

# ARSENIC REMOVAL FROM CONTAMINATED WATER USING NON-IMPRINTED POLYMERS

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## **ABSTRACT**

Arsenic contamination presents serious health concerns for the public. Elevated arsenic concentrations are a worldwide issue, effecting millions of people through contamination of drinking water, irrigation water and food crops. Exposure to arsenic can result in skin lesions, developmental problems and cancer. Previous technologies for the removal of arsenic in most cases require either several pre-treatment steps or have long turn over times between treatments. Production of arsenic contaminated waste is also an issue.

This study has investigated the possibility of using non-imprinted polymers (NIP) for the treatment of arsenic contaminated water, that can provide both sufficient and efficient removal of contaminants.

NIP showed an adsorption capacity of 27 mg arsenic per g of media at pH 5. Adsorption capacity decreased with increasing pH. Rate of adsorption was rapid due to the small particle size of the media and high surface area. Adsorption was best modelled by the Dubinin – Radushkevich isotherm and the pseudo-second order model which gave average R<sup>2</sup> of 0.93 and 0.99 respectively. NIP would be better suited for acidic solutions containing high arsenic concentrations, such as mining waste water, but would not be suitable for river water where arsenic concentrations are 0.02 mg/L and neutral pH.

## **KEYWORDS**

Heavy Metals, Product Development, Arsenic, Potable Water, New Technology

## **PRESENTER PROFILE**

Norton Holtz is a Research Technologist and Scale Up Chemist at Ligar LP based at the Ruakura Research Campus in Hamilton. Ligar produces materials capable of removing heavy metals, pesticides, flavor taints and valuable compounds from water, wine/beverages and industrial waste streams.

# 1 INTRODUCTION

Heavy metal contamination of water is a growing global concern. Arsenic is a naturally occurring persistent toxic heavy metal which is commonly found in water sources (Langsch et al., 2012). Natural sources of arsenic release include volcanic activity, erosion and forest fires. Agricultural use, geothermal power generation, mining and smelting are common human activities which can release arsenic into water sources (WHO, 2016). Arsenic is used in rat poisons, insecticides, semi-conductors, bronzing, pyrotechnics, lead shot hardening, paints, dyes, drugs, glass manufacture and preserving wood.

Many countries have identified high levels of naturally occurring arsenic in their ground water. These include Argentina, Bangladesh, China, India and the United States of America. Countries such as Peru where mining occurs will also be at risk of high arsenic concentrations in water sources as the mining waste water is often discharged into waterways used to source drinking and irrigation water. Exposure to high levels of arsenic through drinking contaminated water or using contaminated water for food preparation and irrigation is the greatest threat for public exposure to arsenic (Nicomel et al., 2016). The maximum contaminant level (MCL) for arsenic in drinking water is 10 ppb (EEA, 2017, Nicomel et al., 2016). Short term exposure to arsenic can result in vomiting, abdominal pain, diarrhea and extremity numbness. Death will occur in cases where the concentration is high. Long term arsenic exposure can result in skin lesions, cancer and developmental problems (WHO, 2016, Clancy et al., 2013).

Suggested methods to reduce arsenic levels in drinking water include substituting rain water for ground water, diluting high arsenic concentration water with low arsenic concentration water or installing arsenic removal technologies (WHO, 2016). Existing arsenic removal technologies include ion exchange, adsorptive media filtration, coagulation combined with flocculation, iron co-precipitation and electrocoagulation. These methods produce arsenic contaminated waste which must be disposed (Ito et al., 2001, Clancy et al., 2013, Langsch et al., 2012).

Disposal of arsenic contaminated waste is one of the main factors that limits the use of current arsenic removal technologies. Other factors include cost, regeneration, processing time and maintenance. In developed countries, arsenic contaminated wastes can be stabilized and disposed into hazardous waste landfills. If the arsenic contaminated waste is disposed of into general waste landfills or not stabilized, the arsenic can be released in the landfill leachate due to the inappropriate conditions of the landfill. In developing countries arsenic contaminated waste is often disposed into ponds or open fields (Clancy et al., 2013).

Molecularly imprinted polymers (MIP) consist of functional and crosslinking monomers. Polymerization takes place in the presence of a template molecule. The interaction between the functional monomers and the template molecule results in the formation of complementary shaped binding sites during polymerization. The template molecule is then removed from the MIP using different cleaning methods leaving behind free complementary shaped binding sites which can selectively bind the template molecule out of different solutions.

Using MIPs for contaminated water remediation has several advantages such as good resin stability, fast binding rates and fast elution rates. The most attractive advantage is the ability to selectively recover the contaminant/target in a purer form than other options. This allows the recovered contaminant/target to be used in useful applications instead of disposed of. Alternatively, where disposal is still the preferred option contaminants recovered using MIPs will have less mass to be disposed of due to lower percentages of other materials being present e.g. co-precipitated metals and sludges etc.

The main disadvantage of using MIPs for contaminant removal is that the contaminant must be used during the synthesis of the MIP and then removed from the MIP different cleaning steps. An alternative to using MIPs is to use Non-Imprinted Polymers (NIPs). NIPs are polymerized in the absence of the template which creates generic binding sites able to bind a wide range of templates. This is useful in situations where more than one type of contaminant needs to be removed. However, NIPs do not allow the selective recovery of the contaminants (Alvarez-Lorenzo and Concheiro, 2013). NIPs have been suggested as an alternative to MIPs where the desired template to be recovered is considerably hazardous. As no template is used during polymerization, no cleaning is required and the manufacturing process is simpler and faster. NIPs are also used in preliminary studies to investigate the binding ability of polymers made with different functional and crosslinking monomers.

This study investigated the use of NIPs for the removal of arsenic from water. It was completed as preliminary work prior to using MIPs for the removal of arsenic from water. It will cover the binding rate and ability of the NIP at different pHs and discuss different models for the binding data.

## **2 EXPERIMENTAL**

NIP was supplied by Ligar Polymers (Hamilton) and consists of a proprietary crosslinked polymer with groups that can participate in electrostatic interactions. Lab grade arsenic (V) was purchased from Sigma, while distilled water, sodium hydroxide, nitric acid, and hydrochloric acid were all supplied by the University of Waikato.

### **2.1 ISOTHERM EXPERIMENTAL**

Distilled water was adjusted to pH 5 and spiked with arsenic concentrations ranging from 0.03 to 18 mg/L arsenic. 0.01 gram of NIP was suspended in 0.1 litres of the test solution in conical flasks and agitated for 24 hours at room temperature (19.8 °C) on a shaker table at 130 rpm. The NIP was allowed to settle, a 10 ml sample of the test solution was collected filtered through a 0.45 µm filter, stabilized by adding 0.2 ml of concentrated nitric acid, and taken for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to analyze the change in arsenic concentration. The method was repeated for pH 6, pH 7 and pH 8.5.

### **2.2 KINETIC BINDING EXPERIMENTAL**

Distilled water was adjusted to pH 5 and spiked with 0.06 mg/L of arsenic. 1 gram of NIP was suspended in 0.5 litres of the test solution and agitated. 10 ml samples of the suspension were taken at regular intervals up to 24 hours. The test solution was filtered through a 0.45 µm filter after collection, stabilized by adding 0.2 ml of concentrated nitric acid, and taken for Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to analyze the change in arsenic concentration. The method was repeated for pH 6, pH 7 and pH 8.5. Kinetic binding models were fit using the Microsoft Excel Solver function and the sum of square errors method.

### **2.3 DATA ANALYSIS**

The amount of arsenic adsorbed,  $q_t$  (mg/g) at time  $t$ , was calculated according to equation (1):

$$q_t = \frac{[(C_0 - C_t)V]}{W} \quad (1)$$

Where  $C_o$  (mg/L) is the starting liquid phase concentration of As and  $C_t$  (mg/L) is the arsenic concentration at time  $t$  respectively,  $V$  is the volume of the Arsenic solution (L) and  $W$  is the mass (g) of NIP used.

The percentage of As removal was calculated according to equation (2):

$$R \% = \left[ \frac{C_o - C_e}{C_o} \right] \times 100 \quad (2)$$

Where  $C_e$  is the equilibrium concentration in the solution (mg/L).

The Langmuir, Freundlich, Langmuir-Freundlich and Dubinin-Radushkevich (D-R) (Mandal et al., 2013; Zeng, 2004) adsorption isotherms were used in this study to model the interaction between NIP adsorbent and the arsenic.

The Langmuir equation is:

$$q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (8)$$

Equation (8) is linearized to give:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (9)$$

Where  $q_e$  is the amount of As adsorbed at equilibrium (mg/g),  $C_e$  represents the equilibrium concentration of As in the aqueous solution (mg/L),  $q_m$  is the maximum adsorption capacity (mg/g) and  $K_L$  is the Langmuir constant (L/mg).

The Freundlich equation is:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (10)$$

Equation (10) is linearized to give:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (11)$$

Where  $K_F$  is a Freundlich constant (mg/g) and  $n$  is a constant.

The Langmuir-Freundlich equation is:

$$q_e = \frac{K_L q_m C_e^{\frac{1}{n}}}{1 + K_L C_e^{\frac{1}{n}}} \quad (12)$$

The Dubinin - Radushkevich equation is:

$$q_e = q_s \exp(-K_{DR} \varepsilon^2) \quad (13)$$

$$\varepsilon = RT \ln \left( 1 + \frac{1}{C_e} \right) \quad (14)$$

Equation (13) is linearized to give:

$$\ln q_e = \ln q_s - K_{DR} \varepsilon^2 \quad (15)$$

Where  $K_{DR}$  is D-R isotherm constant ( $\text{mol}^2/\text{KJ}^2$ ),  $\epsilon$  is the Polanyi potential,  $q_s$  is the isotherm saturation capacity ( $\text{mg/g}$ ),  $R$  is the universal gas constant ( $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ) and  $T$  is the temperature in Kelvin (K).

Isotherm models were fitted using the Microsoft Excel Solver function and the sum of square errors method.

The pseudo-first-order, pseudo-second-order and Elovich kinetic models were applied to the kinetic data for As adsorption onto NIP. The pseudo-first-order non-linear model is:

$$q_t = q_e(1 - \exp^{-K_1 t}) \quad (3)$$

The non-linear form of pseudo-second-order model is given as:

$$q_t = \frac{K_2 q_e^2 t}{(1 + q_e K_2 t)} \quad (5)$$

Where  $K_1$  and  $K_2$  is the pseudo-first order ( $\text{min}^{-1}$ ) and pseudo-second-order ( $\text{g/mg.min}$ ) rate constant respectively,  $t$  is the time (min),  $q_e$  and  $q_t$  represent the quantity of As adsorbed ( $\text{mg/g}$ ) on the surface of NIP at equilibrium and at time  $t$  (min) respectively (Gulnaz et al., 2005).

Elovich kinetic model can be expressed as:

$$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln(t) \quad (7)$$

Where  $\alpha$  ( $\text{mg/g min}$ ) and  $\beta$  ( $\text{g/mg}$ ) are the initial adsorption rate constant and the Elovich adsorption constant respectively (Sen Gupta and Bhattacharyya, 2011).

The isotherm and kinetic models were fitted using the Microsoft Excel Solver function and the sum of square errors and coefficient of determination ( $R^2$ ) method.

### 3 RESULTS AND DISCUSSION

Figure 1 shows the effect of solution pH on the adsorption of As by NIP. At pH 5 the adsorption was greatest reaching 27 mg/g and gradually decreased as pH increased. At pH 5 the majority of As is in the form of  $\text{H}_2\text{AsO}_4^-$ , while at pH 6 only 65% is in that form with the remainder in the form  $\text{HAsO}_4^{2-}$ , and at pH 7 and 5 37% and 5% is  $\text{H}_2\text{AsO}_4^-$  respectively (Henke 2009). The polymer used for NIP is a weak base and becomes protonated and forms a positive charge at low pH, hence showing good binding capacity for As.

The isotherms for all pH were not favourable requiring higher concentrations of arsenic for adsorption to occur at increasing pH. This is problematic if NIP was to be used for arsenic removal as the arsenic could not be removed to low concentrations, and would not be useful for concentrations as low as 0.020 mg/L as found in the Waikato river and at pH 7, twice as much media would be needed. NIP would be useful for acidic mining waste water that was rich in arsenic at concentrations greater than 5 mg/L.

The Dubinin – Radushkevich isotherm gave the best fit for the isotherm data, representing well the unfavourability of adsorption (parameters shown in Table 1), while the Freundlich, Langmuir and Langmuir Freundlich models were unable to do so.

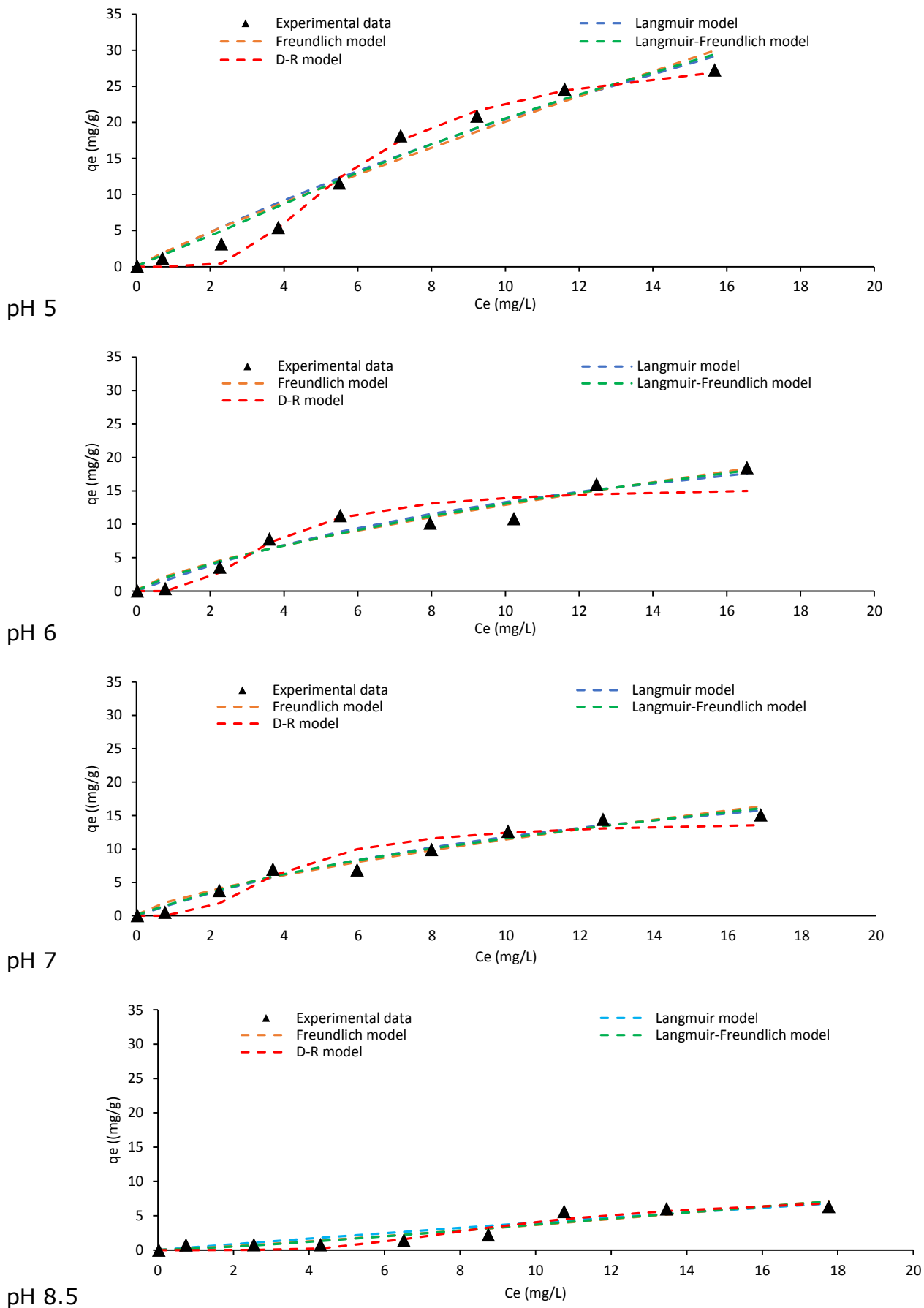


Figure 1: Adsorption isotherms for arsenic adsorption onto NIP at different pH.

Table 1: Fitted parameters and goodness of fit for the Dubinin – Radushkevich isotherm for arsenic adsorption onto NIP at different pH.

pH	$K_{DR}$ ( $\text{mol}^2/\text{KJ}^2$ )	$q_s$ ( $\text{mg}/\text{g}$ )	SSE	R2
5	5.47	30.49	10.33	0.99
6	2.15	15.65	33.92	0.90
7	2.54	14.26	21.24	0.92
8.5	14.21	8.78	4.18	0.92

Kinetic data (Figure 2) showed rapid removal within the first 100 minutes, but taking up to 800 minutes in some cases to reach equilibrium. The initial rapid uptake is due to the media being relatively small, 5-15  $\mu\text{m}$ , and therefore having a large surface area for adsorption. Once the surface sites were occupied, adsorption appeared to be controlled by diffusion of arsenic into the media. Percentage removal was 40% for pH 8.5, which was unexpected due to the media showing greater adsorption capacity at lower pH. The result could be due to the solution reaching 0.038 to 0.043 mg/L arsenic concentration (Figure 3), while the media reached 0.0013 mg/g arsenic concentrations, so concentrations might be too low to give accurate results. For the NIP to be of use in removal of arsenic from river water, it needs to be able to reduce the arsenic concentration to below 0.01 mg/L which is the New Zealand drinking water standard, but with the adsorption isotherm being unfavourable, NIP is not likely to be a successful adsorbent.

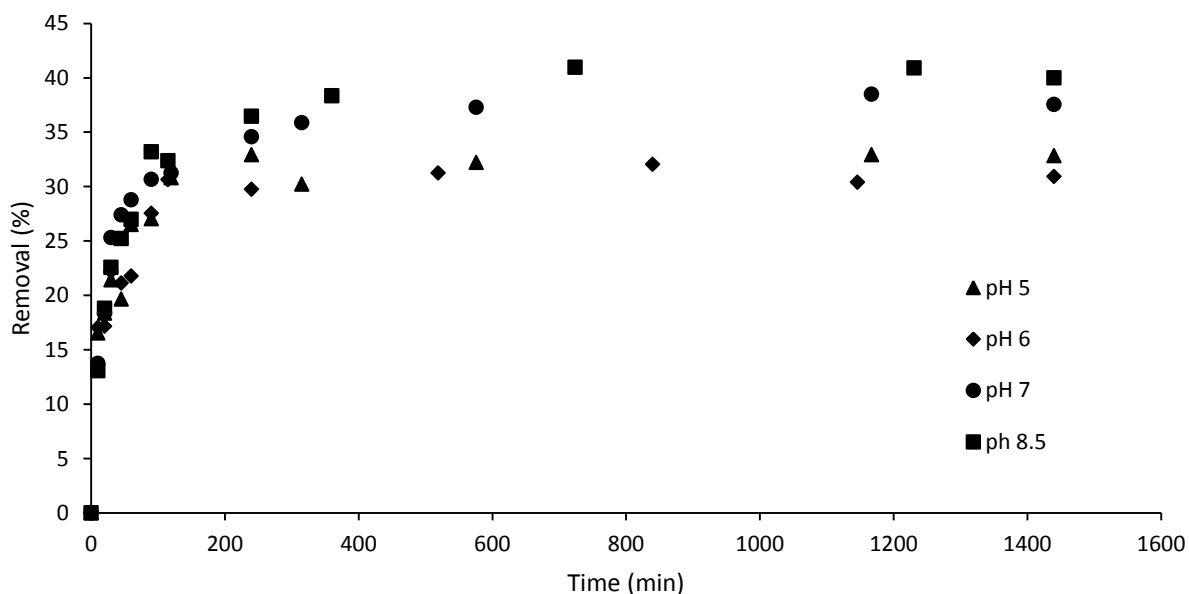


Figure 2: Percentage removal with time for arsenic adsorption onto NIP at different pH.

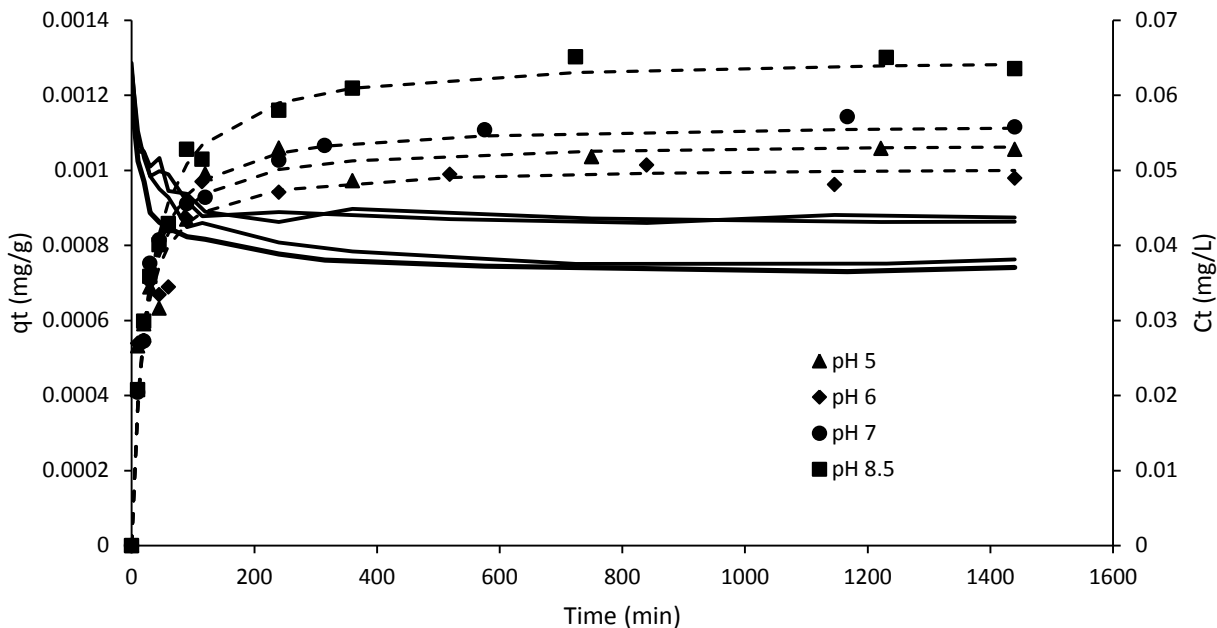


Figure 3: NIP and solution concentrations of arsenic over time. Data points are the experimental arsenic concentrations on the media, dashed lines are the pseudo-second-order model arsenic concentrations on the media, while solid lines are the solution concentrations.

The pseudo-second order model gave the best fit for the kinetic data (Figure 3) with an average  $R_2$  value of 0.99 when the data was linearized and the linearized model fitted. The pseudo first order and Elovich models gave bad fits for both linearized and non-linearized data with average  $R_2$  of 0.69 and 0.87 respectively. Fitted parameters for the pseudo second order model are shown in Table 2. Pseudo second order models have been successfully used for a range of other metal adsorptions such as nickel, chromium, copper, cadmium and lead onto fly ash, peat, plant leaves, and other adsorbents (Ho 1999) because they readily fit adsorptions that include various reaction mechanisms and diffusion.

Table 1: Fitted parameters and goodness of fit for the pseudo-second-order model for arsenic adsorption onto NIP at different pH.

pH	$K_2$ (g/mg.min)	$q_e$ (mg/g)	$R_2$
5	53.5	0.0011	0.9996
6	62.4	0.0010	0.9992
7	46.8	0.0011	0.9997
8.5	35.6	0.0013	0.9995

## 4 CONCLUSION

While NIP showed an adsorption capacity of 27 mg arsenic per g of media, the polymer chemistry required the water to be adjusted to pH 5 for NIP to hold a charge that would bind the arsenic. Adsorption capacity decreased with increasing pH and was unfavourable. This meant the media did not have a high affinity for the arsenic and the arsenic concentration needed to be high for adsorption to occur. Rate of adsorption was rapid due to the small particle size of the media and high surface area, but did not result in high removal of arsenic. Adsorption was best modelled by the Dubinin – Radushkevich



isotherm and the pseudo-second order model which gave average  $R_2$  of 0.93 and 0.99 respectively. NIP would be better suited for acidic solutions containing high arsenic concentrations, but would not be suitable for river water where the arsenic concentrations are 0.02 mg/L and neutral pH.

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