

Adsorption of Iron(III) from Phosphoric Acid Solution on Aminotrimethylene Phosphonic Acid Impregnated Resin

A. Sh. Saleh¹ and A. A. El-Zahhar^{1,2}

¹*Nuclear Chemistry Department, Hot Laboratories Center, Atomic Energy Authority, Cairo, Egypt*

²*Chemistry Department, College of Science, King Khalid University, Abha, Kingdom of Saudi Arabia*

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ABSTRACT

The phosphonate compound aminotrimethylene phosphonic acid (ATMP) was impregnated onto Amberlite® XAD4 resin and studied for adsorption of ferric ions from phosphoric acid solution by the batch equilibration and column techniques. The adsorption process was studied as a function of influencing parameters such as ATMP concentration, solution pH, initial iron concentration, H₃PO₄ concentration and anion concentration in solution. The removal of Fe(III) by ATMP-impregnated resin was found to decrease as the concentration of ATMP increased on the resin. The presence of anionic species (chloride, nitrate and sulphate at certain concentrations) was found to increase the removal of iron from phosphoric acid solution. The column breakthrough capacity for Fe(III) onto ATMP-impregnated resin was found to be 1.79 meq/g.

Keywords: *Amberlite® XAD4, phosphonate, iron, phosphoric acid*

INTRODUCTION

Iron is one of the highly important contaminants, which is routinely detected in municipal waste effluents, particularly in cities where iron and steel are manufactured. Iron readily complexes with sulphates in the sediments of many surface waters. The presence of iron in drinking water creates an objectionable taste, which can be easily detected even at low concentrations of iron 1.8 mg/l.⁽¹⁾ The iron toxicity causes many problems such as anorexia, oliguria, diarrhoea, hypothermia, diphasic shock, metabolic acidosis and even death.⁽²⁾ The presence of iron with other impurities (originally present in the phosphate rocks) in phosphoric acid produced by the wet process highly affects the grade of the acid. The presence of these impurities especially iron, affects the quality of the product. Consequently, the majority of phosphoric acid produced by the wet process (about 95%) is used as fertilizers

and excluded from the use in non-fertilizer applications.⁽³⁾ The usage of phosphoric acid in some industrial and food grade applications (e.g. food beverage, toothpaste and cleaning markets) requires application of high purification techniques which enables the removal of the above mentioned impurities.⁽⁴⁾ Different procedures were studied for purification of phosphoric acid including precipitation, ion-exchange, liquid-liquid extraction⁽⁵⁻⁹⁾, adsorption on activated carbon⁽¹⁰⁾ and membrane technologies such as electrodialysis (ED), reverse osmosis and nanofiltration.⁽¹¹⁻¹³⁾ Purification of H_3PO_4 through the removal of heavy metals was studied by precipitation of these metals as sulfides.⁽¹⁴⁾ Further purification of wet H_3PO_4 could be performed by precipitation of cationic impurities, especially Fe, Al, Mg and Ca, through increasing the pH of H_3PO_4 until the precipitation.⁽⁴⁾ Fertilizer grade phosphoric acid of 50% P_2O_5 should contain no more than 1.5% Fe_2O_3 .⁽¹⁵⁾ Adsorption of ferric ions from aqueous solution was studied on chitin (a long chain polymer of a N-acetylglucosamine) by the batch equilibration method and different parameters were studied.⁽¹⁶⁾ The purification of phosphoric acid was studied by electroextraction of mineral impurities by electrodeionization process (EDI) combining ion-exchange membranes (IEM) and textiles (IET).⁽¹⁷⁾ High iron content in fertilizer grade phosphoric acid decreases the solubility of P_2O_5 in water ⁽⁴⁾. The Egyptian phosphate concentrates leached with H_2SO_4 contain 50% P_2O_5 and 4% Fe_2O_3 , while that leached with recycled H_3PO_4 contain 50% P_2O_5 and 2.7% Fe_3O_4 .⁽⁴⁾ Decreasing iron content in wet phosphoric acid was studied using different precipitating reagents as sodium silicate, silicon dioxide, potassium sulfate, (silicon dioxide + sodium carbonate + potassium sulfate (0.8885:1.5672:4.0000)), calcium sulfate and potassium amyl xanthate (0.01–6.00 g/100 ml H_3PO_4).⁽⁴⁾ Aminotrimethylene phosphonate compound was also studied for decreasing the iron content in the wet-process phosphoric acid.⁽¹⁸⁾

In the present work, the phosphonate compound aminotrimethylene phosphonic acid (ATMP) was impregnated onto Amberlite® XAD4 resin. The produced adsorbent was studied for the removal of Fe(III) from phosphoric acid solution by studying the effect of pH, contact time, adsorbent dose, Fe(III) concentration, acid concentration and temperature. The prepared adsorbent was applied for the removal of iron from phosphoric acid using batch technique. Column experiments were also performed for adsorption of Fe(III) from phosphoric acid.

EXPERIMENTAL

Materials:

Aminotrimethylene phosphonic acid (ATMP) was purchased from E-Chemical Source Company while Amberlite® XAD4 was supplied by Rohm and Haas. Extra pure phosphoric

acid was obtained from Scharlau, Spain and was used for solutions preparation. Crude black phosphoric acid was supplied from Abu Zaabal Fertilizer and Chemical Company (AZFC). This black acid was firstly purified from suspended matter to obtain green acid.⁽⁵⁾ The constituents of the obtained green acid are given in Table 1. All the chemicals used were of analytical grade and used without further purification.

Table (1): Constituents of green wet process phosphoric acid

Constituent	Concentration
P ₂ O ₅	20%
Fe ₂ O ₃	0.25%
Mn	2.4 ppm
Cd	<0.3 ppm
As	2 ppm
Pb	<1 ppm
Zn	1.2 ppm
U	<1ppm

Preparation of ATMP-Impregnated Resin:

An appropriate volume of 5% ATMP solution in water was mixed with a weighed amount of Amberlite XAD4 resin. The ATMP-impregnated resin was then dried for 24 hours.

Adsorption Experiments:

The removal of iron from phosphoric acid solution with ATMP- impregnated resin was studied as a function of pH, ATMP concentration, iron concentration, acid concentration and anion concentration. 10 mL of the acid solution containing Fe(III) were mixed with 0.1 g of solid adsorbent and were shaken at 25 ± 1 °C till equilibrium. The solution pH was measured and adjusted using NaOH or HCl solutions. After equilibration, the aqueous solution was separated from the solid adsorbent, and the concentration of iron was measured using atomic absorption spectroscopy. The sorption percentage (Sorption%) was calculated as follows:

$$\text{Sorption}\% = \frac{c_o - c_e}{c_o} \times 100 \quad (1)$$

Where C_o is the initial iron concentration in the aqueous solution (mg/L), C_e is the equilibrium iron concentration in the aqueous solution (mg/L), V is the solution volume (mL) and m is the weight of adsorbent (g). After optimizing the sorption conditions, batch sorption experiments were performed similarly on the green wet phosphoric acid obtained from AZFC.

Column Studies:

Column adsorption experiments were performed to evaluate the impregnated resin for adsorption of Fe(III) from wet process phosphoric acid through column operation. Vertical down flow glass column of 0.5 cm inner diameter and 50 cm length packed with 2 g of the prepared ATMP-impregnated resin was used. The effluent flow rate was adjusted at 0.1 ml/min. The effluent solution was collected in 2 ml fractions and the concentration of Fe(III) was determined using atomic absorption spectroscopy. The adsorption capacity of the ATMP-impregnated resin column was determined using the equation:

$$Q_e = [(C_o - C_e)/m] b_v \quad (2)$$

Where C_o and C_e denote the initial and effluent concentration of metal ion in mole/L for Fe(III), b_v is the breakthrough volume of the Fe(III) solution in liters and m is the mass of the adsorbent packed in the column in gram.

RESULTS AND DISCUSSION

Effect of ATMP Concentration:

The removal of Fe(III) from phosphoric acid solution was studied using ATMP-impregnated resin (impregnated with different concentration of ATMP). The results represented in Fig. 1 obviously show that the sorption percentage decreases with increasing the ATMP concentration in the impregnation solution. This could be due to cluster formation of the chelating phosphonate compound on the surface of the resin which inhibits the chelation reaction. The results indicate that the resin impregnated with 0.1% ATMP gives the highest removal percentage of Fe(III). Therefore, this ATMP-impregnated resin was used in further experiments, unless otherwise stated.

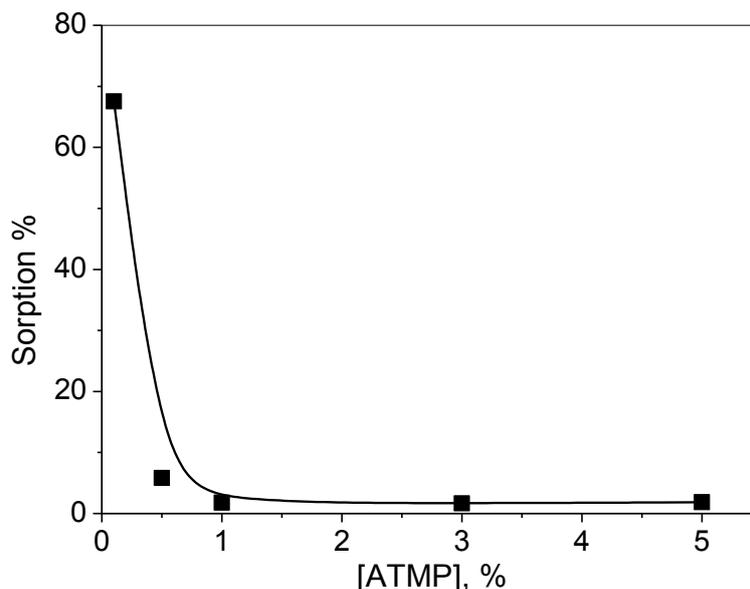
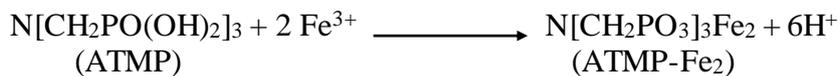
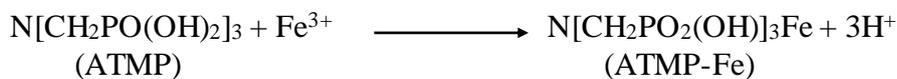


Fig.(1): Effect of ATMP concentration on sorption of Fe(III); [Fe(III)]_i = 50 mg/L, pH = 1.7.

Effect of pH :

The predominant species of Fe(III) ions in aqueous solution depends greatly on the pH, which affects the adsorption reaction of these ions with the active sites on the adsorbent surface. Within acidic to neutral pH conditions, ferric iron may form a number of soluble species include Fe^{3+} , $\text{Fe}(\text{OH})^{2+}$, and $\text{Fe}(\text{OH})_2^+$. Dimerized species (e.g. $\text{Fe}_2(\text{OH})_2^{4+}$) could be formed depending on solution concentration. The removal of Fe(III) from phosphoric acid solution of variable pH was studied using AMTP-impregnated resin and the obtained results are represented in Fig. 2. The results show evident dependence of Fe(III) adsorption on pH. In highly acidic solutions the surface of the chelating phosphonate compound ATMP reacts with Fe^{3+} according to the following chelation reactions⁽¹⁸⁾:



Firstly, as the pH increases to near 4.0, the above chelation reactions increase in the forward direction and hence, the Fe(III) adsorption increases. Then, with further increase in pH, the surface active sites of the ATMP go blocked, and hence, the chelation reactions are inhibited and the adsorption greatly decreases. This observation emphasizes the importance of

the role of ATMP and the chelation reactions. At pH higher than 4.0, soluble hydrolyzed species ($\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^+$) are formed which inhibit the exchange reactions on the resin. Further increase of pH causes complete hydrolysis and precipitation which renders the residual Fe(III) concentration in solution highly decreased (due to precipitation not because of adsorption).^(16,19)

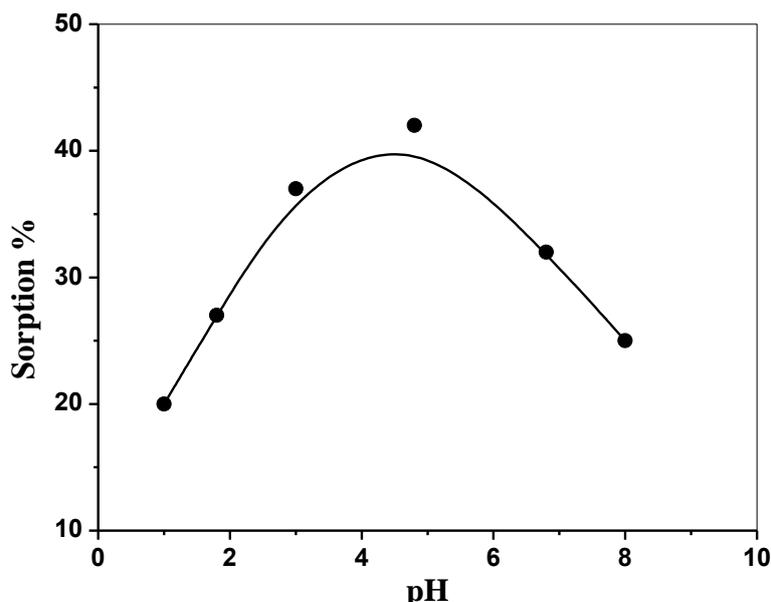


Fig. (2): Effect of pH on sorption of Fe(III) onto ATMP-impregnated resin; $[\text{ATMP}] = 0.5\%$, $[\text{Fe}(\text{III})]_i = 50 \text{ mg/L}$.

Effect of Fe(III) Concentration:

The removal of Fe(III) by ATMP-impregnated resin was studied from phosphoric acid solutions containing different Fe(III) concentrations. The dependence of the adsorption reaction on the concentration of Fe(III) can be explained as follows: at low Fe(III) concentration, i.e. the Fe(III) to adsorbent ratio is low, the fractional adsorption becomes independent of the initial Fe(III) concentration.⁽²⁰⁾ While at higher Fe(III) concentrations, the available sites of adsorption and chelation become fewer and hence the percentage removal of iron(III) decreased with increasing Fe(III) concentration. The adsorption of Fe(III) from solutions containing different initial concentrations of Fe(III) is shown in Fig. 3. It is clear that the adsorbed amount of Fe(III) increases with increasing Fe(III) concentration.

Effect of Acid Concentration (H_3PO_4):

The removal of Fe(III) by ATMP-impregnated resin was studied from phosphoric acid solutions containing different acid (H_3PO_4) concentrations. The results in Fig. 4 clarify that the removal percentage of Fe(III) decreases with increasing acid concentration. This observation could be attributed to the release of the chelated or adsorbed Fe(III) with increasing acid concentration.⁽¹⁸⁾

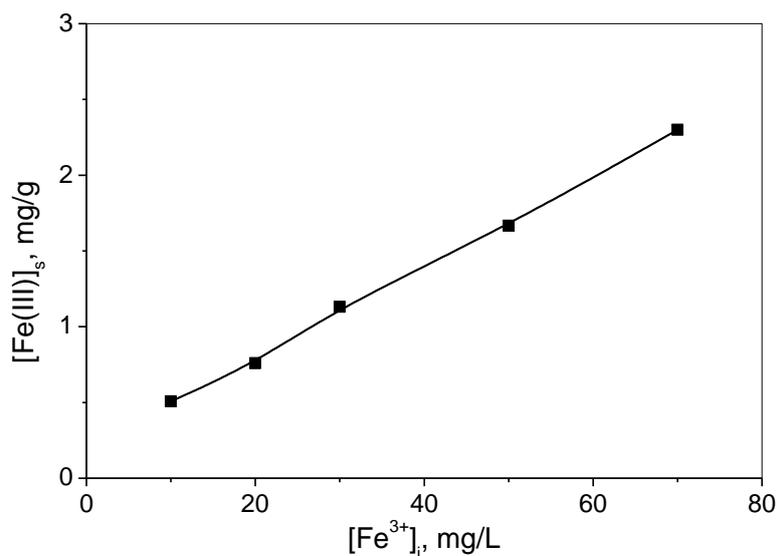


Fig. (3): Effect of initial ion concentration on Fe(III) adsorption on ATMP-impregnated resin; [ATMP] = 0.1%, pH = 2.

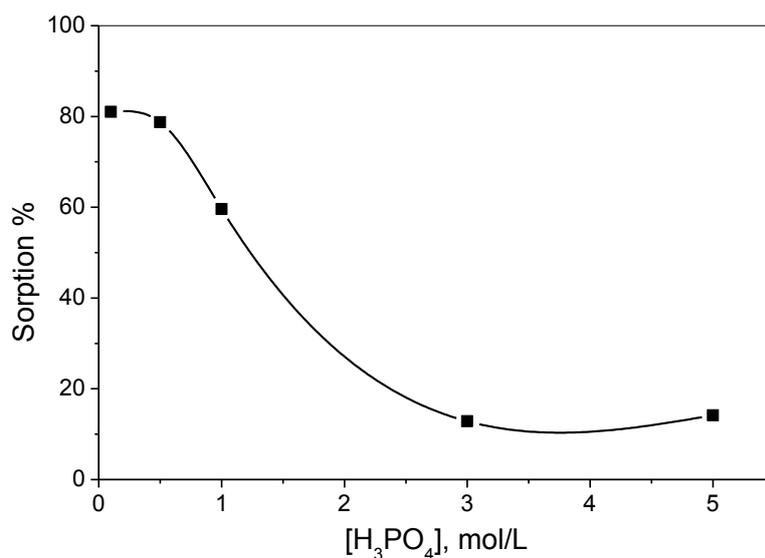


Fig. (4): Effect of H_3PO_4 concentration on Fe(III) adsorption on ATMP-impregnated resin; [ATMP] = 0.1%, $[Fe(III)]_i = 50$ mg/L.

Effect of Chloride, Nitrate and Sulphate Anions:

The removal of Fe(III) from phosphoric acid solution by AMTP-impregnated resin was studied as a function of anions concentration (Cl^- , NO_3^- , SO_4^{2-}). The results in Figs. 5, 6 and 7 show that increasing chloride ion concentration increases the removal of iron(III) by AMTP-impregnated resin, while increasing nitrate and sulphate concentrations firstly decreases the adsorption, but a further increase in nitrate and sulphate concentrations increases the adsorption. This could be attributed to the presence of these anions in certain concentrations that increase the formation of anionic complexes⁽²¹⁾ which, in turn, may increase the affinity towards the chelate formation with AMTP. The results in this concern reflect a relative increase in the chelation ability of Fe(III) in presence of certain concentrations of Cl^- , NO_3^- and SO_4^{2-} .

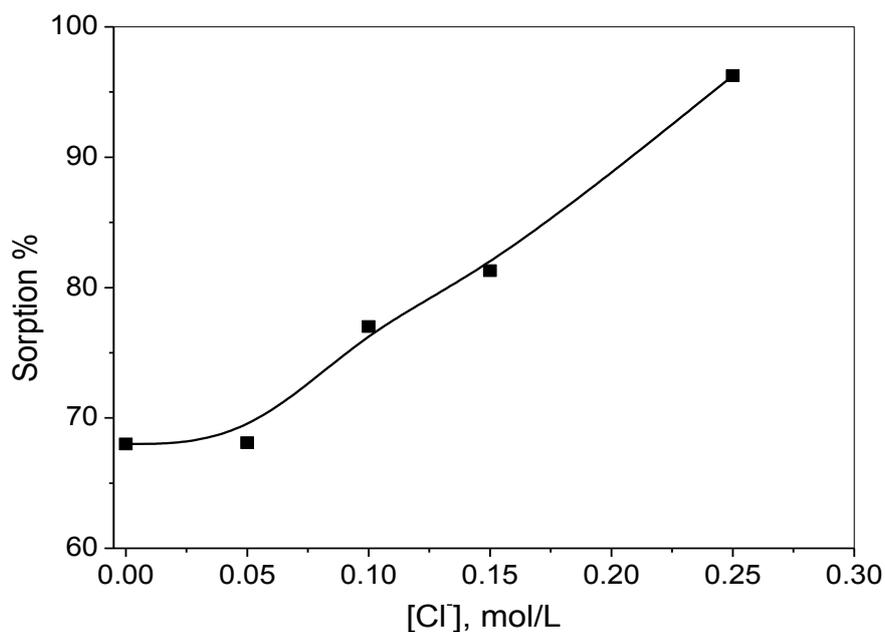


Fig. (5): Effect of Cl^- ion concentration on adsorption of Fe(III) on ATMP- impregnated resin; $[\text{ATMP}] = 0.1\%$, $[\text{Fe(III)}]_i = 100 \text{ mg/L}$, $\text{pH} = 1.5$.

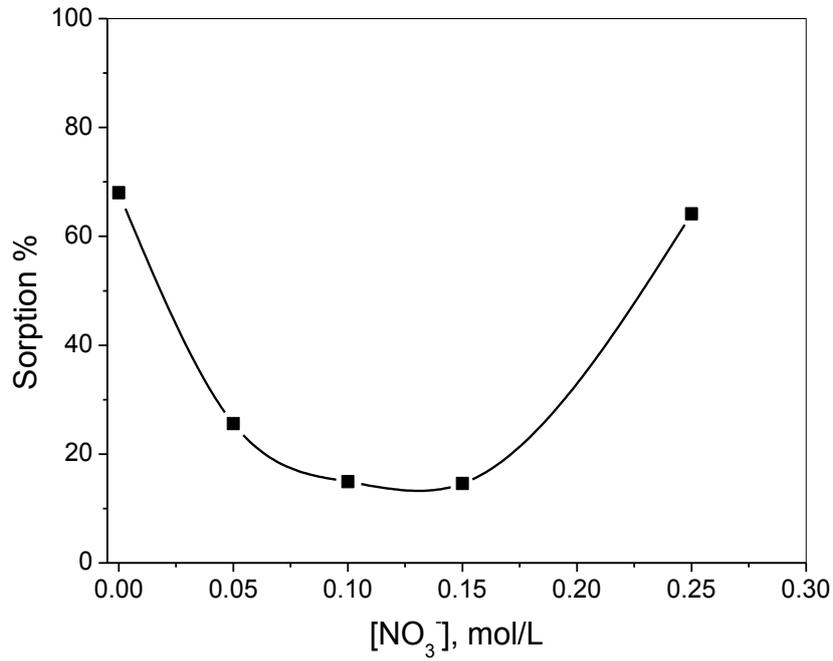


Fig. (6): Effect of NO_3^- ion concentration on sorption of Fe(III) on ATMP- impregnated resin; [ATMP] = 0.1%, $[\text{Fe(III)}]_i = 100$ mg/L, pH = 1.5.

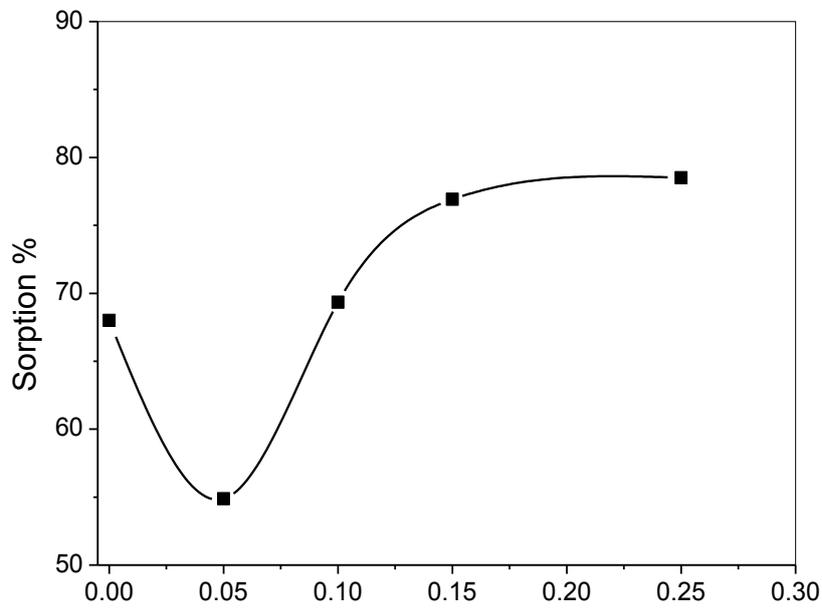


Fig. (7): Effect of SO_4^- ion concentration on sorption of Fe(III) on ATMP-impregnated resin; [ATMP] = 0.1%, $[\text{Fe(III)}]_i = 100$ mg/L, pH = 1.5.

Column Studies:

The adsorption of Fe(III) from green wet process phosphoric acid solution was dynamically studied on ATMP-impregnated resin column at room temperature and at a flow rate of 0.1 ml/min. The influent solution (wet phosphoric acid with the constituents in Table 1) was passed through the column beads. The breakthrough of Fe(III) was obtained by plotting the ratio of C_e/C_o against the effluent volume, Fig. 8. It was observed that the column gets saturated after passing 60 ml of iron solution. The estimated breakthrough sorption capacity (Q_e) was found to be 1.79 meq/g for Fe(III).

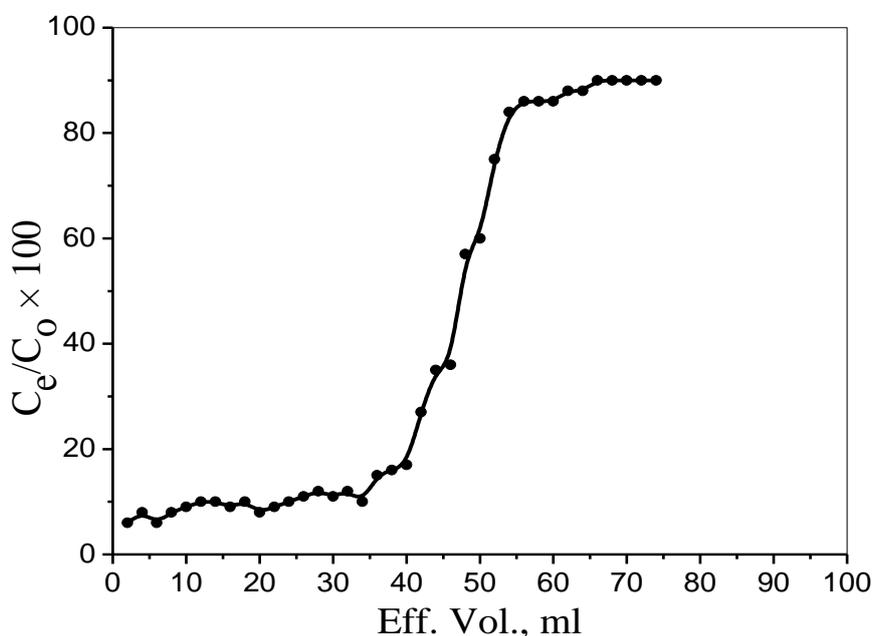


Fig. (8): Breakthrough curve for adsorption of Fe(III) on ATMP-impregnated resin column, $m = 2$ g.

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