

# Kinetic Performance of Aluminum and Iron Oxides in the Removal of Arsenate from Aqueous Environment

E. Bilgin Simsek and U. Beker

**Abstract**—Arsenate (As(V)) adsorption from aqueous solution onto clinoptilolite incorporating iron or aluminum oxides was investigated. The modified samples were characterized by nitrogen adsorption isotherms, TEM-EDX analysis. Kinetic models were applied to describe As(V) adsorption on each modified clinoptilolite samples. The kinetic data, explained best by the pseudo-second-order model by good regression coefficients.

**Index Terms**—Arsenic, adsorption kinetics, metal oxides.

## I. INTRODUCTION

Arsenic presents in ground water in one of two oxidation states: arsenite (As(III)) and arsenate (As(V)). Arsenic is stable in several oxidation states, of which the arsenite, As(III), and arsenate, As(V), are the most common forms in natural waters. The dominant species of arsenic depend greatly on its surrounding environment. The As(V) is stable in oxidizing environment, whereas the As(III) is mainly found in reducing one [1]. Arsenic exposure is known to be associated with skin, lung, liver, kidney and prostate cancer (NRC 1999). There were regions including high arsenic concentrations such as Taiwan (~34-558 µg/L [2]; 10-1820 µg/L [1]) and Vietnam (~3050 µg/L b in rural groundwater samples [3]).

The USEPA changed the maximum contaminant level for arsenic from 50 µg/L in 1974 to 10 µg/L in 2001 due to its long-term health effect [4].

Metallic oxides like iron, aluminum or manganese oxides have gained special attention in environmental remediation technologies in recent years. Especially widespread application of iron and aluminum oxides for water treatment has encouraged in evaluating them for arsenic adsorption. Toxicity of inorganic arsenic has caused various health effects [5], thus, different kinds of metal oxides were synthesized for estimating their arsenic removal efficiency. The challenge of these oxides, problems might occur owing to their fine particles [6]. An effective method to overcome these problems is to incorporate these oxides into/onto carriers of larger size such as zeolites.

The aim of this work is to carry out kinetic and isotherm studies on the adsorption of As(V) on iron or aluminum oxides modified clinoptilolite samples.

## II. MATERIALS AND METHODS

### A. Preparation of Adsorbents

The previous study [7] concluded that the pretreated zeolites exhibited low or no adsorption capacities for As(V). However, major increases were observed for all metal oxide coated zeolites especially for bimetallic oxides coated ones. For that reason, further studies were carried out with iron or aluminum oxide doped ones.

Iron and aluminum oxides impregnated zeolites were prepared as described in previous study [7]: A defined amount of NC-Na was immersed in 200 ml of metal solution and pH of the solution was raised to 7.0 by addition of NaOH. The stirring was continued for 1 h and then the suspension was filtered and washed with deionized water in column and dried at 338 K. The iron oxide immobilized NC-Na was prepared with FeCl<sub>2</sub> solution and sample was designated as NC-Fe. Similarly, aluminum oxide immobilized NC-Na was synthesized by using AlCl<sub>3</sub> solution and sample was coded as NC-Al.

### B. Characterization Studies

The nitrogen adsorption experiments were conducted with Quantachrome Autosorb instrument. The specific surface area ( $S_{BET}$ ), micropore volume and pore size distribution of samples were calculated using BET (Brunauer, Emmett, Teller), t-plot and BJH (Barett-Joyner-Halenda) methods, respectively. Transmission electron microscopy (TEM) observations and elemental analysis of samples were performed with a high resolution electron microscope (FEI Tecnai G2 F20 X-Twin) operated at 200 kV with an Energy Dispersive X-ray spectroscopy system attachment (TEM-EDX).

### C. Adsorption Experiments

As(V) adsorption kinetic studies were carried out by adding defined amount of modified samples into 500 mL of As(V) solutions at different temperatures (25, 45 and 65 °C). The arsenic concentration was detected at 193.7 nm using an atomic absorption spectrometer (Analytik Jena ContrAA 700 TR).

Arsenate sorption capacity was calculated by using the following equation (Eq. (1)):

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (1)$$

where  $q_e$  is the arsenate adsorption capacity (mg/g),  $C_0$  is the initial concentration of arsenate (mg/L),  $C_e$  is the equilibrium As(V) concentration (mg/L),  $V$  is the solution volume (L) and  $m$  is the adsorbent dosage (g).

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The experimental data was applied by the pseudo-first- and pseudo-second order kinetic models.

### III. RESULTS AND DISCUSSION

#### A. Characterization Results

The textural properties of samples from the nitrogen adsorption isotherm are summarized in Table I. The total pore volume values of NC-Fe and NC-Al samples were found 0.221 and 0.173 cm<sup>3</sup>/g, respectively.

TABLE I: TEXTURAL PROPERTIES OF SAMPLES

Sample	NC-Fe	NC-Al
S <sub>BET</sub> (m <sup>2</sup> /g)	69.62	22.20
V <sub>a</sub> (cm <sup>3</sup> /g)	0.221	0.173

S<sub>BET</sub>: Specific surface area, V<sub>a</sub>: Total pore volume

The increases in total pore volume of modified samples are probably due to the higher content of iron or aluminum in the composite. This could be explained by the formation of secondary pore structure during the precipitation of the metal oxide particles [8]. But the formation of small pores had no significant effect to the total pore volume due to the zero values of micropore volume for modified zeolites.

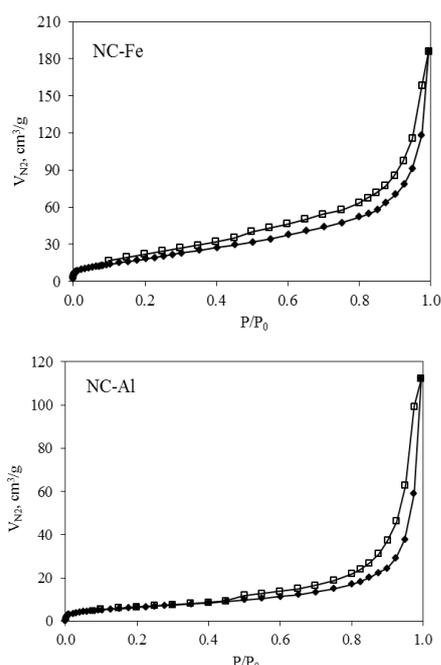


Fig. 1. Nitrogen adsorption-desorption isotherms (◆: adsorption ; ◻: desorption)

Nitrogen adsorption and desorption isotherms of all samples (Fig. 1) were fitted to Type-V with a B- or H3-type of hysteresis loop in accordance with the IUPAC classification [9]. The isotherms showing hysteresis loops depict characteristic feature of mesopores [10].

The TEM image of NC-Fe (Fig. 2) was confirmed by the morphology of the crystals which form thin plates could be identified as δ-FeOOH (feroxyhyte) or α-FeO(OH) (goethite) forms [11]. TEM-EDX analysis shows that approximately 47.1 wt% Fe ions were aggregated at the surface of zeolite support.

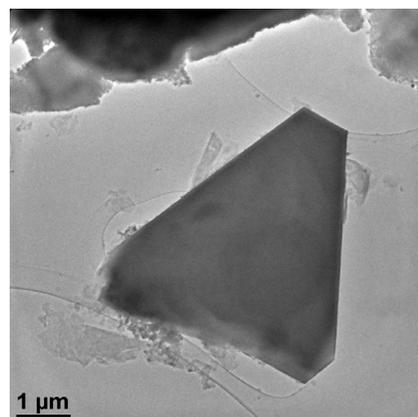


Fig. 2. TEM image of NC-Fe sample

#### B. Kinetic Models

Adsorption kinetic plays an important role on the physical and/or chemical characteristics of the sorbent material, which also influenced the sorption mechanism [12]. Although many models like homogeneous diffusion model or the pore diffusion model have been proposed to interpret the transport of solutes inside adsorbents, the mathematical complexity of these models makes them inconvenient for practical use. From a viewpoint of system design, lumped analysis of the adsorption rates is thus considered to be sufficient for practical operation [13].

The experimental results showed that NC-Fe and NC-Al samples removed 74% and 65% of As(V) at the end of 8 hour. For NC-Fe sample, maximum As(V) adsorption capacity was obtained as 2.716 mg/g while that of NC-Al was found as 1.338 mg/g at equilibrium (Fig. 3).

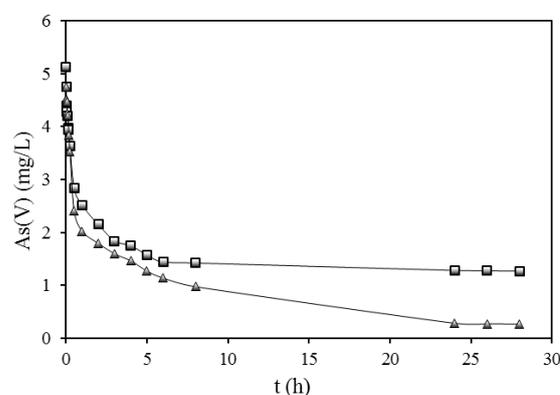


Fig. 3. As(V) adsorption uptake of (▲) NC-Fe; (■) NC-Al

The prediction of adsorption rate provides important information for designing batch adsorption systems. Information on the kinetics of pollutant uptake is needed for selecting optimum operating conditions for full-scale batch process. In the present work, general kinetic equations were applied to the experimental data. The pseudo-first-order rate expression of Lagergren is generally described by the following equation [14]:

$$\frac{dq_t}{dt} = k_1 \cdot (q_e - q_t) \quad (2)$$

where  $q_e$  and  $q_t$  are the amounts of As(V) adsorbed on the adsorbents at equilibrium and at time,  $t$  (min), respectively and  $k_1$  is the rate constant (1/min). Integrating and applying

the boundary conditions,  $t=t$  and  $q_t=q_e$  takes the form:

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right)t \quad (3)$$

The other main kinetic model was described as pseudo-second-order process [15] by the following equation:

$$\frac{dq_t}{dt} = k_2 \cdot (q_e - q_t)^2 \quad (4)$$

where,  $q_e$  and  $q_t$  have the same meaning as mentioned previously, and  $k_2$  is the rate constant for the pseudo second-order kinetics. Rearranging this equation to a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t \quad (5)$$

The plots of  $t/q_t$  versus  $t$  are shown in Fig. 4 for NC-Fe and NC-Al. The theoretical  $q_t$  values estimated from the first-order kinetic model gave significantly different values compared to experimental values, and the correlation coefficients were also found to be lower. These results showed that the first-order kinetic model did not well describe As(V) sorption system.

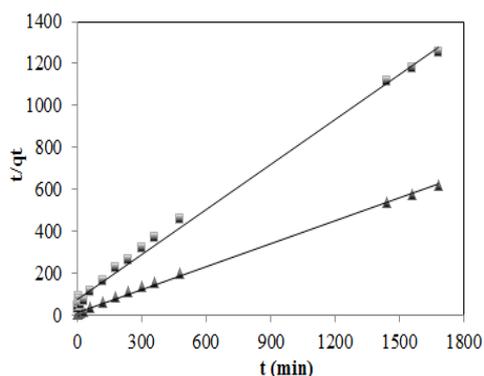


Fig. 4. Pseudo-second-order kinetic model of (▲) NC-Fe; (■) NC-Al

TABLE II: KINETIC PARAMETERS

Temperature	298 K	318 K	338 K
<b>NC-Fe</b>			
$q_e$ (mg/g)	2.716	2.839	3.183
<b>Pseudo-first-order</b>			
$q_t$ (mg/g)	1.742	1.533	1.083
$k_1$ (1/min)	0.007	0.006	0.002
$R^2$	0.930	0.967	0.565
<b>Pseudo-second-order</b>			
$q_t$ (mg/g)	2.728	2.835	2.960
$k_2$ (g/mg.min)	0.009	0.011	0.032
$R^2$	0.998	0.997	0.997
<b>NC-Al</b>			
$q_e$ (mg/g)	1.338	1.401	1.473
<b>Pseudo-first-order</b>			
$q_t$ (mg/g)	1.076	1.051	1.058
$k_1$ (1/min)	0.006	0.005	0.007
$R^2$	0.959	0.966	0.932
<b>Pseudo-second-order</b>			
$q_t$ (mg/g)	1.395	1.393	1.494
$k_2$ (g/mg.k)	0.006	0.009	0.011
$R^2$	0.991	0.993	0.996

However, the theoretical  $q_t$  values for the both sorbents were very close to the experimental  $q_e$  values in the case of second-order kinetics (Table II). Based on the values of linear regression coefficients ( $R^2$ ) of each applied kinetic model, it could be suggested that As(V) adsorption kinetics for both sorbents described the pseudo-second order equation ( $R_{NC-Na}^2 = 0.9982$ ;  $R_{NC-Al}^2 = 0.9964$ ).

The pseudo-second-order model is based on the assumption that the rate-determining step may be a chemical sorption involving valence forces through sharing or exchange of electrons between adsorbent and sorbate [16].

The presence of aluminum and iron in zeolite enhanced the As(V) uptake significantly. NC-Fe sample was found more effective adsorbent than NC-Al sample as observed by others [17]-[19].

#### IV. CONCLUSION

The results indicated that iron oxide incorporated clinoptilolite was better adsorbent for As(V) removal than the aluminum one suggesting the As(V) adsorption depends on the metallic species in the zeolite surface.

This study provides an insight into arsenic adsorption onto metal oxides supported onto natural, cheap and eco-friendly material.

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