  $30\text{ g l}^{-1}$ ).

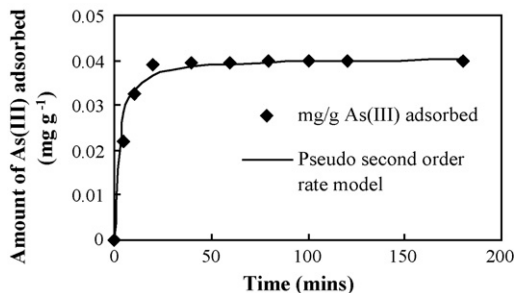


Fig. 4. Adsorption kinetics of As(III) on IOCC adjusted by pseudo-second order rate model ( $\text{pH } \sim 7$ ;  $T: 27 \pm 2^\circ\text{C}$ ; sorbent dose:  $30\text{ g l}^{-1}$ ).

whereas the adsorbent surface also becomes negatively charged ( $\text{pH}_{\text{PZC}} 11.1$ ); thus, electrostatic repulsion results in decreased adsorption. However, as very little change on As(III) uptake was observed with varying pH ( $3\text{--}9$ ), all further experiments were carried out at  $\text{pH } \sim 7$ .

#### 3.2.3. Adsorption kinetics

Fig. 4 shows the adsorption kinetics of As(III) onto IOCC at  $27 \pm 2^\circ\text{C}$  and at neutral pH. A study of the kinetic curve reveals a rapid uptake within the first 20 min to achieve the equilibrium conditions. The uptake is then stabilized after the first 40 min of contact implying that the equilibrium has been reached. Therefore, an optimum agitation time of 2 h was chosen.

The adsorption kinetics may be expressed as [34]

$$R = k_t t^m \quad (2)$$

Eq. (2) can be expressed in linearized form as

$$\ln R = \ln k_t + m \ln t \quad (3)$$

where  $R$  is the As(III) removal efficiency (%),  $t$  the contact time (min) and  $k_t$  and  $m$  are the constants. A plot of  $\ln R$  versus  $\ln t$  (Fig. 5) shows that the sorption kinetics can be divided into two linear phases: (i) the first phase, corresponding to the rapid removal phase and (ii) the second phase, where the removal becomes constant indicating equilibrium condition. Applying Eq. (3) to the first linear phase, as maximum occurs in this phase, the values of  $\ln k_t$  and  $m$  as calculated from Fig. 5 are 3.25 and 0.42, respectively. For pore diffusion to be the rate limiting step, the value of  $m$  should have been 0.5, i.e. the rate of adsorption should have varied with the square root of time ( $t^{0.5}$ ). However, in the present case, the rate of adsorption varies with  $t^{0.42}$ , which

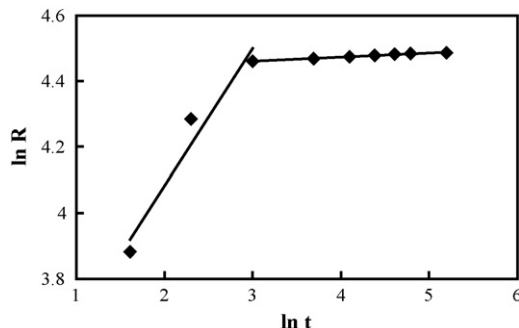


Fig. 5. Plot of  $\ln R$  vs.  $\ln t$ .

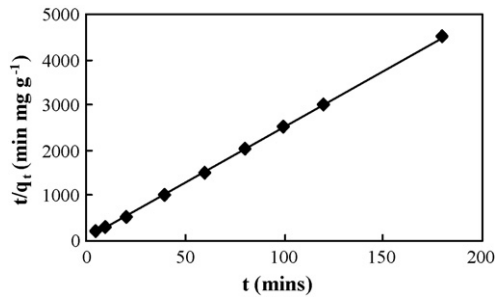


Fig. 6. Linear plot of  $t/q_t$  vs.  $t$  of the pseudo-second order rate equation for As(III) adsorption onto IOCC.

implies that pore diffusion is not the rate limiting step. Therefore, the rate limiting step may be film diffusion. Furthermore, as is evident from Fig. 5 that the plots do not pass through the origin, which augments the fact that pore diffusion is not the rate-limiting step [35] and the process may be controlled by film diffusion mechanism.

In order to analyze the sorption of As(III) on the IOCC medium, the modified equation of Lagergren developed by Ho and McKay [36] was also applied. Assuming that the adsorption capacity of IOCC is proportional to the number of active sites on its surface, then according to Ho and McKay the modified Lagergren equation can be written as

$$\frac{dq_t}{dt} = k_{ads}(q_e - q_t)^2, \quad t = 0, q_t = 0, \quad (4)$$

where  $k_{ads}$  is the equilibrium rate constant of pseudo-second order sorption kinetics ( $\text{g mg}^{-1} \text{min}^{-1}$ ),  $q_e$  the amount of soluted sorbate sorbed at equilibrium ( $\text{mg g}^{-1}$ ) and  $q_t$  is the amount of soluted sorbate on the surface of the sorbent at any time  $t$  ( $\text{mg g}^{-1}$ ).

Integrating Eq. (4) gives

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_{ads}t, \quad (5)$$

which can be rearranged into

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t, \quad (6)$$

where  $h = k_{ads}q_e^2$  representing the initial sorption rate ( $\text{mg g}^{-1} \text{min}$ ).

The values of  $q_e$  and  $k_{ads}$  calculated from the slope and intercept of the straight line, obtained from the linear plot of  $t/q_t$  versus  $t$  (Fig. 6), were  $0.04 \text{ mg g}^{-1}$  and  $11.4 \text{ g mg}^{-1} \text{min}^{-1}$ .

As is evident from Fig. 4, highly significant regression curve ( $R^2 > 0.99$ ) was obtained from this pseudo-second order model which indicated that the adsorption kinetics followed the pseudo-second order model.

### 3.2.4. Adsorption isotherms

In order to determine the adsorption capacity of As(III) onto IOCC, and to diagnose the nature of adsorption, the equilibrium adsorption isotherms are of fundamental importance. Four different isotherm models were studied to determine the isotherm constants and regression coefficients of the adsorption experi-

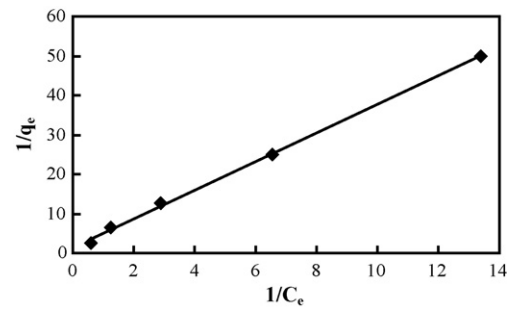


Fig. 7. Langmuir adsorption isotherm plot at different initial As(III) concentrations with IOCC (pH  $\sim 7$ ;  $T$ :  $27 \pm 2^\circ\text{C}$ ;  $t_{eq}$ : 2 h; sorbent dose:  $30 \text{ g l}^{-1}$ ).

mental results: the Langmuir model, the Freundlich model, the Redlich–Peterson (R–P) model, and the Dubinin–Radushkevich (D–R) model. The Langmuir model assumes monolayer sorption onto a homogeneous surface with a finite number of identical sites while the D–R model is more general than the Langmuir model because it does not assume a homogeneous surface or constant sorption potential. It was applied to distinguish between the physical and chemical adsorption [37] of As(III) on IOCC. The Freundlich and R–P models are empirical in nature.

The following Langmuir equation was used to describe the equilibrium data,

$$\frac{1}{q_e} = \frac{1}{bQ_0C_e} + \frac{1}{Q_0} \quad (7)$$

where  $Q_0$  and  $b$  are the Langmuir constants related to saturated monolayer adsorption capacity ( $\text{mg g}^{-1}$ ) and the binding energy of the sorption system, respectively,  $C_e$  the equilibrium solute concentration ( $\text{mg l}^{-1}$ ), and  $q_e$  is the amount of As(III) adsorbed at equilibrium ( $\text{mg g}^{-1}$ ).

The slope and intercept of the linear plot of  $1/q_e$  versus  $1/C_e$  (Fig. 7) gave the values of the Langmuir constants  $b$  and  $Q_0$  and the same are presented in Table 3.

The affinity between As(III) and the IOCC adsorbent can be predicted using the Langmuir parameter  $b$  from the dimension-

Table 3

Isotherm parameters and  $R^2$  values for adsorption of As(III) onto IOCC at pH 7

Parameter	Value	$R^2$
Langmuir isotherm		
$Q_0$ ( $\text{mg g}^{-1}$ )	0.69	0.999
$b$	0.40	
Freundlich isotherm		
$k_f$	0.22	0.994
$n$	1.08	
Dubinin–Radushkevich isotherm		
$Q_m$ ( $\text{mg g}^{-1}$ )	0.24	0.879
$k$ ( $\text{mol}^2 \text{kJ}^{-2}$ )	0.06	
$E$ ( $\text{kJ mol}^{-1}$ )	2.86	
Redlich–Peterson isotherm		
$K$	0.289	0.993
$F$	0.292	
$N$	0.0271	



Table 4  
Thermodynamic parameters for the adsorption of As(III) on IOCC

$C_0$ (mg l <sup>-1</sup> )	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta G$ (kJ mol <sup>-1</sup> )			
			288 K	298 K	308 K	318 K
1.35	-11.83	-0.02	-6.07	-5.87	-5.67	-5.47

less separation factor  $R_L$  [38,39], as

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

where  $C_0$  is the initial As(III) concentration (mg l<sup>-1</sup>) and  $b$  is the Langmuir isotherm constant. According to Hall et al. [38] and others researcher's [40,41] study, it has been shown using mathematical calculations that the parameter  $R_L$  indicates the shape of the isotherm. Value of  $R_L < 1$  represents the favourable adsorption and value  $R_L > 1$  represents unfavourable adsorption.

The values of  $R_L$  (shown in Fig. 8), for adsorption of As(III) on the IOCC adsorbent, were found to be within 0 and 1 which indicates a highly favourable adsorption with increased adsorption efficiency at higher As(III) concentrations.

The Freundlich model assumes that the uptake of metal ions occur on a heterogeneous surface and is described by the following equation:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (9)$$

The common terms in Eqs. (7) and (9) are described above and  $k_f$  and  $n$  are the Freundlich constants representing the adsorption capacity and the adsorption intensity, respectively.

The linear plot between  $\ln q_e$  and  $\ln C_e$  (Fig. 9) gives a slope that is the value of  $1/n$ , and the y-intercept is  $\ln k_f$ . A high value of  $n$  (i.e. a relatively slight slope) means a good adsorption over the entire range of concentrations studied, while a small  $n$  (i.e. a steep slope) indicates that adsorption is good at high concentrations but much less at lower concentrations.

The values of  $k_f$  and  $1/n$  are presented in Table 3. The numerical value of  $n$  indicates that adsorption capacity is slightly suppressed at lower equilibrium concentration. The sorption data is obeyed well. The Freundlich sorption isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. This isotherm does not predict any saturation of the sorbent by the

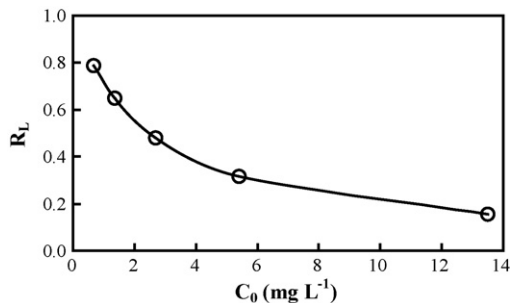


Fig. 8. Separation factor of As(III) adsorbed onto IOCC (pH ~7;  $T$ :  $27 \pm 2^\circ\text{C}$ ; sorbent dose:  $30 \text{ g l}^{-1}$ ).

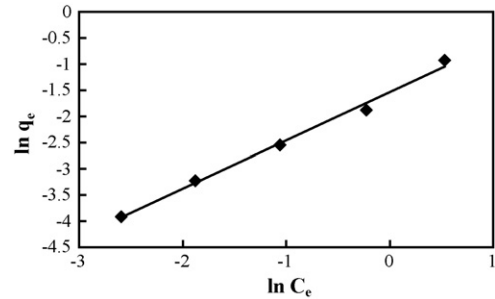


Fig. 9. Freundlich adsorption isotherm plot at different initial As(III) concentrations with IOCC (pH ~7;  $T$ :  $27 \pm 2^\circ\text{C}$ ;  $t_{\text{eq}}$ : 2 h; sorbent dose:  $30 \text{ g l}^{-1}$ ).

sorbate, thus infinite surface coverage is predicted mathematically, indicating a multilayer sorption of the surface [42].

The D–R isotherm has the form

$$\ln q_e = \ln Q_m - k\varepsilon^2 \quad (10)$$

where  $\varepsilon$  (Polanyi potential) is  $[RT \ln(1 + 1/C_e)]$ ,  $Q_m$  the theoretical saturation capacity (mg g<sup>-1</sup>),  $k$  a constant related to mean adsorption energy (mol<sup>2</sup> kJ<sup>-2</sup>),  $R$  the gas constant (kJ mol<sup>-1</sup> K<sup>-1</sup>) and  $T$  is the temperature (K).

The slope of the plot  $\ln q_e$  versus  $\varepsilon^2$  (Fig. 10) gives  $k$  and that of the intercept yields  $Q_m$ , the values of which are listed in Table 3. As is evident from Fig. 10, the plot of  $\ln q_e$  against  $\varepsilon^2$  for As(III) sorption on IOCC is not exactly linear which also accounts for the low  $R^2$  value. Nevertheless, its various parameters give certain information on the nature of the ongoing adsorption process. The sorption capacity  $Q_m$  is found to be  $0.24 \text{ mg g}^{-1}$ .

The mean free energy of adsorption ( $E$ ) was calculated from the  $k$  value using the following relation [43]:

$$E = -(2k)^{-0.5} \quad (11)$$

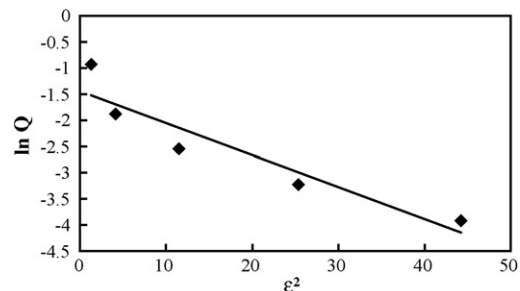


Fig. 10. Dubinin–Radushkevich (D–R) adsorption isotherm plot at different initial As(III) concentrations with IOCC (pH ~7;  $T$ :  $27 \pm 2^\circ\text{C}$ ;  $t_{\text{eq}}$ : 2 h; sorbent dose:  $30 \text{ g l}^{-1}$ ).

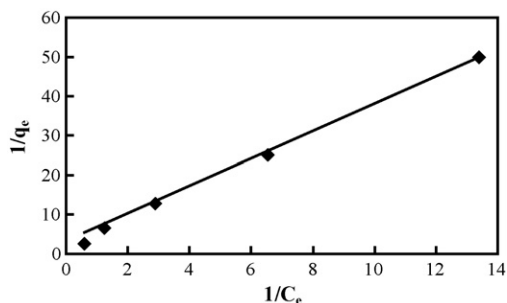


Fig. 11. Redlich–Peterson (R–P) adsorption isotherm plot at different initial As(III) concentrations with IOCC (pH  $\sim$ 7;  $T$ :  $27 \pm 2^\circ\text{C}$ ;  $t_{\text{eq}}$ : 2 h; sorbent dose:  $30 \text{ g l}^{-1}$ ).

As shown in Table 3, the  $E$  value is  $2.86 \text{ kJ mol}^{-1}$  for As(III) on the IOCC adsorbent medium. The numerical value of mean free energy is in the range of 1–8 and 9–16  $\text{kJ mol}^{-1}$  for physical and chemical adsorption, respectively [44]. In the present study, as is evident from the results, the  $E$  value is less than  $8 \text{ kJ mol}^{-1}$ , which is within the energy range of physical adsorption which implies that the type of adsorption is physical.

The R–P incorporates the features of both the Langmuir and the Freundlich isotherms. It considers, as the Freundlich model, heterogeneous adsorption surfaces as well as the possibility of multilayer adsorption. The R–P isotherm model [45] is expressed as:

$$\frac{1}{q_e} = \frac{1}{KC_e} + \frac{1}{FC_e^N} \quad (12)$$

where  $K$ ,  $F$ , and  $N$  are the R–P isotherm constants and  $C_e$  is the concentration of As(III) in solution at equilibrium ( $\text{mg l}^{-1}$ ).

Fig. 11 shows the plot of R–P isotherm model. The values of the constants were determined by the trial and error optimization method and are presented in Table 3.

According to the results shown in Table 3, the data fitted reasonably well the Langmuir isotherm in the adsorption studies carried out. It has been reported that the adsorption of As(III) by hematite [21], As(III) and As(V) by activated carbon, activated bauxite, activated alumina [46] and amorphous iron hydroxide [47], followed Langmuir isotherm. Langmuir isotherm which leads the adsorption process indicates that the reaction is a reversible phenomenon and the coverage is monolayer [27].

The reported values of  $Q_0$ , the Langmuir constant related to saturated monolayer adsorption capacity for hematite [21], iron(III) hydroxide loaded coral lime stone (Fe-coral) [22], iron oxide impregnated activated alumina [25], iron oxide coated sand [24], and red mud [27] are 0.19, 0.013, 0.734, 0.028, and  $0.66 \text{ mg g}^{-1}$ , respectively. In the present study, As(III) adsorption capacity of IOCC at  $27 \pm 2^\circ\text{C}$ , estimated from Langmuir isotherm is  $0.69 \text{ mg g}^{-1}$ , which is more effective than the adsorbents hematite, iron(III) hydroxide loaded coral lime stone (Fe-coral), iron oxide coated sand, and red mud, stated here.

### 3.2.5. Thermodynamic parameters

The amount of sorption of As(III) by IOCC were measured at temperatures of 15, 25, 35, and  $45^\circ\text{C}$ . The thermodynamic

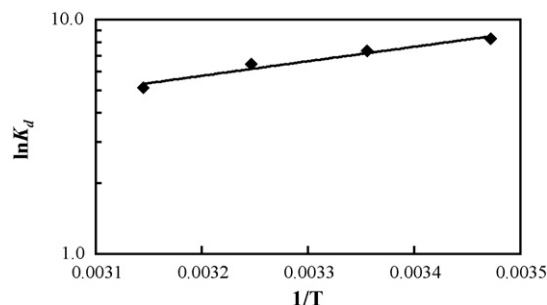


Fig. 12. Plot of  $\ln K_d$  vs.  $1/T$  for As(III) adsorption onto IOCC (pH  $\sim$ 7;  $C_0$ :  $1.35 \text{ mg l}^{-1}$ ;  $t_{\text{eq}}$ : 2 h; sorbent dose:  $30 \text{ g l}^{-1}$ ).

parameters obtained for the adsorption systems were calculated using the following equations and the values are given in Table 4:

$$K_d = \frac{C_{\text{ads}}}{C_e} = \frac{a}{1-a} \quad (13)$$

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (14)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (15)$$

where  $K_d$  is the equilibrium constant,  $C_{\text{ads}}$  the adsorbed amount of As(III) at equilibrium,  $a$  the uptake percentage of adsorbate at equilibrium,  $\Delta G^\circ$  the change in Gibbs free energy ( $\text{kJ mol}^{-1}$ ),  $\Delta H^\circ$  the change in enthalpy ( $\text{kJ mol}^{-1}$ ),  $\Delta S^\circ$  the change in entropy ( $\text{kJ mol}^{-1} \text{ K}^{-1}$ ),  $T$  the temperature (K), and  $R$  is the universal gas constant.

The equilibrium constant ( $K_d$ ) values decreased with the increase in temperature indicating the exothermic nature of sorption. The values of enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were obtained from the slope and intercept of the plot of  $\ln K_d$  versus  $1/T$  (Fig. 12). The values of the thermodynamic parameters for the adsorption of As(III) on IOCC are given in Table 4. The negative values of enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) show that the adsorption process is exothermic in nature from which it can be further concluded that the adsorption type is physisorption [48]. The negative  $\Delta G^\circ$  values as presented in Table 4 confirm the feasibility of the adsorption process and the spontaneous nature of As(III) adsorption onto IOCC medium. However, as is evident from the results presented in Table 4, the spontaneity decreases with the rise in temperature confirming the exothermic nature of the ongoing process.

## 4. Conclusions

In order to optimise the adsorption conditions for As(III) removal from aqueous solution by IOCC, kinetic, isotherm, and thermodynamic studies have been performed. Kinetic studies revealed that the Ho and McKay pseudo-second order equation suitably described the adsorption kinetics of As(III) on IOCC. pH studies showed that maximum As(III) removal could be achieved at more neutral pH values ( $6 < \text{pH} < 8$ ). Isotherm studies showed good fits with the Langmuir, Freundlich and R–P isotherm models, but D–R isotherm model was not able to describe the adsorption equilibrium properly. However, it gave

a rough idea of the nature of the ongoing adsorption process. The temperature dependence of As(III) adsorption on IOCC was investigated and the values of the calculated thermodynamic parameters ( $\Delta H^\circ$ ,  $\Delta G^\circ$ , and  $\Delta S^\circ$ ) showed exothermic nature of sorption and spontaneous nature of sorption. Batch study results showed that IOCC can be effectively used for As(III) removal from the aqueous environment as both kinetics and capacity are highly favourable.

## References

- [1] S. Kundu, A.K. Gupta, Analysis and modeling of fixed bed column operations on As(V) removal by adsorption onto iron oxide-coated cement (IOCC), *J. Colloid Interface Sci.* 290 (2005) 52.
- [2] J.C. Saha, A.K. Dikshit, M. Bandyopadhyay, K.C. Saha, A review of arsenic poisoning and its effects on human health, *Crit. Rev. Env. Sci. Technol.* 29 (1999) 281.
- [3] V. Lenoble, O. Bouras, V. Deluchat, B. Serpaud, J.-C. Bollinger, Arsenic adsorption onto pillared clays and iron oxides, *J. Colloid Interface Sci.* 255 (2002) 52.
- [4] WHO Guidelines for Drinking-Water Quality, 2nd ed., vol. 1, 1993.
- [5] USEPA National Primary Drinking Water Regulations, Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring, Federal Register 66(14) (2001) 6975.
- [6] WHO, Arsenic, Environmental Health Criteria 18, IPCS International Programme of Chemical Safety, Vammala (Finland): Vammalan Kirjapaino Oy., 1981.
- [7] The U.S. Environmental Protection Agency, Implementation Guidance for the Arsenic Rule, EPA 816-D-02-005, USEPA, Washington, DC, 2002.
- [8] A.I. Zouboulis, I.A. Katsoyiannis, Recent advances in the bioremediation of arsenic-contaminated groundwaters, *Environ. Int.* 31 (2005) 213.
- [9] I. Katsoyiannis, A. Zouboulis, Application of biological processes for the removal of arsenic from groundwaters, *Water Res.* 38 (2004) 17.
- [10] G.N. Manju, C. Raji, T.S. Anirudhan, Evaluation of coconut husk carbon for the removal of arsenic from water, *Water Res.* 32 (1998) 3062.
- [11] S. Bajpai, M. Chaudhuri, Removal of arsenic from groundwater by manganese dioxide-coated sand, *J. Environ. Eng.—ASCE* 125 (1999) 782.
- [12] S.A. Wasay, Md.J. Haron, A. Uchiumi, S. Tokunaga, Removal of arsenite and arsenate ions from aqueous solution by basic yttrium carbonate, *Water Res.* 30 (1996) 1143.
- [13] T.S. Singh, K.K. Pant, Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina, *Sep. Purif. Technol.* 36 (2004) 139.
- [14] J. Patanayak, K. Mondal, S. Mathew, S.B. Lalvani, A parametric evaluation of the removal of As(V) and As(III) by carbon-based adsorbents, *Carbon* 38 (2000) 589.
- [15] S. Bang, M. Patel, L. Lippincott, X. Meng, Removal of arsenic from groundwater by granular titanium dioxide adsorbent, *Chemosphere* 60 (2005) 389.
- [16] M.J. DeMarco, A.K. Sengupta, J.E. Greenleaf, Arsenic removal using a polymeric/inorganic hybrid sorbent, *Water Res.* 37 (2003) 164.
- [17] S. Bang, G.P. Korfiatis, X. Meng, Removal of arsenic from water by zero-valent iron, *J. Hazard. Mater.* 121 (2005) 61.
- [18] H.-L. Lien, R.T. Wilkin, High-level arsenite removal from groundwater by zero-valent iron, *Chemosphere* 59 (2005) 377.
- [19] N.P. Nikolaidis, G.M. Dobbs, J.A. Lackovic, Arsenic removal by zero-valent iron: field, laboratory and modeling studies, *Water Res.* 37 (2003) 1417.
- [20] M.L. Pierce, C.B. Moore, Adsorption of arsenite and arsenate on amorphous iron hydroxide, *Water Res.* 16 (1982) 1247.
- [21] D.B. Singh, G. Prasad, D.C. Rupainwar, V.N. Singh, As(III) removal from aqueous solution by adsorption, *Water, Air, Soil Pollut.* 42 (1988) 373.
- [22] S. Maeda, A. Ohki, S. Saikoji, K. Naka, Iron(III) hydroxide-loaded coral limestone as an adsorbent for arsenic(III) and arsenic(V), *Sep. Sci. Technol.* 27 (1992) 681.
- [23] A. Joshi, M. Chaudhuri, Removal of arsenic from ground water by iron oxide-coated sand, *J. Environ. Eng.—ASCE* 122 (1996) 769.
- [24] V.K. Gupta, V.K. Saini, N. Jain, Adsorption of As(III) from aqueous solutions by iron oxide-coated sand, *J. Colloid Interface Sci.* 288 (2005) 55.
- [25] S. Kuriakose, T.S. Singh, K.K. Pant, Adsorption of As(III) from aqueous solution onto iron oxide impregnated activated alumina, *Water Qual. Res. J. Canada* 39 (2004) 258.
- [26] B. Petrusevski, J. Boere, S.M. Shahidullah, S.K. Sharma, J.C. Schippers, Adsorbent-based point-of-use system for arsenic removal in rural areas, *J. Water SRT—Aqua* 51 (2002) 135.
- [27] H.S. Altundoğan, S. Altundoğan, F. Tümen, M. Bildik, Arsenic removal from aqueous solutions by adsorption on red mud, *Waste Manage.* 20 (2000) 761.
- [28] J.S. Noh, J.A. Schwarz, Estimation of the point of zero charge of simple oxides by mass titration, *J. Colloid Interface Sci.* 130 (1989) 157.
- [29] W.H. Kuan, H.S. Lo, M.K. Wang, C.F. Lin, Removal of Se(IV) and Se(VI) from water by aluminum-oxide-coated sand, *Water Res.* 32 (1998) 915.
- [30] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, APHA Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, Washington, DC, 1998.
- [31] H.F.W. Taylor, Cement Chemistry, Academic Press, New York, 1990.
- [32] W. Stumm, J.J. Morgan, Aquatic Chemistry, 3rd ed., Wiley Interscience, New York, 1981.
- [33] C. Su, R.W. Puls, Arsenate and arsenite removal by zero-valent iron: kinetics, redox transformation, and implications for in situ groundwater remediation, *Environ. Sci. Technol.* 35 (2001) 1487.
- [34] S.B. Lalvani, T. Wiltowski, A. Hubner, A. Weston, N. Mandich, Removal of hexavalent chromium and metal cations by a selective and novel carbon adsorbent, *Carbon* 36 (1998) 1219.
- [35] V.J.P. Poots, G. McKay, J.J. Healy, Removal of basic dye from effluent using wood as an adsorbent, *J. Water Pollut. Control Fed.* 50 (1978) 926.
- [36] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, *Process Biochem.* 34 (1999) 451.
- [37] S.-H. Lin, R.-S. Juang, Heavy metal removal from water by sorption using surfactant-modified montmorillonite, *J. Hazard. Mater.* 92 (2002) 315.
- [38] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore-and-solid-diffusion kinetics in fixed-bed absorption under constant-pattern conditions, *Ind. Eng. Chem. Fund.* 5 (1966) 212.
- [39] G. McKay, M.J. Bino, A.R. Altamemi, The adsorption of various pollutants from aqueous solutions on to activated carbon, *Water Res.* 19 (1985) 491.
- [40] Y.S. Ho, C.T. Huang, H.W. Huang, Equilibrium sorption isotherm for metal ions on tree fern, *Process Biochem.* 37 (2002) 1421.
- [41] T.W. Weber, R.K. Chackravorti, Pore solid diffusion models for fixed bed adsorbents, *J. Am. Instrum. Chem. Eng.* 20 (1974) 228.
- [42] R. Donat, A. Akdogan, E. Erdem, H. Cetisli, Thermodynamics of Pb<sup>2+</sup> and Ni<sup>2+</sup> adsorption onto natural bentonite from aqueous solutions, *J. Colloid Interface Sci.* 286 (2005) 43.
- [43] S.M. Hasany, M.H. Chaudhary, Sorption potential of Haro river sand for the removal of antimony from acidic aqueous solution, *Appl. Radiat. Isot.* 47 (1996) 467.
- [44] M.M. Saeed, Adsorption profile and thermodynamic parameters of the pre-concentration of Eu(III) on 2-thenoyltrifluoroacetone loaded polyurethane (PUR) foam, *J. Radioanal. Nucl. Chem.* 256 (2003) 73.
- [45] A. Benhammou, A. Yaacoubi, L. Nibou, B. Tanouti, Adsorption of metal ions onto Moroccan stevensite: kinetic and isotherm studies, *J. Colloid Interface Sci.* 282 (2005) 320.
- [46] K.S. Gupta, K.Y. Chen, Arsenic removal by adsorption, *J. Water Pollut. Control Fed.* 50 (1978) 493.
- [47] T.R. Harper, N.W. Kingham, Removal of arsenic from wastewater using chemical precipitation methods, *Water Environ. Res.* 64 (1992) 200.
- [48] M. Ajmal, A.H. Khan, S. Ahmad, A. Ahmad, Role of sawdust in the removal of copper(II) from industrial wastes, *Water Res.* 32 (1998) 3085.