

SYNTHESIS OF ALUMINIUM OXIDE FROM ALUMINIUM WASTE TO REMOVE PHOSPHATES AND NITRATES FROM WASTEWATER

See Jae Wey Tristan (3I1), Ernest Tan Rui Yang (3I1), Joshua Ng Yong Quan (3I3)

Group 1-49

ABSTRACT

Excess phosphate in water bodies causes eutrophication which is harmful to the ecosystem. In this study, aluminium oxide was successfully synthesised from waste aluminium foil. Studies were conducted on the aluminium oxide to determine its effectiveness in removing phosphate and nitrate. Effect of pH and initial concentration of phosphate on adsorption were also investigated. Synthesised aluminium oxide is made up of spherical particles with sizes less than 50 nm. It is able to remove both phosphate and nitrate ions. The adsorption of phosphate is more effective, with close to 100% of phosphate being removed. Through isotherm studies, the maximum adsorption capacity of the aluminium oxide on phosphate was determined to be 74.6 mg g⁻¹. Phosphate adsorption is affected by both concentration and pH of solution, with the optimal pH being pH 10. Synthesised aluminium oxide was also found to be comparable with both commercial aluminium oxide and other phosphate adsorbents such as iron (III) oxide and tantalum hydroxide in removing phosphate. Aluminium oxide synthesised from waste aluminium is promising to be used in wastewater treatment plants to remove phosphate from industry effluents.

1. INTRODUCTION

Water eutrophication is a major environmental problem worldwide, which results in the degradation of the water ecosystem and the destruction of the self-purification capacity of water (Smith, 2003). Nitrogen and phosphorus, the two major contributors to water eutrophication, rapidly increase with human activities, including the discharge of agricultural, industrial, and domestic wastewater (Paerl, 2009). Inorganic nitrogen and phosphorus commonly exist in the form of NH₄⁺, NO₃⁻, and PO₄³⁻ in the water system. Eutrophication in water is usually caused by the combined action of two or three kinds of nutrients: NH₄⁺, NO₃⁻, and PO₄³⁻, and these may vary with the season and the trophic status of water (Kolzau et al., 2014).

Phosphates and nitrates are nutrients that are a natural part of aquatic ecosystems which support the growth of algae. Excess nitrates and phosphates in water promote growth of algae. Excessive algae block the sunlight needed by aquatic plants which are submerged in the water. The rate of photosynthesis of these plants decreases and the amount of dissolved oxygen in the

river decreases as a result, causing aquatic organisms to slowly die and release more carbon dioxide. Water bodies become polluted and become dead zones (Kann & Smith, 1999).

Aluminium is one of the most valuable component materials of municipal refuse in terms of cans, doors, siding, car engine and body parts, wrapping foil and pie plates (Buryakovskaya, Meshkov, Vlaskin, Shkolnikov, & Zhuk, 2017). One of the main sources of aluminium waste is the aluminium foil which is difficult to recycle and takes a very long time to degrade in landfills; therefore, it is either incinerated or disposed of in the landfill (Bayus, Ge, & Thorn, 2016). For example, in 2017, the US disposed a total of 2.4 million tonnes of aluminium (United States Environmental Protection Agency, 2020).

To prevent eutrophication, aluminium oxide (Al_2O_3) is widely used to remove phosphates from wastewater. Aluminium oxide is mainly obtained from bauxite ore in the Bayer process. However, mining activities have negative effects on the environment including soil, air and water as well as people's health and well-being. Respiratory problems, skin diseases, malaria, diarrhoea and heavy metal ion poisoning are health problems prevalent in communities exposed to mining activities (Feisal, Hashim, & Jalaludin, 2019).

The chemical properties of the aluminium oxide such as hardness, having a high melting point, resistivity to both oxidation and corrosion and non-volatility have resulted in industries extensively using it in the production of aluminium, ceramics and refractories. Aluminium oxide has also been extensively used as a catalyst or catalytic support for numerous chemical reactions. Moreover, since aluminium oxide is a robust adsorbent, it can be used as an ion amphoteric exchanger for the treatment of industrial and hazardous waste solutions (Ghoniem, Sami, El-Reefy, & Mohamed, 2014). It also has a high-surface area and exists in different configurations; therefore, it has the potential to adsorb anionic pollutants such as phosphates and nitrates from industrial wastewater (Naiya et al., 2009).

Objectives

This study aims to synthesise aluminium oxide from the reaction between waste aluminium foil and hydrochloric acid, followed by precipitation using sodium hydroxide, to investigate the effectiveness of synthesised aluminium oxide in removing phosphates and nitrates from solutions and thus compare with commercial aluminium oxide. This study also aims to evaluate the effect of initial concentration of phosphates and nitrates on the adsorption capacity of aluminium oxide of these pollutants, and finally, study the effect of pH on the adsorption of phosphate by synthesised aluminium oxide.

Hypotheses:

This study hypothesises that aluminium oxide synthesised from aluminium foil is comparable to commercial aluminium oxide in removing nitrates and phosphates from water, and that the initial concentration and pH of the phosphate/nitrate solution will affect the adsorption of phosphates and nitrates by aluminium oxide.

2. MATERIALS AND METHODS

2.1 Materials

Waste aluminium foil was obtained from laboratories. Potassium dihydrogen phosphate, zinc nitrate, and sodium hydroxide were procured from GCE Chemicals while commercial aluminium oxide was purchased from Sigma Aldrich. Hydrochloric acid was procured from Scharlau.

2.2 Synthesis of aluminium oxide

Waste aluminium foil (2 g) was cut into 1cm by 1cm pieces. The aluminium pieces were reacted with 75 ml of 5 mol dm⁻³ hydrochloric acid to form aluminium chloride, as shown in equation 1.

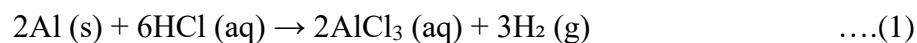
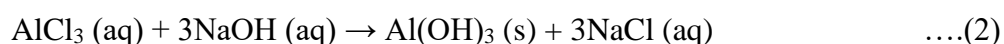


Figure 1. Waste aluminium foil



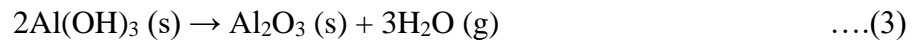
Figure 2. Reaction of waste aluminium foil with hydrochloric acid

The mixture was vacuum-filtered, after which drops of 5 mol dm⁻³ sodium hydroxide were added to the filtrate to induce the precipitation of aluminium hydroxide. The reaction is shown in equation 2.



The precipitate was filtered and washed with deionised water until the washing was free of chloride. This was done by testing the washing with aqueous silver nitrate until there was

no more white precipitate observed. The precipitate was then dried in an oven until constant mass. Finally, it was calcined at 500°C for 4 hours to obtain aluminium oxide (Al₂O₃).



The morphology and particle size of the synthesised aluminium oxide was determined using a Scanning Electron Microscope (SEM). Its identity was confirmed by the use of X Ray Diffraction (XRD).

2.3 Adsorption studies

Solution containing phosphate or nitrate was prepared by dissolving desired amount of potassium dihydrogen phosphate and zinc nitrate in deionised water.

Aluminium oxide (0.1 g) was added to 20 ml of solution containing 50 mg/L phosphate or nitrate. The control was the solution containing 50 mg/L phosphate or nitrate without any aluminium oxide. The mixture was stirred for 24 hours, after which it was centrifuged to obtain the supernatant. The concentration of phosphate or nitrate remaining in the supernatant was analysed using a colorimeter (HACH DR/890). To evaluate the effectiveness of the aluminium oxide synthesised, its adsorption capacity was determined using the following formula:

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

q_e is the adsorption capacity (mg g⁻¹)
 C_0 is the initial concentration of phosphate/nitrate in the solution (mg l⁻¹)
 C_e is the concentration of phosphate/nitrate at equilibrium (mg l⁻¹)
 V is the volume of the solution (l)
 m is the mass of aluminium oxide (g)

The percentage of phosphate or nitrate removed will be determined using the following formula:

$$R\% = \frac{C_0 - C_e}{C_0} * 100$$

R is the percentage of removal
 C_0 is the initial concentration of phosphate/nitrate (mg l⁻¹)
 C_e is the final concentration of phosphate/nitrate (mg l⁻¹)

The effectiveness of aluminium oxide synthesised using aluminium waste foil was compared with commercially-available aluminium oxide.

2.4 Effect of pH on adsorption

The purpose of this study is to determine the optimum pH for adsorption of phosphate, and to investigate the mechanism of adsorption by aluminium oxide. The pH of the solution

containing 50 mg^l⁻¹ phosphate was varied from pH 2 to pH 12 using hydrochloric acid (HCl) or sodium hydroxide (NaOH). Adsorption was then carried out as described in section 2.3.

2.5 Effect of initial concentration of phosphate or nitrate on adsorption

The initial concentration of nitrate and phosphate was varied from 50 to 500 mg^l⁻¹. The equilibrium concentration data of these studies was fitted into Langmuir isotherm to determine the maximum adsorption capacity as well as the mechanism of adsorption. The Langmuir isotherm assumes that adsorbed material (such as phosphate) is adsorbed over a uniform adsorbent surface at a constant temperature.

The linear form of Langmuir isotherm equation is given by:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

Where C_e is the equilibrium concentration of pollutant (mg/L), q_e is the equilibrium capacity of the aluminium oxide (mg/g), b is the Langmuir constant that indicates the sorption intensity and q_m is the maximum sorption capacity (mg/g).

If the equilibrium concentration data fits the Langmuir isotherm, adsorption can be inferred to be monolayer. Maximum adsorption capacity of the aluminium oxide can be derived from the inverse of the gradient of Langmuir linear equation.

3. RESULTS AND DISCUSSION

3.1 Characterisation of aluminium oxide

The Scanning Electron Micrograph (SEM) image shows aluminium oxide as discrete spherical particles of sizes less than 50 nm (Figure 3). The particle size of the synthesised product was similar to those synthesized by Sol-gel technology (Dhawale, Khobragade, & Kulkarni, 2018).

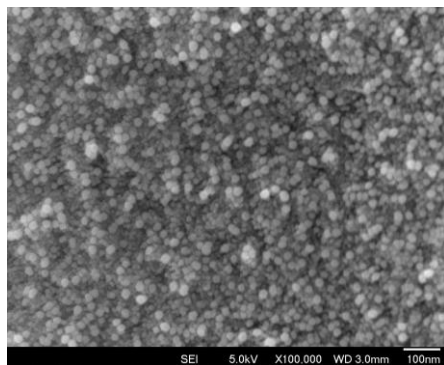


Figure 3. SEM of aluminium oxide synthesised

The Energy Dispersive Spectrum (EDS) analysis reveals that both aluminium and oxygen were present in the synthesised sample (Figure 4).

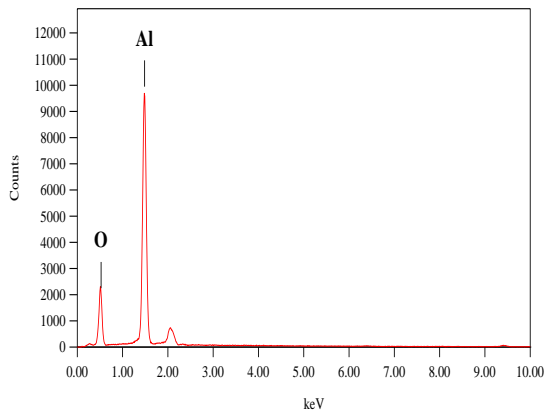


Figure 4. EDS of aluminium oxide synthesised

X-Ray Diffraction (XRD) pattern of aluminium oxide synthesised displayed characteristic diffraction peaks at 2 Theta of 37.6°, 46.0°, 66.9° (Figure 5). The results were consistent with other studies (Zhang & Jia, 2016; Liu, Luo, Wang & Guo, 2015).

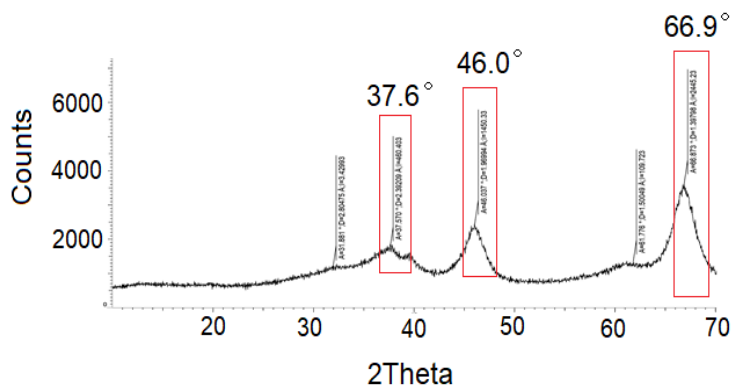


Figure 5. XRD of aluminium oxide synthesised

3.2 Adsorption Studies

3.2.1 Comparison between synthesised and commercial aluminium oxide

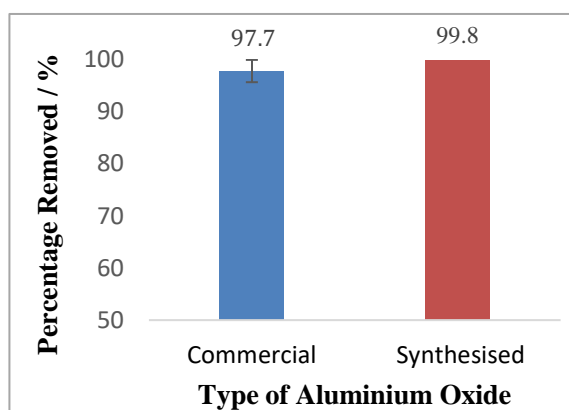


Figure 6. Comparison of adsorption of phosphate by commercial and synthesised aluminium oxide. N=3

The synthesised aluminium oxide from waste aluminium foil is comparable to commercial aluminium in the adsorption of phosphate ions, adsorbing close to 100% of

phosphate ions. Percentage removal of phosphate ions by synthesised aluminium oxide was identical and consistent for all the triplicates studied, accounting for the absence of an error bar on the bar corresponding to synthesised aluminium oxide.

3.2.2 Comparing adsorption of phosphate with nitrate

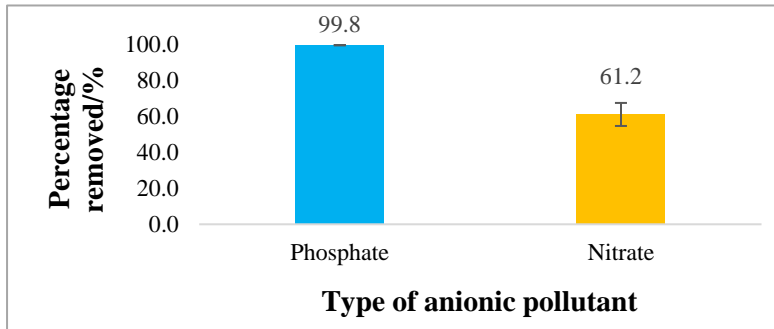
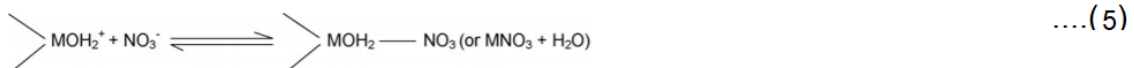


Figure 7. Comparison of adsorption of phosphate with nitrate by aluminium oxide at 50 ppm. N=3

The synthesised aluminium oxide is able to remove close to 100% of phosphate and 61% of nitrate. Hence it is more effective in adsorbing phosphate than nitrate. Aluminium oxide adsorbs phosphate by several mechanisms including ion exchange, complexation and Lewis acid-base interactions (Li, Liu, Xu, & Qian, 2016). On the other hand, nitrates are adsorbed through a 2-step reaction involving ligand exchange as shown in equation 4 and 5 (Bhatnagar, Kumar & Sillanpääc, 2010).



where M represents metal ions (Al)

3.2.3 Effect of initial concentration of phosphate and nitrate on adsorption capacity

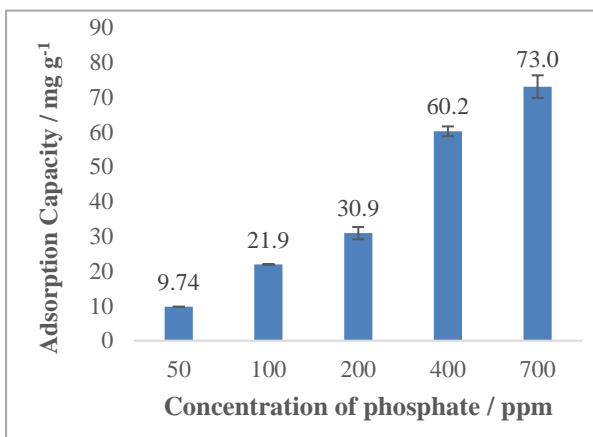


Figure 8. Effect of initial concentration of phosphate on adsorption. N=3

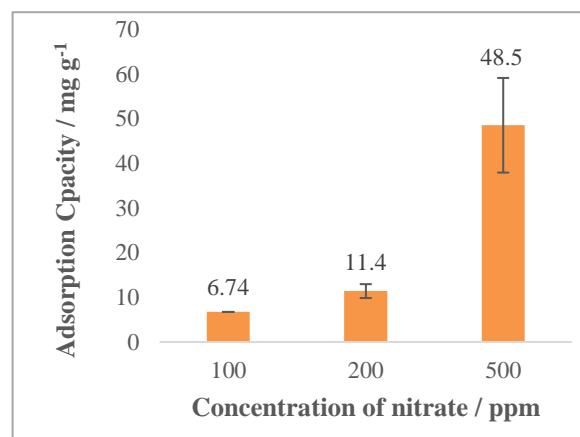


Figure 9. Effect of initial concentration of nitrate on adsorption. N=3

As shown in Figure 8 the adsorption capacity of aluminium oxide increases as the concentration of phosphate increases. This could be due to the abundance of phosphate ions present at higher concentrations and the fact that aluminium oxide has not reached its maximum adsorption capacity yet. The adsorption capacity at 700 ppm is almost 8 times that at 50 ppm, suggesting that aluminium oxide is an effective adsorbent over a wide range of concentrations. The same trend is observed for nitrate. The adsorption capacities on phosphate are also higher than on nitrate at 100 and 200 ppm concentration.

3.2.4 Isotherm studies

Data from Figure 8 was fitted into the Langmuir isotherm model. The graph of $\frac{C_e}{Q_e}$ against C_e was plotted. C_e is the equilibrium concentration while Q_e is the adsorption capacity. A straight-line graph was obtained with an R^2 value of 0.9846 which is close to 1 (Figure 10). Thus, it can be inferred that phosphate adsorption on aluminium

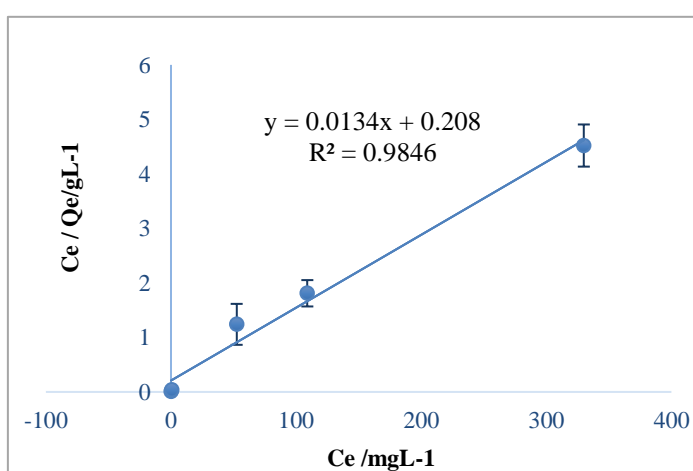


Figure 10. Langmuir isotherm plot for aluminium oxide

oxide is a good fit for Langmuir isotherm model, suggesting that the adsorption of phosphate ions is monolayer. By taking the inverse of the gradient of the straight-line graph obtained, the maximum adsorption capacity, q_m , was determined to be 74.6 mg g⁻¹.

The Q_e of aluminium oxide synthesised was compared with other phosphate adsorbents (Table 1). The synthesised aluminium oxide has a relatively high adsorption capacity compared to other metal oxide and hydroxide adsorbents, except for tantalum hydroxide which has the highest adsorption capacity in the list. Hence, synthesised aluminium oxide has great potential to be used in wastewater treatment to remove phosphates.

Table 1. Comparison of q_e of aluminium oxide with other adsorbents

| Adsorbent | Maximum Adsorption Capacity (q_e)/ $\text{m}g\text{g}^{-1}$ | Reference |
|-------------------------------------|---|-----------------------------------|
| Aluminium Oxide | 74.6 | This study |
| Tantalum Hydroxide | 78.5 | Yu, Dong, Gong, Jiang & Liu, 2012 |
| Iron (III)/Chromium (III) Hydroxide | 6.5 | Namasivayam & Prathap, 2005 |
| Iron (III)-Zirconium Binary Oxide | 13.7 | Long et al., 2011 |
| Iron (III) Oxide | 12.6 | Zeng, Li, & Liu, 2004 |

3.2.5 Effect of pH on adsorption of phosphate

Figure 11 shows that the optimal pH for adsorption of phosphate is 10. pH 2 had the lowest percentage of adsorption since some of the aluminium oxide reacted with the very acidic solution, reducing the amount of aluminium oxide available for adsorption. However, aluminium oxide has very high adsorption over a range of pH, with the percentage of phosphate removed being above 90%, again suggesting that it is a feasible adsorbent to be used in water purification.

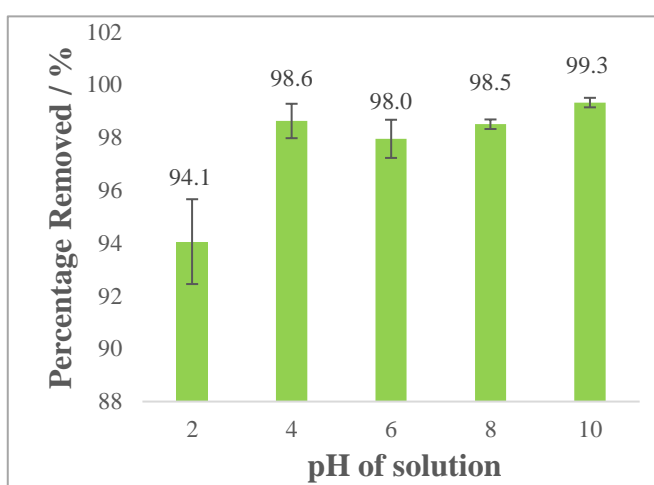


Figure 11. Effect of pH on adsorption of phosphate

At lower pH, ion exchange is the dominant type of adsorption mechanism on the surface of aluminium oxide. Hydroxyl ions (OH^-) which form coordinate bonds with aluminium oxide are released and exchanged for phosphate ions, which exist as the monovalent ionic species, H_2PO_4^- . At neutral pH, there are mainly ion-dipole interactions between the divalent phosphate ions (HPO_4^{2-}) and aluminium oxide. Finally, at higher pH, there are predominantly Lewis acid-base interactions

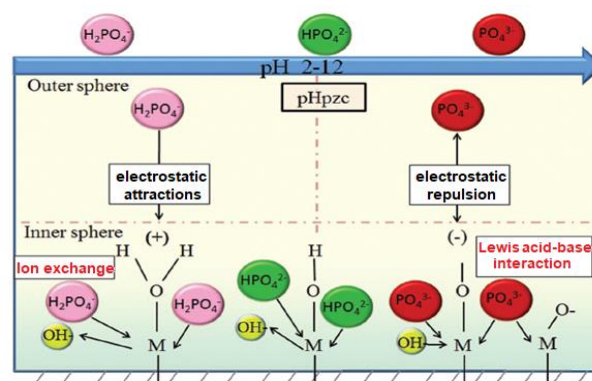


Figure 12. Adsorption mechanism of phosphate at different pH (Li, Liu, Xu & Qian, 2016)

between the trivalent phosphate ions (PO_4^{3-}) and the surface of aluminium oxide (Li, Liu, Xu & Qian, 2016). The different types of interactions at different pH are summarised in Figure 12.

4. CONCLUSION AND FUTURE WORK

Aluminium oxide was successfully synthesised from waste aluminium foil. It is able to remove close to 100% phosphate and 61% nitrate. It has a higher adsorption capacity for phosphates as compared to that of nitrates. Adsorption capacity of aluminium oxide increases as the concentration of phosphate and nitrate increases. The adsorption of phosphate ions by aluminium oxide fits the Langmuir isotherm model and is hence monolayer. Aluminium oxide is also effective in removing phosphate ions from solutions over a wide range of concentrations and pH. Aluminium oxide has the potential to be used as a phosphate adsorbent since its adsorption capacity is comparable with commercial aluminium oxide and other phosphate adsorbents, including tantalum hydroxide. The optimal pH for adsorption of phosphate is pH 10, while the maximum adsorption capacity for phosphate is 74.6 mg g^{-1} .

In the future, isotherm and pH studies can be extended to nitrates. Kinetic studies could also be investigated to determine the rate of adsorption of phosphate and nitrate by aluminium oxide. It is also important to find out whether aluminium ions will leach out from the aluminium oxide during the adsorption process. Finally, a prototype which purifies water using aluminium oxide can also be fabricated (Figure 13). The top sliding gate is first opened to allow wastewater to mix with the aluminium oxide, while the lower sliding gate remains closed. After adsorption is complete, the lower sliding gate is opened to allow the treated effluent to flow out.

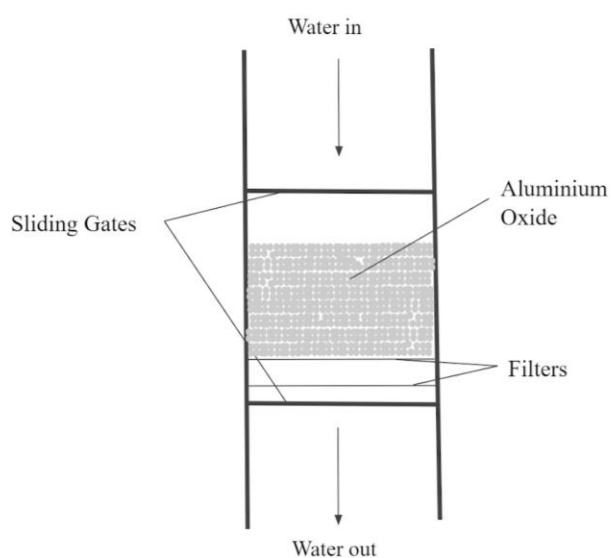


Figure 13. Prototype containing aluminium oxide for wastewater treatment

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