# REMOVAL OF As(V) BY Ce(IV)-EXCHANGED ZEOLITE P USING COLUMN METHOD

(Penyingkiran As(V) oleh  Ce(IV)-Zeolit P Menggunakan Kaedah Turus)

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**Abstract**

Zeolite P was modified by ion exchange with Ce(IV) cation (Ce4ZP) and its performance for removal of As(V) anion using column method is described.   The removal of As(V) was strongly depending on the bed depth, influent flow rate and initial As(V) concentration.  The increase in bed depth enable more water can be treated, but with a slight reduction in adsorption capacity.  At lower flow rate, the quantity of treated water and adsorption capacity were found to increase.  At higher influent concentrations, better adsorption capacity was observed.  The theoretical service times evaluated from bed depth service time (BDST) model for different flow rates and influent As(V) concentrations shows good correlation with the experimental data.

**Keywords**: Arsenate, BDST model, Ce(IV)-zeolite P, column, adsorption

**Abstrak**

Zeolite P telah diubahsuai secara penukaran ion dengan kation cerium (IV)  (Ce4ZP) dan kebolehannya untuk penyingkiran anion As(V) menggunakan kaedah turus dilaporkan.  Penyingkiran As(V) bergantung kepada  ketinggian turus, kadar aliran masuk dan kepekatan awal As(V).  Penambahan ketinggian turus menghasikan lebih banyak air yang dapat dirawat tetapi ia merendahkan sidikit muatan jerapan.  Pada kadar aliran masuk yang rendah, kuantiti air yang dirawat dan muatan jerapan meningkat.  Sample air dengan kepekatan arsenik lebih tinggi menghasilkan muatan jerapan yang lebih tinggi.   Jangka masa operasi turus yang dikira dari model BDST hampir sama dengan jangka masa operasi yang didapati secara eksperimen.

**Kata kunci** :  Arsenat, model BDST, Ce(IV)-zeolit P, turus, jerapan

## Introduction

Arsenic is harmful to man and living organisms and a suspected carcinogen [1].  It enters the environment through anthropogenic activities such as petroleum refineries, fossil fuel power plants and non-ferrous smelting as well as through natural weathering of arsenic rock.   Arsenic is also used in many industries such as in wood treatment that use the largest amount of arsenic compounds, lead shot, storage batteries, semiconductors, pesticides and fertilizers [2].   The arsenic levels in many international standards for drinking water and industrial waste effluent have been lowered to 0.01 mg L$^{-1}$ and 0.05 mg L$^{-1}$, respectively [3-4].  Conventional precipitation methods for arsenic removals using iron and aluminum salts have not been successful to meet these drinking and effluent standards for arsenic due to the solubility of the resultant products.  On the other hand, adsorption appears to be one of the promising methods for removal of arsenic from water [5].  Among these processes, the removal of As(V) using metal oxides such as antimony and manganese [6], iron hydroxide [7] and iron coated catalysts [8] have been studied.

Zeolites are crystalline, hydrated aluminosilicate minerals containing exchangeable alkaline and alkaline earth metal cations, in particular, sodium, potassium, magnesium and calcium as well as water molecules in their structural frameworks.  The compounds are based on three dimensional networks of AlO$_4$ and SiO$_4$ tetrahedra linked to each other by sharing all the oxygen atoms [9].  Since zeolites have a permanent negative charge on their surface, they have no affinity for anions.  Recent studies have shown that modification of zeolites with certain cations resulted in  sorbents with a strong affinity for many anions [10]. Cationic-surfactant-modified zeolites have been shown to remove arsenate from aqueous solutions [11]. Since the presence of the arsenate anion in water covers a wide pH range, the removal of As(V) by zeolites could be enhanced after loading them with various metal cations such as aluminium [12] and iron [13].  Cerium hydroxide has been

known to adsorb As(V) effectively from aqueous solution.  Recently hydrous cerium oxide was shown to possess a high anion exchange capacity for As(V) [14].  Furthermore cerium doped iron oxide adsorbed As(V) at a higher capacity than alumina [15].  Our previous study showed that Ce(IV)-exchanged Zeolite P could sorb As(V) at higher capacity than several cerium- and zeolite-based adsorbents using batch method [16].

This paper describes the use of Ce(IV)-exchanged Zeolite P (Ce(IV)ZP) to sorb As(V) from aqueous solution using column method.  Parameters investigated were effect of bed depth, flow rate and also initial influent concentration.  The evaluation of column performance and analysis of breakthrough curves were done by the Bed Depth ServiceTtime (BDST) model [17].  The BDST approach was used for prediction of breakthrough time and exhaust time of column bed under different flow rate and influent concentration. All experiments for column method were performed at room temperature (25±2 °C).

## Experimental

Zeolite P prepared from rice husk silica was donated by the Ibnu Sina Institute, University Technology Malaysia.  Ce(IV)-loaded Zeolite P (Ce4ZP) was prepared by stirring of Zeolite P (5.0 g) in 45 cm$^3$ of 0.1 mol L$^{-1}$ ceric ammonium nitrate (Merck) in distilled water at 90 °C for 24 h. The Zeolite was separated from the solution by vacuum filtration rinsed with distilled water and oven dried at 60 °C for 24 h. The concentration of Ce(IV) in the supernatant was determined using ICP-AES model Perkin-Elmer Plasma 1000. The loading capacity of Ce(IV) in Zeolite P was found to be 170 mg g$^{-1}$ [16].  A stock solution of As(V), 1000 mg/L, was prepared by dissolving NaH$_2$AsO$_4$.7H$_2$O (Sigma) in distilled water.  Test As(V) sample solutions were prepared by dilution of the stock solution.

The Ce4ZP adsorbent was packed inside borosilicate glass columns (Omnifit USA) with internal diameter of 10 mm and length of 100 mm equipped with teflon frit. The experiments were conducted in the up flow mode. The As(V) spiked water was pumped through the packed bed of Ce4ZP with a double reciprocating piston pump (model Pharmacia P 50).  The effect of process parameters such as bed height, inlet flow rate, initial As(V) concentration were studied. The effluent samples were collected in a glass test tubes at definite interval using a fraction collector (model Pharmacia GradiFrac) and analyzed for As concentration using ICP-AES (model Perkin Elmer l000).  The As(V) spiked water was allowed to pass through Ce4ZP bed in up flow mode at a flow rate of 0.5 mL/min.  The bed depths of 1.0, 1.5 and 2.0 cm and initial As(V) concentration of 25 mg/L were selected for experimental evaluation of column parameters.  The effect of flow rate on As(V) removal was studied at 0.5 and 1 mL/min for a fixed bed depth of 1.0 cm and As(V) concentration of 25 mg/L. The performance of Ce4ZP at a bed depth of 1.0 cm was also evaluated at a higher As(V) concentration of 50 mg/L at 0.5 mL/min.

## Results and Discussion

### Effect of Column Bed Height

The breakthrough curves which is the plots C/C$_o$ as a function of lapse time of water treated for an initial As(V) concentration of 25 mg/L  for three different bed depths of 1.0, 1.5 and 2.0 cm at a flow rate of 0.5 mL/min are shown in Fig. 1.  For the low bed depth, the breakthrough curve is steeper showing faster saturation of the bed. The point on the breakthrough curve at which arsenic concentration reaches its maximum allowable value for wastewater of 0.05 mg/L (corresponding to $C/C_o = 0.002$ or 0.2% of the influent concentration) was taken as 'breakthrough point' and the value of $C/C_o = 90\%$ was taken as 'exhaustion point'. The time corresponding to breakthrough and exhaustion points with respective volumes of water treated are shown in Table 1.  The data showed that the increase in bed depth increased the volume of treated water at breakthrough and exhaustion points.  This could be due to the availability of more adsorbent binding sites with the increase of bed depth [18]. However reduction in adsorption capacity of As(V) was observed with increased bed heights which could be due more active sites of the adsorbent may be remained inaccessible for adsorption of As(V) ions [19].

### Effect of initial As(III) concentration

The performance of Ce4ZP column for influent As(V) concentrations of 25 and 50 mg/L for the bed depth of 1.0 cm at 0.5 mL/min are shown in Fig. 2 and the breakthrough and the exhaustion data are shown in Table 1. The breakthrough time and time of exhaustion for 50 mg/L As(V) concentration obtained were 120 and 220 min, respectively which are lower compared the values of 180 and 360 min for corresponding concentration of 25 mg/L.  The quantities of treated water at breakthrough were also reduced to 60 mL for 50 mg/L concentration, compared to 90 ml for 25 mg/L As(V) concentration.  However the column adsorption capacities obtained was higher for higher concentrations.  A decrease in breakthrough as well as time of exhaustion at higher initial

concentration may be due to the rapid exhaustion of the adsorption sites since a higher concentration gradient caused a faster transport of ions as a result of increase in diffusion coefficient [20].
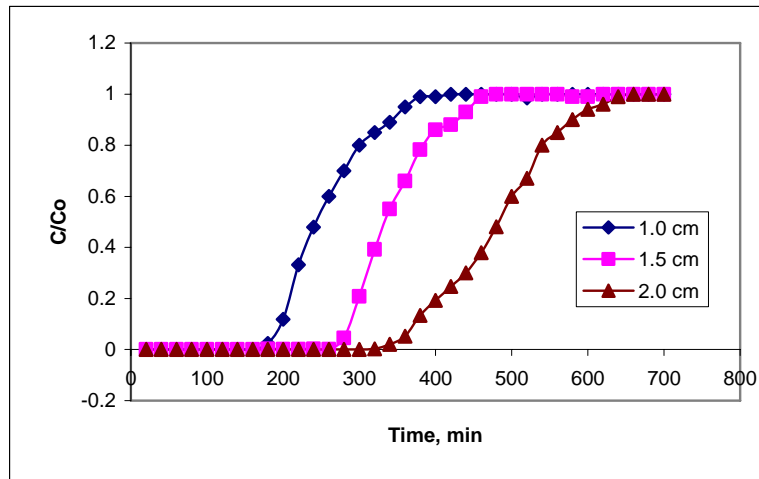


Fig.1  Breakthrough curves of As(V) adsorption on Ce4ZP for different bed depths (initial As(V) conc. = 25 mg/L, flow rate = 0.5 mL/min).

Table 1.  The volumes water treated at different bed depths, initial As(V) concentrations and flow rates

| Bed depth (cm) | Initial concentration mg/L | Flow rate ml/min | Break-through time (min) | Time of exhaustion (min) | Volume of water treated at breakthrough (ml) | Volume of water treated before exhaust (ml) | Adsorption capacity (mg/g) |
|---|---|---|---|---|---|---|---|
| 1.0 | 25 | 0.5 | 180 | 360 | 90 | 180 | 6.8 |
| 1.5 | 25 | 0.5 | 260 | 440 | 130 | 220 | 6.4 |
| 2.0 | 25 | 0.5 | 380 | 560 | 190 | 280 | 5.9 |
| 1.0 | 50 | 0.5 | 120 | 220 | 60 | 110 | 8.1 |
| 1.0 | 25 | 1.0 | 80 | 260 | 40 | 130 | 4.3 |

**Effect of flow rate**
The effect of flow rate was investigated at 0.5 and 1.0 mL/min for an influent As(V) concentration of 25 mg/L, bed depth of 1.0 cm and column diameter of 1 cm.  The breakthrough curves for different flow rates are shown in Fig. 3. The quantity of water treated at breakthrough point and exhaust point are shown in Table 1. There is a reduction in the adsorption capacity of Ce4ZP with increase in flow rate.  This may be due to relatively low contact time between the adsorbate and adsorbent there by reducing the diffusion of As(V) ions into pores of Ce4ZP [21].  Also, at higher flow rates, the movement of adsorption zone along the bed is faster which in turn reducing the time for adsorption of As(V) ions on adsorbent bed.

**Bed depth service time model (BDST)**
According to Hutchins only three column tests are necessary to collect data required for column design using BDST model.  The bed depth (*x*) and service time (*t*) can be express as [17]:

$$t = ax \ + \ b \tag{1}$$

where

$$a = \text{slope} = \frac{N_0}{C_0 V} \tag{2}$$

$$b = \text{intercept} = \frac{1}{K C_0} \ln\left( \frac{C_0}{C_B} - 1 \right) \tag{3}$$

where $C_0$ = initial solute concentration (mg/L); $C_B$ desired solute concentration at breakthrough (mg/L); K adsorption rate constant (L/mg min); $N_0$ adsorption capacity (mg solute/L sorbent); x = bed depth of sorbent (cm); V = linear flow velocity of feed to bed (cm/min); and t = service time of column under above conditions (min).
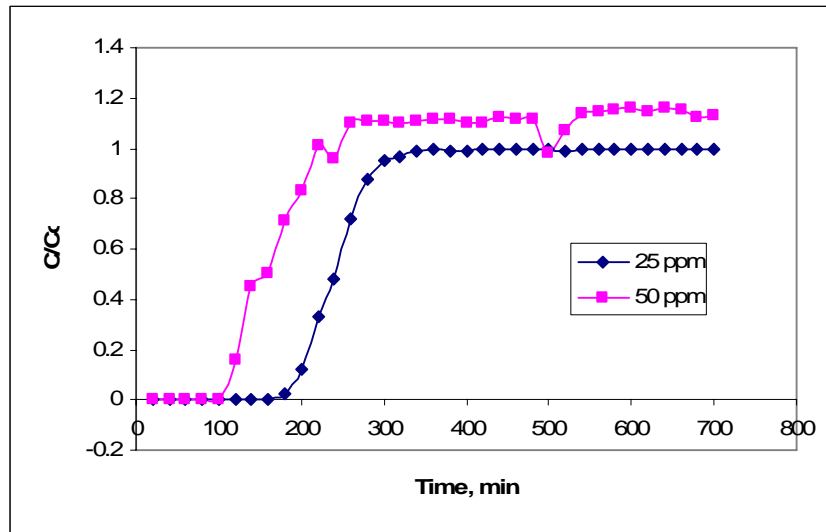


Fig. 2  Effect of initial concentrations on the breakthrough curves for As(V) adsorption on Ce4ZP.  Bed depth = 1.0 cm and flow rate = 0.5 mL/min.
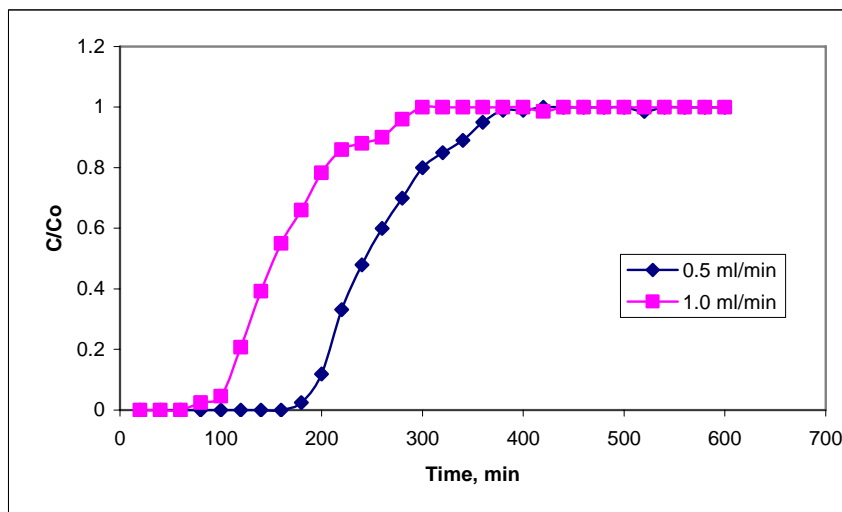


Fig. 3  Effect of flow rates on the breakthrough curve of As(V) adsorption on Ce4ZP.  Bed depth = 1.0 cm and initial As(V) conc. = 10 mg/L.

From breakthrough times corresponding to $C/C_0 = 0.002$ (0.2% saturation) and the exhaust times corresponding to $C/C_0 = 0.9$ (90% saturation) for bed depth of 1.0, 1.5 and 2 cm, a plots service time versus bed depth for 0.2 % breakthrough and 90% saturation of Ce4ZP bed were made and given in Fig. 4. The equations of these lines are:

$$t = 200x + 153.33 \qquad \text{(90\% saturation)} \qquad (4)$$

$$t = 200x - 26.667 \qquad \text{(0.2\% saturation)} \qquad (5)$$

Since those lines were parallel the equations can be used to predict the service time at breakthrough and at exhaustion for different flow rates and initial influent concentrations for practical used as discussed below [17].
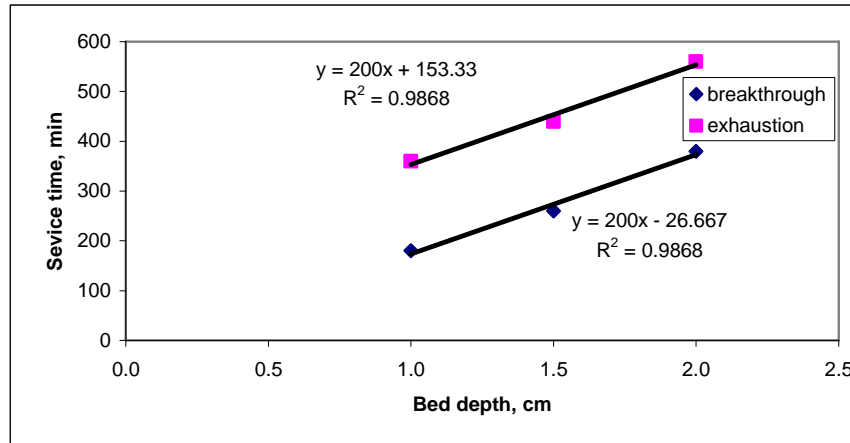


Fig. 4. Bed depths versus service time plot at 0.2% and 90% saturation of Ce4ZP
fixed bed. Initial As(V) 25 mg/L, flow rate 0.5 mL/min.

**Prediction of service times of columns under new operating conditions using BDST model**

**New flow rate**
According to BDST approach (equation 1) , if the value of slope '$a_1$' is determined for one flow rate '$f_1$', value of '$a_2$' for the other flow rate '$f_2$' can be calculated as [21]:

$$a_2 = a_1 \frac{f_1}{f_2} \qquad (6)$$

In this case the value of intercept '$b$' is not affected significantly with flow rates. For flow rates of 1.0 mL/min, the calculated value of '$a_2$', is 100. With this value the BDST equation for flow rate of 1.0 mL/min can be written as:

$$t = 100x + 153.33 \text{ (for 90\% saturation)} \qquad (7)$$

$$t = 100x - 26.667 \text{ (for 0.2\% saturation)} \qquad (8)$$

From Eqs. (7) and (8), the breakthrough and exhaust times for new flow rate of 1.0 mL/min at a bed depth of 1.0 cm were calculate and presented in Table 2. The data show that the experimental and theoretical values are well comparable with error less than 10%.

**New concentration**
From the BDST equation of the experimental data of a solute concentration $C_1$, it is also possible to predict the
equation for another concentration $C_2$ as [17]

$$a_2 = a_1 \frac{C_1}{C_2} \tag{9}$$

$$b_2 = b_1 \frac{C_1}{C_2} \frac{ln(C_2/C_F - 1)}{ln(C_1/C_B - 1)} \tag{10}$$

where $a_1$ is the slope at concentration $C_1$; $a_2$ the new slope at concentration $C_2$; $b_1$ the intercept at concentration
$C_1$; $b_2$ the new intercept at concentration $C_2$; $C_F$ the effluent concentration at influent concentration $C_2$ and $C_B$ is
the effluent concentration at influent concentration $C_1$.  For As(V) concentration of 50 mg/L, the values of $a_2$
and $b_2$ calculated from Eqs. (9) and (10) at breakthrough are 100 and −3.63 and for exhaust are 100 and 80.56,
respectively.  The equations of service time/bed depth for the new concentration can be written as

$$t = 100x + 80.56 \quad \text{(for 90\% saturation)} \tag{11}$$

$$t = 100x - 3.65 \quad \text{(for breakthrough)} \tag{12}$$

The theoretical exhaust time and breakthrough calculated from Eqs. (11) and (12) are 96 and 180 min,
respectively, which are comparable to the experimental values (with errors less than 10%) as shown in Table 2.
These equations can be used to prediction service times for different As(V) influent concentrations with
acceptable accuracy.

Table 2  Comparison of the experimental service times with theoretical service times predicted using BDST
model

| Flow rate ml/min | Influent concentration mg/L | Breakthrough time min | | | Exhaust time min | | |
|---|---|---|---|---|---|---|---|
| | | Experimental | Theoretical | Error (%) | Experimental | Theoretical | Error (%) |
| 1.0 | 25.0 | 80 | 73 | 8 | 260 | 253 | 3 |
| 0.5 | 50.0 | 100 | 96 | 3 | 200 | 180 | 9 |

**Conclusion**
The adsorption of As(V) on Ce4ZP in a fixed bed, was observed strongly depending on the influent flow rate,
initial concentration and bed depth of column.  Increase in bed depth enable more water can be treated, but with
a slight reduction in column capacity. The quantity of treated water and adsorption capacity were found higher
at a lower flow rate.  At higher influent concentration, the adsorption capacity was higher. The service times
predicted from the theoretical BDST equations agreed well with the service time obtained experimentally at
different concentration and flow rate. The results suggest the practical applicability of Ce4ZP in As(V) removal
in fixed bed columns.

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