



## Research article

## Phosphorus removal from secondary wastewater effluent using copper smelter slag

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## ABSTRACT

This study investigated the use of copper smelter slag for the removal of phosphorus from secondary wastewater effluent through batch tests. The media was physically and chemically characterized and showed presence of Fe<sub>2</sub>O<sub>3</sub> (45.22%), SiO<sub>2</sub> (14.98%), Al<sub>2</sub>O<sub>3</sub> (3.21%), CaO (1.99%), SO<sub>3</sub> (1.77%) and MgO (1.33%). Scanning electron microscopy monographs revealed smooth and flat surface and no heterogeneity on the surface of the slag with visible micro pores before the experiment and less visible after the experiment. The point of zero charge of the media was 5.0. Equilibrium was reached after 4 h at 29.5 ± 0.71% phosphorus removal efficiency and media dosage of 0.4/100 mL. The kinetic data was best described by Pseudo second order equation. More than one mechanisms were involved in the adsorption of phosphorus onto copper smelter slag as suggested by multi-linearity of intra particle diffusion model. Ninety seven percent (97.5 ± 0.0%) removal efficiency was achieved at an equilibrium dosage of 160 gL<sup>-1</sup>. The equilibrium isotherm was described better by Langmuir equation with observed maximum adsorption capacity of 0.16 mg P g<sup>-1</sup> media and the experimental maximum adsorption capacity was 0.26 mg P g<sup>-1</sup> media. Regeneration studies showed low performance with maximum efficiency of 11.7% revealed during the first regeneration trial therefore low practical benefits. Copper smelter slag is a poor adsorbent for phosphorus and further studies on the media should be conducted.

## 1. Introduction

Elevated phosphorus (P) levels in water bodies have resulted in detrimental effects which declines water quality. The primary source of phosphorus in the environment is anthropogenic activities occurring as both point sources (domestic and industrial wastewater) and non-point sources (agricultural runoffs) [1]. Phosphorus concentration as low as 2.0 mg L<sup>-1</sup> can cause eutrophication leading to environmental degradation, aesthetic problems in lakes, coastal areas and some confined water bodies in short and long term periods [2].

To date several conventional technologies are used for the removal of phosphorus from wastewater and these include chemical precipitation [3], biological removal [4], ion exchange [5] and coagulation [6]. The main disadvantages of these conventional technologies are their high capital, operational and maintenance costs. In addition they require more energy hence are not considered economically viable and they have high carbon footprint and produce toxic sludge. It is also difficult to recover P when using these technologies. Adsorption is emerging as an attractive option for phosphorus removal from wastewater effluents. The major

advantage of using industrial by-products as phosphorus adsorbents is that they are normally perceived as wastes and believed to have no future use and are available in large quantities. Many rural areas in the world especially in the developing countries do not have centralized wastewater treatment systems and instead have onsite facilities. These facilities discharge into open environment and creating a high risk of surface and underground water pollution and therefore a need for P removal onsite. Recent studies have focused on conducting research on media that can be used as adsorbents for phosphorus. Some of the media have been modified to enhance their performance and synthetic P solutions are still used during the studies. For instance, Park et al. [7] investigated the efficiency of rapid cooled basic oxygen furnace slag on P removal using synthetic P solution of 10–200 mg P L<sup>-1</sup>. In that study, the maximum adsorption capacities were 3.6 and 2.5 mg P g<sup>-1</sup> media at initial pH values of 5.0 and 7.0 respectively. Nguyen et al. [8] investigated the adsorption of P from aqueous solutions and sewage using Zirconium loaded okara in fixed bed columns of 120 cm height and 1.75 cm inner diameter. Several parameters such as flow rate, bed height, initial P concentration, media size and pH and were investigated to establish their

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influence. Adsorption capacity of 16.43 mg P g<sup>-1</sup> media was reported as well as successful desorption and regeneration using 0.2 NaOH and 0.1 HCl respectively. Another study by Zuo et al. [9] investigated P removal from wastewater using lanthanum oxide-loaded ceramic adsorbent using synthetic P solution of 2–50 mg P L<sup>-1</sup>. Removal efficiencies between 98 and 100% were observed for P solution of 2–15 mg P L<sup>-1</sup>. Effects of pH, temperature, initial P concentration and interfering anions were also investigated. Removal efficiency was between 98 and 100% for initial P concentrations of 2–15 mg P L<sup>-1</sup> but decreased when P concentration was increased. From initial pH < 3 efficiency was increasing but decreased at pH ≥ 8. Xie et al. [10] examined P removal from eutrophic lakes using dispersed magnesium oxide Nano flake – modified diatomite adsorbent and observed experimental capacities between 44.44 – 52.08 mg P g<sup>-1</sup> media. The adsorption capacity was observed increasing with increasing temperature and contact time but decreasing with increasing pH. On coexisting substances investigated only carbonates (CO<sub>3</sub><sup>2-</sup>), sulphates (SO<sub>4</sub><sup>2-</sup>) and silicates (SiO<sub>3</sub><sup>2-</sup>) showed negative effects on P removal. Bentonite surface was modified through acid thermo-activation, Rewoquate, Irasoft, calcium Fe and Al treatment. It was observed that Fe-Al treated bentonite achieved 99% efficiency in 30 min at pH 2–10 and there was no effect of coexisting ions [11].

Table 1 reveals results of modified and not modified media under varying conditions. Serious thought should be considered when using modified media which include availability and modification costs during field scale application after pilot scale trials. The other factor that should be taken into account is the use of synthetic solutions. Real wastewater will be treated during field application therefore a likelihood of many background pollutants or constituents competing with P. It is therefore necessary to consider looking for materials that are readily and or locally available at less or no costs and utilising real wastewater. Very fine materials are sometimes used which will facilitate clogging and reduce hydraulic conductivity in the fixed bed columns [19] therefore need to use bigger diameter media and will negatively reduce surface area and adsorption capacity. The introduction of roughing filter to reduce suspensions and materials that can facilitate bed clogging. Sibrell and Tucker [20] used fine grained media <0.15 mm and synthetic P solution of 1.0–50 mg P L<sup>-1</sup> for investigate P removal using acid mine drainage sludge and 96% efficiency was achieved. The other observation was different shaking speeds employed during these tests. Some shaking speeds as high as 250 rpm were used and in reality wastewater will not be passing through fixed beds at such high turbulence. High shaking speeds might give unrealistic results. Media might breakup during shaking and developing new adsorption sites which will increase media adsorption capacity due to the forces of attraction increasing [19]. The other disadvantage of high agitation speed might be collision of media particles resulting in low adsorption of pollutants. Many of these studies predict the adsorption capacity basing on the isotherm models which has been reported to be unrealistic and overestimates the lifespan of the treatment facility such as constructed wetlands. For instance, Wang et al. [18] calculated a theoretical lifetime of wetlands as 232 years and concluded that it was over-estimation. Some of the solutions used for the studies have unrealistic P concentrations. Wang et al. [18] used synthetic solutions of up to 1000 mg P L<sup>-1</sup>. Such solutions will have high diffusion gradients resulting in high adsorption efficiency hence misleading results which might be used for designing fixed bed systems. Not all media modifications give positive results. For instance, Yan et al. [21] conducted studies on two types of iron oxide organic matter for P removal and observed a decrease in adsorption capacity of 22.17, 5.43, 4.67 and 3.27 mg P g<sup>-1</sup> media for the treated adsorbents and the decrease was attributed to media coatings decreasing specific surface area of iron oxide (FeO). Similarly, Mahardika et al. [22] investigated ferrihydrite-impregnated granular activated carbon for efficient removal of phosphorus from secondary wastewater and observed that P sorption rate and adsorption capacity was influenced by surface area and Fe content. The modification of granular activated carbon was aimed at creating active functional groups such as carboxyl and phenolic. In their study of adsorption characteristics of phosphorus from aqueous

Table 1. Summary of some recent studies on phosphorus removal by different adsorbents.

Adsorbent	Type	Adsorption capacity/Percent P removal	Comments	Mode of test	Reference
Magnetic layered double hydroxide (media size not stated)	Synthetic	74.8, 80.8 and 67.8 mg P g <sup>-1</sup>	Al, Zn-Al and Mg-Fe were used to synthesize the adsorbent layer. Synthetic solution was used. Shaking speed not stated.	Batch	[12]
Surface buffer sediments (0.15 mm)	Natural	0.54–41.47 mg P g <sup>-1</sup>	Synthetic solution was used. Pseudo second Order kinetics, Langmuir isotherm	Batch	[13]
10 Sediments (passing through 100 mm sieve)	Natural	430.2–1424.2 mg P g <sup>-1</sup>	Synthetic solution of 0.5–20 mg P L <sup>-1</sup> . Langmuir isotherm Agitation speed not stated	Batch	[14]
Aluminum modified eggshell and parent eggshell (passing through 100 mm sieve)	Synthetic Natural	3.45, 4.38, and 6.22 mg P g <sup>-1</sup> 0.20, 0.33, and 0.55 mg P g <sup>-1</sup>	Synthetic solutions 10 mg P L <sup>-1</sup> for parent eggshell and 5 mg P L <sup>-1</sup> for modified eggshell. Agitation of 200 rpm	Batch	[15]
Lake sediments (passing through 100 mesh sieve) Ignited sediments	Natural Modified	5.818 mg P g <sup>-1</sup> 13.18 mg P g <sup>-1</sup>	Synthetic solutions of 0.05–80 mg P L <sup>-1</sup> Agitation speed of 250 rpm	Batch	[16]
La-modified bentonite (passing through 80 mesh sieve)	modified	0.52 mg P g <sup>-1</sup> at pH 3.0 to 0.93 mg P g <sup>-1</sup> at pH 7.0	Synthetic solution of 0.1–10 mg P L <sup>-1</sup> Agitation speed 150 rpm Adsorption followed Pseudo-second order kinetic and Langmuir isotherm model	Batch	[17]
Cement based mortar or alternative cementitious materials (0.45 mm)	Man made	30.96, 23.75, 20.20 and 12.7 mg P g <sup>-1</sup>	Synthetic solution of 20–1000 mg P L <sup>-1</sup> Agitated at 175 rpm Adsorption described by both Freundlich (1 mortar) and Langmuir isotherms (3 mortars)	Batch	[18]

solutions onto phosphate mine wastes, Jellali et al. [23], observed phosphorus removal increasing with initial aqueous phosphorus concentrations, adsorbent dosage and temperature but decreased with increasing pH values. It was concluded that the material could be considered as one of the most efficient natural materials for phosphorus retention and recovery and an option of reuse as agricultural fertiliser [23]. Phosphorus recovery from wastewater has been investigated by other researchers since the source is declining. For example, Yin et al. [24] used dolomite for removing and recovering 92% of P from livestock wastewater. Investigations on the cost effectiveness of different P removal technologies revealed that the use of reactive media through filtration was cost effective compared to the other five technologies [25], signalling that many studies should be conducted on reactive media for use in this technology. In their study of removing phosphorus from aqueous solutions using Lanthanum modified pine needles, Wang et al. [26], observed that pre-treated pine needles with alkali-isopronol failed to effectively remove P while pine needles modified with Lanthanum hydroxide showed relatively high removal efficiency. There was no competing effect of phosphorus shown by  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  but  $\text{CO}_3^{2-}$  showed significant competing effect with increasing concentration. The various studies have demonstrated that currently modification of adsorbents to enhance efficiency is high though modification is not a guarantee of improved performance. Some modification sometimes block the pores of the adsorbents resulting in lowered performance and might as well increase costs.

The objective of this study was to investigate the efficiency of copper smelter slag, a by-product of the smelting of copper at a copper/nickel mine, for the removal of phosphorus from secondary treated wastewater. The authors aimed to investigate the virgin material first without any modifications which will then later be conducted during another study. It will be necessary to know the performance of the virgin material first. Copper smelter slag is stock piled in tons as mine waste. There is no disposal option for the waste in place and it might be detrimental to the receiving environment through heavy metals leaching. To our knowledge this material has not been investigated for its efficiency on P removal from wastewater. Utilising the material for wastewater treatment will be both economic and environmental beneficial to the country and the mining company.

## 2. Materials and methods

### 2.1. Copper smelter slag

Copper smelter slag was collected from the BCL LTD mine, a copper nickel mine located in Selibi Phikwe, Botswana, (21.97S and 27.84E). By August 2016 the mine was producing approximately 81 000 tons of copper smelter slag per month (BCL, 2016). This waste has been piled in dumping sites at the mine for many years. The material is a by-product after limestone, sand and copper ore concentrate (Chalcopyte,  $\text{CuFeS}_2$ ) mixture has been blown with oxygen in a blast furnace. The oxygen reacts with the iron to form iron oxide ( $\text{FeO}$ ) and copper is left in the form of copper sulphide ( $\text{CuS}$ ) whilst the silicon dioxide ( $\text{SiO}_2$ ) in the sand reacts with limestone and iron oxide to form a less dense material called smelter slag, ( $\text{FeSiO}_3$ ).

### 2.2. Media preparation

Media was washed several times with deionized water to remove materials adhered to particles and any soluble materials which could dissolve during batch experiments. Particle size was segregated by mechanical sieving (BS 3310-1) and media retained between 0.425 and 1.18 mm sieves was used.

### 2.3. Wastewater

Wastewater was sourced locally from Palapye wastewater treatment plant. The system consists of waste stabilisation ponds and a biological

filter comprised of trickling filter system. The incoming organic load is broken down in stabilisation ponds before final treatment is carried out in trickling filters. The existing ponds serve as primary facility whilst the trickling filter represents secondary treatment facility.

### 2.4. Media characterization

Media was characterised by determining the particle and bulk densities, porosity and hydraulic conductivity. The particle density of the media was determined as described by Sima et al. [27] where 60 mL of deionised water was added to a 100 mL measuring cylinder and volume recorded. Smelter slag weighing 50 g was then added into the cylinder and stirred to remove air trapped between particles. The new volume was then recorded and the difference in the two volumes was recorded as the volume of the media particles. Particle density was calculated from the equation:

$$\rho_p = \left( \frac{\text{Mass of media (g)}}{\text{Media volume (mL)}} \right) \quad (1)$$

where  $\rho_p$  is particle density ( $\text{g cm}^{-3}$ ).

The bulk density was determined from the volume displacement method as described by Dan-Asabe et al. [28]. Media sample was weighed to determine its mass (M) and placed into a measuring cylinder to determine the volume ( $V_1$ ). A known volume of distilled water was added into the cylinder and the final volume ( $V_2$ ) noted. The bulk density was calculated according to the equation:

$$\rho_b = \frac{M}{V_2 - V_1} \quad (2)$$

where:  $\rho_b$  = bulk density ( $\text{g cm}^{-3}$ ), M = mass (g),  $V_2$  and  $V_1$  are final and media volumes ( $\text{cm}^3$ ) respectively.

The hydraulic conductivity (K) was determined at the Geological Engineering department laboratory using constant head permeameter equipment (38-T0184/A1, 38-T0184/A2 and 38-T0184/A3) according to American Standard Test Method (ASTM). The material was placed into the column and filled with DI water for saturation. The water was allowed to flow through the media at a constant head. The volume of water that passes through at a particular time was collected into the measuring cylinder. The hydraulic conductivity was calculated from the equation:

$$K = \frac{VL}{Ath} \quad (3)$$

where: K = hydraulic conductivity ( $\text{m d}^{-1}$ ), V = volume in cubic meters ( $\text{m}^3$ ), t is time to collect certain amount of volume in days, L is the length of media specimen (m), A is the cross sectional area of permeameter ( $\text{m}^2$ ).

The porosity (n) of the media was determined as described by Sima et al. [27] from the equation:

$$n = \left( 1 - \frac{\rho_b}{\rho_p} \right) \quad (4)$$

where  $\rho_b$  is bulk density ( $\text{g cm}^{-3}$ ) and  $\rho_p$  is particle density ( $\text{g cm}^{-3}$ ).

The elemental composition of the media was determined using the X-Ray Fluorescence (Thermo ArL Advant -X) while the mineralogy was determined using X-Ray diffractometer (Bruker D8 Advance) with  $\text{CuK}\alpha$  as a radiation source with a wavelength of 1.54Å within the values of  $2\theta = 5-80^\circ$ .

Scanning electron microscopy (SEM) images of representative particle samples for media before and after phosphorus removal were obtained using JSM-7100G Field Emission Scanning electron microscope. The samples were each mounted on an 8.5 mm diameter Cambridge stub for inspection. Images were taken at low and high magnifications. The samples were stored in a desiccator overnight prior to analysis.

The point of zero charge was determined as described by Faria et al. [29], through the pH drift method where 2.92 g or 0.05 M of sodium chloride (NaCl), was dissolved in 1 L of deionised (DI) water. Then 0.5 g of smelter slag was placed into six (6) 250 mL Erlenmeyer flasks and 60 mL NaCl solution added. The pH of the solutions was then adjusted between 2 and 12 by adding either 0.1 M HCl or 0.1 M NaOH solutions. The mixtures were duplicated and agitated for 48 h on orbital shakers and flasks removed thereafter and filtered through Whatman size 42 paper and the filtrated pH determined using portable multiparameter Testr™ 35 series meter (Thermo Fisher Scientific, UK).

2.5. Effect of contact time

For determining the effect of contact time and batch kinetics, 2.0 g of media was placed into twelve 250 mL Erlenmeyer flask. Then 100 mL of wastewater was added into each flask. A separate flask containing wastewater only was a control. The flasks were placed onto orbital shaker (Stuart, Cole- Parmer Scientific Experts) and shaken at 120 rpm at room temperature. The flasks were withdrawn at set time intervals of 5, 10, 15, 30, 60, 240, 480, 720, 1440, 2160, 2880 and 4320 min. The mixtures were filtered through a 0.45µm Whatman filter paper and phosphorus concentrations were immediately determined using the molybdenum blue method as described by Murphy and Riley [30] and the UV/Vis spectrophotometer (Agilent technologies carry 60 cuv-vs) at 700 nm wavelength. The pH of the mixture was measured during time intervals using the same meter described earlier. The experimental data was then fitted onto 5 kinetic models, the pseudo first order, pseudo second order, intra-particle diffusion, and the Boyd and Elovich models.

2.6. Data analysis

The statistical analysis was carried out using Microsoft Excel XLSTAT add-on statistical software. The experimental data was in addition analysed through a series of kinetic and equilibrium adsorption models described below:

2.6.1. Kinetic models

Batch kinetics studies provide better understanding on the mechanisms involved during adsorption process and provides useful information for large scale application. The kinetic models and their linear forms as described by different authors are given in Table 2. The symbols are as described by the authors.

In addition for Pseudo second order, h, the initial sorption rate can be calculated from equation as follows:

$$h = k_2 q_e^2 \tag{6}$$

Bt is a time constant and F is a fraction of adsorbate adsorbed at any time t, and is given by t.

$$Bt = -0.4977 - \ln\left(1 - \frac{qt}{q_e}\right) \tag{7}$$

For values of F ranging from 0.86 to 1.

$$Bt = -\ln\frac{\pi^2}{6}(1 - F) \tag{8}$$

A linear plot of Bt vs time was plotted to differentiate between particle diffusion and film diffusion controlled adsorption [35]. If the graph passed through the origin then, intraparticle diffusion was the solely controlling mechanisms otherwise both mass transfer (film diffusion) and intraparticle diffusion were involved in controlling adsorption process. In further determining the rate controlling mechanisms, a dimensionless number, Biot number, was calculated from the equation as described by Muhammad et al [36] and [37]. It has been suggested that if Bi << 1, external mass transfer is the controlling step but for Bi >> 100 internal diffusion is the controlling step whereas 1 << Bi << 100 film diffusion and external diffusion are both controlling steps [37].

$$Bi = k_f \frac{d}{D} \tag{9}$$

where d is the mean particle diameter (m) and D is the surface mass diffusion coefficient (m<sup>2</sup> s<sup>-1</sup>) and k<sub>f</sub> is the film mass coefficient (m s<sup>-1</sup>). The pore and surface diffusion was calculated from the equation:

$$-\log\left(1 - \left(\frac{q_t}{q_e}\right)^2\right) = \left(\frac{4\pi^2 D}{2.3d^2}\right)t \tag{10}$$

2.7. Effect of media dosages

For equilibrium isotherm studies, 100 mL of wastewater was placed into different 250 mL Erlenmeyer flasks containing different amounts of media (0, 0.1, 0.2, 0.3, 0.4, 0.5, 1, 2, 3, 6, 9, 10, 13, 16, 18 and 20 g). The flask were agitated at 120 rpm at room temperature for 4 h determined during kinetic study. After 4 h, flasks were withdrawn and mixtures filtered through a 0.45µm Whatman filter paper. The phosphorus concentration in the filtrate was analysed using the method described earlier. The experimental data was fitted onto the widely known Langmuir and Freundlich isotherm models. The amount of phosphorus adsorbed in the media at equilibrium, q (mg P/g) was calculated as:

$$qt = \frac{C_o - C_e}{M} V \tag{11}$$

where C<sub>o</sub> and C<sub>t</sub> (mg/L) are the initial phosphorus concentration and the concentration at equilibrium time respectively, V is the volume of wastewater (L) and M is the mass of the adsorbent (g).

Adsorption efficiency was calculated as per the following equation as previously described:

$$\%removal = \left(\frac{C_o - C_e}{C_o} \times 100\right) \tag{12}$$

Table 2. Different kinetic models used in batch studies.

Model	Equation	Linear form	References
Pseudo first order	$\frac{dq_t}{dt} = k_1 (q_e - q_t)$	$\ln(q_e - q_t) = \ln(q_e) - \frac{k_1 t}{2.303}$	[31]
Pseudo second order	$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t$	[32]
Elovich	$\frac{dq_t}{dt} = \alpha \exp^{-\beta q_t}$	$q_t = \frac{1}{\beta} \ln \frac{\alpha}{\beta} + \frac{1}{\beta} \ln t$	[33]
Intra-particle diffusion	$q_t = k_p (t^{1/2}) + C$		[34]
Boyd model	$F = \frac{qt}{q_e} = \frac{6}{\pi^2} \exp(-Bt)$		[35]

**Table 3.** Freundlich and Langmuir adsorption isotherms.

Model	Equation	Linear form	Parameters	Reference
Langmuir	$q = \frac{q_{\max} K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{K_L q_{\max}}$	$R_L = \frac{1}{1 + K_L C_o}$	[18]
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$K_F$ (mg g <sup>-1</sup> ) and 1/n	[18]

### 2.8. Equilibrium adsorption isotherms

The Freundlich and Langmuir adsorption isotherms were used to describe the characteristics of P adsorption onto copper smelter slag as described in Table 3.

The models have been widely used in literature for describing adsorption processes and are as described by Wang et al. [18] together with the symbols.

### 2.9. Batch regeneration tests

Media regeneration was carried out by placing 2 g of the media into 250 mL Erlenmeyer flask containing 100 mL wastewater and agitated for 4 h in an orbital shaker at 120 rpm. After 4 h, the flasks were withdrawn, mixture filtered through a 0.45 µm filter paper and the residue rinsed with deionized (DI) water, dried and then weighed before use for the next cycle where 150 mL of 0.1M solution sodium hydroxide (NaOH) was added to each media and shaken again for 4 h. The mixture was filtered and the residual smelter slag was rinsed three times with DI water to remove any NaOH ions. Then the smelter slag was fed again with

**Table 4.** Physical properties of copper smelter slag.

Parameter	Slag
Bulk density (g cm <sup>-3</sup> )	1.21 ± 0.07
Particle density (g cm <sup>-3</sup> )	1.90 ± 0.05
Porosity (%)	36.31 ± 5
Hydraulic conductivity (m s <sup>-1</sup> )	8.06 × 10 <sup>-4</sup>

**Table 5.** XRD and XRF results showing mineralogy and elemental composition of copper smelter slag.

Mineralogy	Percent composition (%)	
Fe <sub>2</sub> O <sub>3</sub>	45.66 ± 0.62	
CaO	2.15 ± 0.22	
Al <sub>2</sub> O <sub>3</sub>	3.35 ± 0.21	
MgO	1.42 ± 0.12	
SiO <sub>2</sub>	15.74 ± 1.1	
SO <sub>3</sub>	1.8 ± 0.03	
Elemental composition	Fresh slag	Used slag (%)
Fe	11.2 ± 0.42	9.83 ± 0.04
Ca	19.82 ± 0.96	17.93 ± 0.81
Mg	5.84 ± 0.52	2.75 ± 0.35
Al	1.80 ± 0.28	9.46 ± 0.06
P	8.79 ± 0.30	8.66 ± 0.49
Minerals related to P removal	Fresh slag	Used slag
	AlPO <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub>
	FeH <sub>4</sub> PO <sub>6</sub>	FeH <sub>4</sub> PO <sub>6</sub>
	Ca <sub>5</sub> HO <sub>13</sub> P <sub>3</sub>	Ca <sub>5</sub> HO <sub>13</sub> P <sub>3</sub>
	CaCO <sub>3</sub>	CaCO <sub>3</sub>
	Nil	MgPO <sub>2</sub> O <sub>7</sub>
	CaO	CaO

wastewater and agitated for 4 h. The filtrate was then analysed for phosphorus concentration and the procedure repeated three times.

## 3. Results and discussion

### 3.1. Media characterization

Table 4 shows the physical parameter results in terms of the bulk density, particles density, porosity and hydraulic conductivity. Both bulk density and particle density were greater than that of wastewater (1.05 g cm<sup>-3</sup>) suggesting that the media might withstand the hydrostatic forces in the fixed bed column. The bulk density was less than 1.74 g cm<sup>-3</sup> of rapid cooled basic oxygen furnace slag reported by Park et al. [7]. It has been reported by Guo and Lua [38] that high density of the adsorbent is desirable to ensure high structural strength. This minimizes weight losses during transportation and handling processes [38]. The low porosity of the media suggests that the media will be saturated in short time hence a likelihood of low phosphorus retention capacity. The porosity of the slag was similar to that of rapid cooled basic oxygen furnace slag of 34% reported by Park et al. [7]. Furthermore the media has low hydraulic conductivity suggesting a possibility of clogging in the fixed bed column resulting in channelling of wastewater hence short circuiting and poor phosphorus removal due to low contact time. This shortfall can be overcome by using media sizes of larger diameter for instance between 5 – 12 mm diameter. It might be desirable to filter the wastewater first in a roughing filter so that suspended solids, turbidity and other pollutants that might encourage clogging are removed.

### 3.2. Elemental and mineralogy composition

The major chemical composition of copper smelter slag as revealed by XRF are  $\text{Fe}_2\text{O}_3$  ( $45.66 \pm 0.62\%$ ),  $\text{SiO}_2$  ( $15.74 \pm 1.1\%$ ),  $\text{Al}_2\text{O}_3$  ( $3.35 \pm 0.21\%$ ),  $\text{CaO}$  ( $2.15 \pm 0.22\%$ ),  $\text{SO}_3$  ( $1.42 \pm 0.12\%$ ),  $\text{MgO}$  ( $1.42 \pm 0.12\%$ ) (Table 5). It has been reported that copper smelter slag is richer in  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  [39]. The composition of copper smelter slag in this study is in agreement with the findings by [40]. However it is worth noting that  $\text{CaO}$  content ( $2.15 \pm 0.22\%$ ) of copper smelter slag was less than that reported in other studies. For instance Han et al. [40] reported  $\text{CaO}$  content of 47.08%, Bowden et al. [41] reported  $\text{CaO}$  of 42.74% whilst Barca et al. [39] reported 34.9%  $\text{CaO}$  content for electric arc furnace slag. The difference in composition could be attributed to difference in raw materials used as well as the production processes. Low content of  $\text{CaO}$  will be an advantage for maintaining low pH since there would be less free  $\text{Ca}$  ions released which will elevate pH hence no need for adjustment if the media was to be used at field scale. The presence of calcite mineral ( $\text{CaCO}_3$ ) has negative implications since the liberated calcium ions has a reversible reaction with carbonate ions therefore limiting the possibility of phosphorus precipitation by calcium ions. High composition of  $\text{Fe}_2\text{O}_3$  suggests that the material could have high affinity for phosphorus because of the presence of Fe. Pratt et al. [42] have reported that Fe and Al rich media adsorb phosphorus through adsorption onto metal oxyhydroxides. Since smelter slag has high  $\text{Fe}_2\text{O}_3$  content, there is a possibility of high phosphorus retention. It has been reported that Fe retains P mainly through ligand exchange where the phosphorus molecules replace hydroxides or water molecules in the oxide; therefore no Fe content is expected to change, except due to leaching. This was observed as there was only a slight difference in the concentrations of Fe in fresh and used (Table 5) media (1.37%). The presence of P in fresh slag suggests reduced adsorption sites and therefore reduced P adsorption capacity of the slag because some of the adsorption sites were already filled up with P.

The results show that Fe and Ca ions (Table 5) had decreased by 1.37 and 1.89% respectively, in the used slag. A higher decrease of 3.09% was observed for magnesium but a very significant increase of 7.66% for aluminum. There was residual P in fresh slag but a slight reduction of 0.13% was observed in used slag. The slight reduction of Ca suggests that the ions were released in low concentration to precipitate P. This is supported by a decrease in P concentration in used media instead of the expected increase. The presence of phosphorus minerals in fresh media ( $\text{Ca}_5(\text{PO}_4)_3$ ,  $\text{AlPO}_4$  and  $\text{Fe}_4\text{PO}_6$ ) suggests that adsorption sites of the media were already occupied with phosphorus before the experiment hence low phosphorus retention. Phosphorus minerals in used slag were,  $\text{Ca}_5(\text{PO}_4)_3$ ,  $\text{Fe}_4\text{PO}_6$  and  $\text{Mg}_2\text{P}_2\text{O}_7$ . Only  $\text{Mg}_2\text{P}_2\text{O}_7$  was not present in fresh slag and reduction of Mg in used media was high compared to the other ions, this suggests that it was the main removal mechanism of phosphorus through either ion exchange or precipitation processes. The

presence of  $\text{Ca}_5(\text{PO}_4)_3$  in fresh slag should have been a seed for the precipitation of P hence a higher chance of P removal. However, this was not the case as P reduction was observed in the used slag suggesting desorption instead.

In order to examine the surface morphology of the media, SEM images for the media before and after phosphorus removal were obtained and the micrographs are presented in Figure 1 (a) and (b). A significant difference is noted on the surface of the media. The micrographs indicate the presence of micro pores in the media before the experiments. The micro pores were not highly visible Figure 1 (a), confirming that slag is not highly porous naturally. The media showed a rather smooth and flat surface and the lack of heterogeneity on the surface of the slag could contribute to low phosphorus removal capacity. The surface morphology of the media after phosphorus sorption was also examined through SEM. The morphology of the material exhibited changes as shown in Figure 1 (b). This suggests that phosphorus was slightly removed by the media. Discrete aggregates on the surface of saturated media can be observed on the surface indicating adsorption process or formation of minerals.

### 3.3. Point of zero charge

The point of zero charge ( $\text{pH}_{\text{pzc}}$ ) for copper smelter slag was found to be 5.0 (Figure 2). At this point, there is no surface charge for neutralisation by ions in the diffuse film and existing adsorbed ions are bound in surface complexes [43]. When the  $\text{pH} < \text{pH}_{\text{pzc}}$  the surface of smelter slag is positively charged and favouring the adsorption of anions, phosphate ions in this case and at  $\text{pH} > \text{pH}_{\text{pzc}}$  the surface of the slag is negatively charged and favouring adsorption of cations [19]. This implies that as pH increases more negatively charged phosphate ions were dominant in the wastewater and increased repulsion between phosphate species in solution and adsorbent surface which was predominantly negative because of  $\text{OH}^-$  ions. The results slightly contrasts the findings by Milonjic et al. [44] who reported  $\text{pH}_{\text{pzc}}$  value of 6.5 for untreated  $\text{Fe}_3\text{O}_4$ . The difference might have been due to the composition of the materials as in this study the media had different minerals. Anions are favourable adsorbed at low pH values due to the presence of  $\text{H}^+$  ions which explains why less phosphate ions were adsorbed since the pH was not favourable.

### 3.4. Water analysis

Table 6 reveals that the effluent from Palapye wastewater treatment facility has high concentration of phosphorus ( $22.6 \pm 0.71 \text{ mg L}^{-1}$ ) and higher than influent P concentration of  $6.5 \pm 0.42 \text{ mg/L}$ . This was in excess of the permissible limit of  $1.5 \text{ mg P L}^{-1}$  as per Botswana Bureau of Standards (BOBS 93:2004) of discharge into the environment. Algae were observed floating in the ponds and these could have exerted

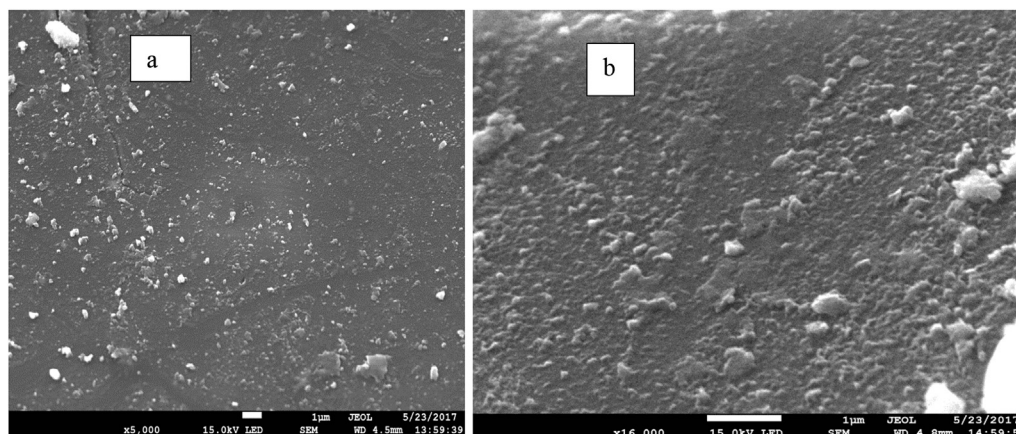


Figure 1. Surface morphology of copper smelter slag before (a) and after (b) phosphorus adsorption.

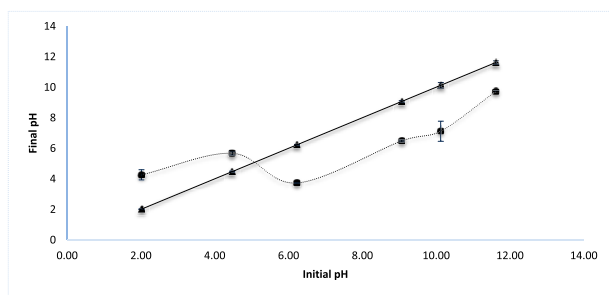


Figure 2. Point of zero charge of copper smelter slag.

phosphorus during die off hence increasing P concentration. The amount of phosphorus in the effluent indicates that overall the system is unable to remove phosphorus to the required limit and therefore a need to investigate on alternative technologies for P removal. Adsorption technology using reactive media have been recommended for use in systems such as filtration and constructed wetlands for onsite wastewater treatment.

### 3.5. Effect of contact times

The adsorption of phosphorus was initially rapid followed by a slower second phase and lastly equilibrium phase during which a plateau like curve was observed (Figure 3). During the first 60 min of the experiment,  $20.5 \pm 0.71\%$  removal efficiency was achieved. The efficiency was  $29.5 \pm 0.71\%$  after 240 min and remained constant until 4320 min when the experiment was stopped, suggesting that all adsorption sites were all used. The presence of residual P in fresh media could have contributed to low P removal efficiency. This observation is in contrast with observation by Blanco et al. [45] where Basic oxygen furnace steel slag was used for P removal from wastewater. In that study, synthetic P solution was used with initial concentration ranging between 5–300 P mg L<sup>-1</sup> and removal efficiency observed was greater than 99%. High P concentration was the driving force and in addition synthetic solution had no competing effect of background constituents which is the case when using real

Table 6. Chemical composition results of wastewater used and corresponding thresholds limits.

Parameters	Influent Concentration (mg L <sup>-1</sup> )	Effluent Concentration (mg L <sup>-1</sup> )	BOBS 93:2004 Wastewater Standard (Other Environments)
Ca	22.6 ± 0.71	6.5 ± 0.42	Not stated
Mg	8.95 ± 0.35	15.25 ± 0.35	Not stated
Al	10.6 ± 0.85	14.95 ± 0.07	Not stated
Fe	0.05 ± 0.01	0.14 ± 0.01	2.0
P	7.35 ± 0.21	21.8 ± 0.71	1.5
Cl	28 ± 1.41	56.2 ± 1.20	600
SO <sub>4</sub>	2.8 ± 0.28	24.1 ± 0.29	400
NO <sub>3</sub>	1.4 ± 0.14	96.85 ± 1.20	50
F	0.15 ± 0.07	0.55 ± 0.07	1.5

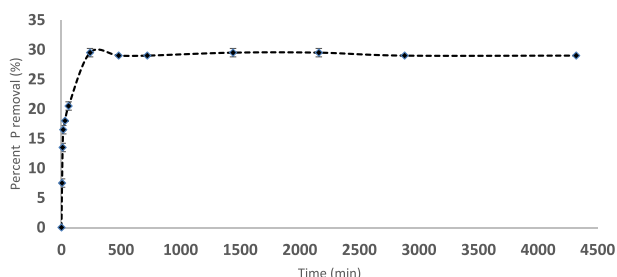


Figure 3. The effect of contact time on phosphorus removal from wastewater.

wastewater. The initial rapid adsorption could be attributed to physical adsorption, where phosphorus was adsorbed onto the adsorption sites on the exterior surface of the media [46], followed by a subsequent diffusion of phosphorus into the pores of slag particle. These findings are comparable to those reported by Kamiyango et al. [47] where kaolinite was used to remove phosphorus from aqueous solutions. However copper smelter slag showed a low phosphorus removal capacity as compared to that study. For instance Blanco et al. [45] reported that phosphorus concentration was reduced from 30 mg L<sup>-1</sup> to 1 mg L<sup>-1</sup> during the first 30 min of the experiment, when basic oxygen steel slag was used. The authors reported that the rapid adsorption by basic oxygen slag was attributed to phosphorus precipitation by CaO at high pH conditions.

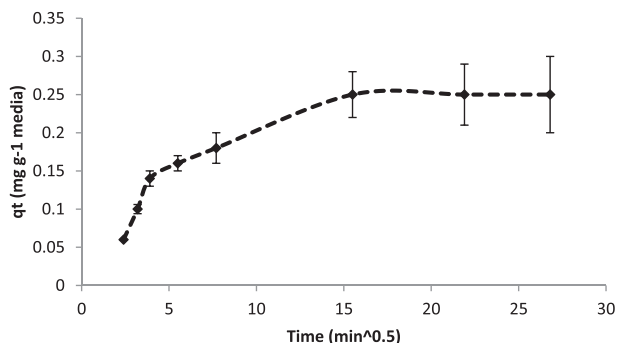
Therefore the low CaO content of smelter slag might have contributed to low removal capacity since calcium precipitation has been reported to be dominant in most P adsorption processes. Han et al. [40], reported that Fe rich minerals in slag can play significant role in P removal, hence high Fe content in smelter slag was expected to increase high P removal. It has been reported that the pH of the wastewater can significantly affect the phosphorus removal capacity of the media [40]. This effect might have affected the removal capacity of slag as the influent pH was 6.8 and filtrate pH was near neutral conditions (6.4–7.4). According to Prochaska et al. [48] P sorption onto aluminum and iron oxides is favoured at acidic pH and low initial P concentration. The concentration of phosphorus in this study was high at 21.3 mg P L<sup>-1</sup> which might have affected the efficiency of the media in P removal and pH was closer to neutral conditions.

### 3.6. Kinetic models

The calculated kinetic parameters and their corresponding regression ( $R^2$ ) values are presented in Table 7. The presented data indicate  $R^2$  of Pseudo-second order was higher than those of  $R^2$  other kinetic models. This indicates that sorption of phosphorus onto slag was better described by the pseudo second order kinetic model. In addition, the calculated adsorption capacity of the media from pseudo second order model (0.2 mg P g<sup>-1</sup> media) was similar to the experimental value (0.19 mg P g<sup>-1</sup> media). It has been reported that most kinetic models are described by Pseudo-second order equation hence superior to other kinetic models [49]. The constant  $k_2$  is a time scale factor that decreases with initial concentration and in this study time to equilibrium was 8.3 min. In the case of pseudo first order and Elovich models the calculated adsorption capacities were 0.16 and 23.2 mg P g<sup>-1</sup> media, respectively, which was not in par with experimental results (0.19 mg P g<sup>-1</sup>). Tan and Hameed [49] reported that for pseudo-first order reaction  $1/k_1$  represents the time scale for the process to reach equilibrium which was 33.3 min if pseudo first order represented P adsorption onto smelter slag. Pseudo-first order model has been reported to be inferior to Pseudo second order model in most cases when using least square ( $R^2$ ) elimination procedure [49]. This is also in agreement to observation by Simonin [50] who reported that in most literature  $k_2$  has been found to provide better correlation with experiment than  $k_1$ . The best fit of the experimental data to the pseudo second order model suggests that chemisorption might have been the dominant phosphorus removal mechanism during adsorption of phosphorus by copper smelter slag. This model describes the chemical nature of the adsorption process, including the exchange of electrons as well as the interaction of valence forces [32]. That is, valence forces existed between phosphorus and ions from copper smelter slag through sharing or exchange of electrons, where OH<sup>-</sup> ions were replaced by PO<sub>4</sub><sup>3-</sup> ions [51]. Desorption of phosphorus from the media might therefore prove difficult since stronger bonds would be formed [52]. However, it must be emphasised that Pseudo Second order model alone does not conclude the mechanisms that were involved during adsorption, several analytical techniques should be used for establishment such as FT-IR, SEM, nitrogen adsorption/desorption and many others where changes in enthalpy, entropy and activation and

**Table 7.** Results of batch kinetic tests.

Pseudo first order		Pseudo second order		Elovich	
$q_e$ calculated (mg g <sup>-1</sup> )	0.16	$q_e$ calculated (mg g <sup>-1</sup> )	0.20	$\beta$ (m/g)	23.20
$q_e$ experimental (mg g <sup>-1</sup> )	0.19	$q_e$ experimental (mg g <sup>-1</sup> )	0.19	$\alpha$ (mg g <sup>-1</sup> /min)	23.42
$k_1$ (1/min)	0.03	$k_2$ (g/mg min)	0.12		
		$h$ (mg g <sup>-1</sup> /min)	0.005		
$R^2$	0.66	$R^2$	0.99	$R^2$	0.88

**Figure 4.** Intraparticle diffusion model for adsorption of phosphorus from wastewater.

adsorption energies are necessary to determine whether chemisorption or physical processes are involved [53].

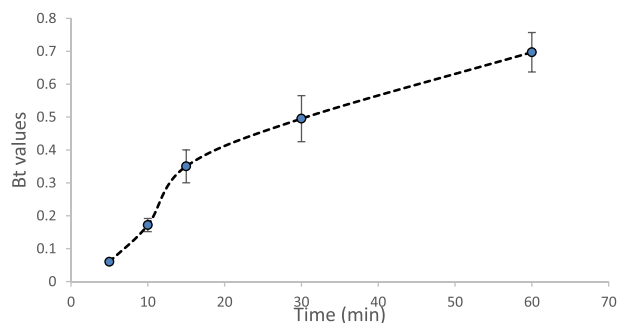
The intra-particle diffusion model also played a role during the adsorption process (Figure 4). The intra-particle diffusion graph indicates deviation from the origin indicating that intra-particle diffusion was not the only rate limiting step. Other rate limiting mechanisms might have been involved in the adsorption process. Multi linearity was observed from the intra particle diffusion graph indicating that three steps were involved in controlling the process. Each linear segment in the graph indicates controlling mechanism or several simultaneous controlling mechanism as stated by Tan and Hameed [49].

The first steeper portion was attributed to the boundary layer diffusion, which is the diffusion of phosphorus from the wastewater to the external surface of the media [54]. The first step lasted for 15 min and was fast. The second part was attributed to gradual adsorption where intra-particle diffusion was rate controlled and lasted for 225 min. The third portion was the equilibrium stage where diffusion remains fairly constant due to unavailability of adsorption sites or low concentration of the phosphorus ions in the wastewater. In this study, this might have been due to unavailability of adsorption sites as P concentration was still high (12.36 mg/L). The size of adsorbate molecules and pore size distribution of the adsorbent can also contribute to the slowdown of the process observed in the third stage [54]. The observation in this study is comparable to that of Cheung et al [54] who reported that the three steps controlled the rate of adsorption of molecules but at a particular range of time only one was rate limiting. The first step revealed intra-particle diffusion rate constant ( $k_p$ ) of 0.075 mg g<sup>-1</sup>/min<sup>0.5</sup> and the second step the gradual adsorption stage with  $k_p$  being 0.009 mg g<sup>-1</sup>/min<sup>0.5</sup>. The two constants indicate that gradual adsorption was the slower of the two stages and was the rate controlling mechanism. The diffusion resistance increases as the phosphorus ions diffuse into the pores of the media resulting in low  $k_p$  in the second stage as compared to the first stage [55]. Similar results were reported by Kumar and Gayathiri [56], on the adsorption of lead ions onto Bael tree leaf powder. The results are also comparable to the findings by Sima et al. [27] who reported that gradual adsorption was rate controlling adsorption of phosphorus onto tailings and clinker ash. Extrapolating the linear portion of the graph to the y-axis gives an intercept of 0.01 mg g<sup>-1</sup>/min<sup>0.5</sup> which gives an idea of boundary layer thickness.

The film mass transfer coefficient,  $k_f$ , was  $-0.287 \text{ cm s}^{-1}$ , with the boundary layer thickness of  $0.01 \text{ mg g}^{-1} \text{ min}^{-0.5}$ ,  $D$ , the diffusion coefficient in the aqueous phase was therefore  $-0.00287 \text{ cm}^2 \text{ s}^{-1}$ , the particle diameter was 0.8 mm and the Biot number was therefore 80. Since  $Bi$  is between 1 and 100, this suggests that adsorption was controlled by both film diffusion and intraparticle diffusion. This contrasts the results observed by Muhammad et al. [36] who reported  $Bi$  values between 422 and 2733 for the kinetics of P removal from wastewater using hybrid ion exchange resin. To further confirm the controlling mechanism between film and intraparticle diffusion, the ratio of time taken for film diffusion to time taken for intraparticle diffusion was calculated and was 0.07. Since this ratio  $<1$ , this indicates that intraparticle diffusion was controlling the adsorption process of phosphorus onto copper smelter slag [35]. This suggests that intraparticle diffusion was the slowest step during the process, hence taking a longer time before equilibrium is reached but was not the only controlling mechanism.

The kinetic data was further analysed through the Boyd model by plotting  $Bt$  against time. In this model, if external transport is greater than internal transport then it indicates that film diffusion controls but if internal transport is greater than external transport it indicates that particle diffusion controls adsorption. For determining the actual rate controlling step during P adsorption onto copper smelter slag Boyd plot was performed as indicated in Figure 5. From the figure, it can be observed that the linear regression of the plot does not pass through the origin suggesting that particle diffusion was not the only rate controlling process for the adsorption.

The rate limiting step during adsorption processes determines the practical options that should be employed to improve adsorption [57]. In the case of film diffusion limiting the adsorption process, mixing or turbulence should be improved. That is if a stirred reactor is used, then stirring speed can be increased to overcome the boundary layer thickness. Similarly, if the limiting step is intraparticle diffusion, use of finer media can be used which will have larger surface areas hence many adsorption sites or instead column depth can be increased thereby increasing contact time and many adsorption sites since finer media can promote bed clogging.

**Figure 5.** Boyd model for the adsorption of phosphorus onto copper smelter slag.



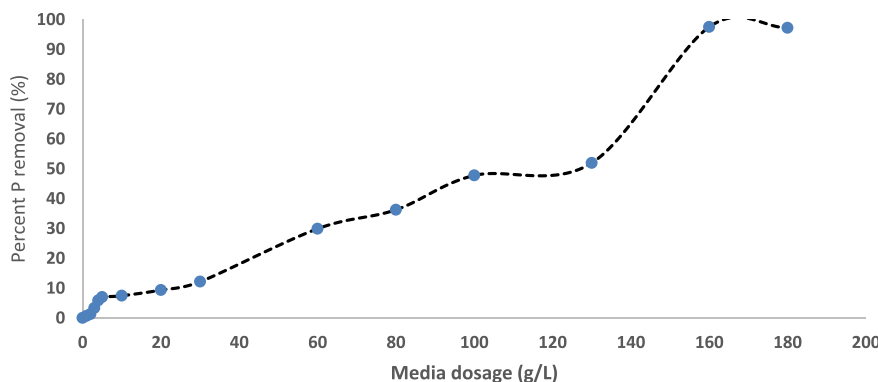


Figure 6. Effect of media dosage on phosphorus removal from wastewater.

### 3.7. Effect of media dosage

The effect of adsorbent dose was investigated by increasing slag dosage from 0.1 to 16 g per 100 mL from initial wastewater pH of  $6.8 \pm 0.4$  with filtrate pH values ranging between  $6.3 \pm 0.25$  and  $6.6 \pm 0.35$  and within the limit of 6.0–9.0. The results also indicate that pH did not change much during the study. As shown in Figure 6, increasing media dosage increased P removal and is comparable to the findings by Moharami et al. [58]. This is due to increased quantity of active sites and surface area therefore increasing adsorption of phosphorus [19]. After a certain dosage further increase of media did not increase the percentage removal of phosphorus from wastewater. This was observed at dosages of 160 and 180 g L<sup>-1</sup>. Similar results were reported by Funes et al. [59] on their study of determining factors controlling phosphorus removal by promising adsorbents used for lake restoration. This was attributed to unavailability of P ions even though adsorption sites were available leading to state of equilibrium. Increasing adsorbent concentration increased adsorbate uptake because of many binding sites and then insufficient P ions for uptake by the adsorbent [60]. Qasemi et al. [61] observed increased P adsorption as adsorbent dose was increased and attributed this to increased adsorption sites in their study of thermally treated aluminium waste fillings as a low cost and efficient adsorbent for P removal from water.

Smelter slag attained  $97 \pm 0.42$  and  $97.2 \pm 0.0\%$  phosphorus removal at high dosages of 16 and 18 g/L respectively which may be attributed to the unavailability of reactive sites. Cucarella and Renman [62] reported that a number of factors such as type of material used, initial phosphorus concentration, sorbent/solution ratio, agitation speed, and temperature can influence equilibrium time. The optimum dosage of slag is 16 g/100 mL of wastewater. It was observed during batch kinetic tests where media dosage was 2 g/100 mL of wastewater that removal efficiency was  $29.5 \pm 0.71\%$  after 4 h. It can be concluded that low removal efficiency was due to unavailability of adsorption sites since when increasing dosage to 16 g/100 mL of wastewater,  $97 \pm 0.42\%$  removal efficiency was achieved. The experimental maximum retention capacity of 0.26 mg P g<sup>-1</sup> media was achieved with media dosage of 0.4 g/100 mL (4 g/L) of P solution. Increasing media dosage for the same initial P concentration makes adsorption process inefficient per gram of adsorbent though oversell removal was high. Low porosity of the media observed earlier might have contributed to Low P adsorption capacity since adsorption sites were few. Low efficiencies observed in some adsorbents has motivated modification with the aim to augment their intrinsic and chemical properties to enhanced P removal. Haddad et al. [46] treated marble wastes and found that only one dose of 10 g L<sup>-1</sup> was required to ensure more than 97% P removal as compared to when untreated marbles were used. However copper smelter slag used in this study is very abundant waste at the mine. Increased media dosage may be compromised over media modification hence reducing costs that might be incurred.

### 3.8. Isotherm models

The equilibrium adsorption isotherms and corresponding constants are presented in Table 8. Langmuir isotherm provided a better fit for phosphorus removal by copper smelter slag with R<sup>2</sup> of 0.52 compared to Freundlich (R<sup>2</sup> = 0.07). This was suggesting a monolayer and a homogeneous distribution pattern during the adsorption process. The findings confirm earlier observation that Pseudo second order kinetic model fits better which also suggests monolayer adsorption [63]. The maximum adsorption capacity (q<sub>max</sub>) as obtained from the Langmuir isotherm was 0.16 mg P g<sup>-1</sup> media less than the experimental results of 0.26 mg P g<sup>-1</sup> media. Langmuir model has been criticized for unrealistic adsorption capacity. Slag showed lower adsorption capacity despite its high Fe<sub>2</sub>O<sub>3</sub> content ( $45.66 \pm 0.62\%$ ). The low removal capacity of slag might be attributed to its surface morphology which was characterized by lack of porous surface as well a smooth and flat surface (Figure 1 (a)) hence making diffusion of the phosphorus ions through the external surface and inner pores difficult. Since real wastewater was used during this study, competing effect of other ions might have reduced P adsorption onto the slag. The presence of residual phosphorus in fresh slag also played a role in the adsorption process. Instead of adsorbing phosphorus, the media could also have been desorbing phosphorus as indicated by low concentration of phosphorus in the used media. Another reason could be that slag got saturated with phosphorus in a short period of time since it already contained phosphorus. The adsorption capacity of P onto copper smelter slag is far less than the findings by Vieira et al. [64] who observed the retention capacities of 1072.85 and 1183.54 mg P g<sup>-1</sup> media for P adsorption onto biochar from poultry manure and biochar from sugarcane straw respectively. The reason for low adsorption capacity compared to the other materials might be due P concentrations used for the experiments. Many studies have used high P concentrations resulting in unrealistic adsorption capacities. The separation factor (R<sub>L</sub>) which is a dimensionless equilibrium constant employed for isotherms that obey Langmuir model [53] was calculated (Table 3) as 0.12. Since the R<sub>L</sub> value was less than 1, the adsorption of phosphorus on slag was favourable.

### 3.9. pH monitoring

Figure 7 shows change in pH with time during batch kinetic studies which ranged between 6.4 and 7.4 from an initial pH of 6.8. These results

Table 8. Langmuir and Freundlich isotherm parameters.

Langmuir		Freundlich	
q <sub>max</sub> (mg P g <sup>-1</sup> )	0.16	K <sub>F</sub> (L g <sup>-1</sup> )	0.10
K <sub>L</sub> (L mg <sup>-1</sup> )	0.35	n	12.8
R <sup>2</sup> value	0.52	R <sup>2</sup> value	0.07
R <sub>L</sub>	0.12		

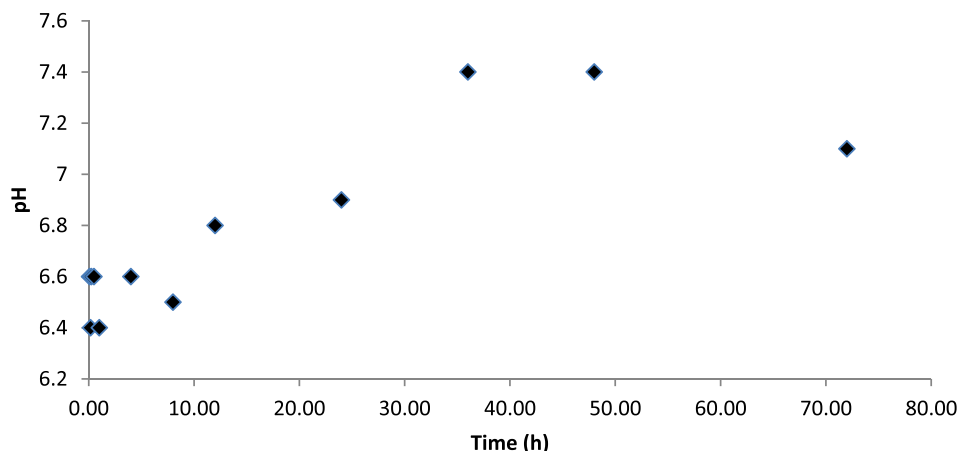


Figure 7. Change of pH with time during batch kinetic studies on phosphorus removal from wastewater.

suggest that copper smelter slag will not elevate effluent pH if used for phosphorus retention from wastewater. The use of smelter slag would not require adjustment of effluent pH either thus being environmentally suitable for use and economical for the treatment technology.

Free lime (CaO) present in slag materials elevates pH of the effluent [40] as a result of liberation of  $\text{Ca}^{2+}$  ions from the material and the formation of  $\text{OH}^-$  ions [65]. Low CaO (1.99%) in smelter slag might have contributed to low pH. Similar findings were reported by Park et al. [7] when using basic oxygen slag for phosphorus removal as the pH ranged between 8.2–8.8. The pH range was lower than that reported by Bowden et al. [31] where values up to 12 were observed. Blanco et al. [36] reported that the final pH increased to 11.3 which can be detrimental to aquatic life and would need adjustment before effluent discharge, hence increasing the costs. Some studies have reported successful phosphorus removal at elevated  $\text{pH} \geq 8$  when calcium precipitation is the dominant removal mechanism [66]. It has been reported that phosphorus adsorption to metal oxides surfaces (Al and Fe oxides, pH 4–7.5) decreases with increasing pH then precipitation is likely to be the removal of phosphorus at elevated pH [41]. Low phosphorus removal observed in this study might have been due to unfavourable pH range and unavailability of adsorption sites. This is despite high content of  $\text{Fe}_2\text{O}_3$  in the slag (45.22%). The  $\text{pH}_{\text{pzc}}$  for the smelter slag was found to be 5.0 and this implies that below this pH the material was positively charged hence high probability of phosphate ions being attracted to the surface of the media. The pH was observed ranging between 6.4 and 7.4 implying that the surface of the media was negatively charged hence repelling the negatively charged phosphate ions and might have contributed greatly to low P retention capacity. There is a need to investigate the influence of pH on the performance of this media. Qasemi et al. observed increase in P removal as pH increased from 4 to 10 and thereafter a decrease. The decline in P retention was attributed to the competition between

negatively charged hydroxide ( $\text{OH}^-$ ) ions and negatively charged phosphate ( $\text{PO}_4^{3-}$ ) ions for available sites.

### 3.10. Batch regeneration studies

From the initial removal efficiency of  $29.5 \pm 0.71\%$ , copper smelter slag efficiencies dropped by 17.4, 7.1 and 4.98% removal respectively in the first, second and third regeneration cycles trials (Figure 8). The results showed that the use of the media would require frequent replacements which would be economically expensive.

When 0.1 M NaOH solution was used, Chitrakar et al. [67] observed a recovery of 67% P from goethite during the second phase of batch reusability trial. The reason was attributed to dissolution of iron from goethite a Fe rich media similar to copper smelter slag. The 0.1 M NaOH solution was the same as that used during this study. During their study of P removal by  $\text{ZnCl}_2$  activated coir pith carbon, Namasivayam and Sangeetha [68] reported that chemisorption and ion exchange were the involved processes. Chemisorption involved zinc-phosphate complex formation hence only ions adsorbed through ion exchange were desorbed and those through complex formation were not. This was comparable to this study where chemisorption was the dominant phosphorus removal mechanisms suggesting the possibility of low desorption during regeneration trial. The findings of this study differ from those reported by Su et al. [51] where 91.67% phosphorus desorption was achieved from am- $\text{ZrO}_2$  nanoparticles using 0.1 M NaOH solution. Other studies have used different reagents for regeneration such as sodium hydrogen carbonate and sodium chloride and observed high P recovery of 98.12 and 82.04% indicating that  $\text{Cl}^-$  and  $\text{HCO}_3^-$  ions exchange phosphate at the surface reaction sites of MAEX resin [69]. Different regenerant of differing concentrations will need to be tried in the future to establish the one having high efficiency for desorption of phosphorus from copper smelter slag.

## 4. Conclusion

Different adsorption media have been used for the removal of P from wastewater. Copper smelter slag efficiency on the removal of P from wastewater was very low. Theoretical and experimental P adsorption capacities were 0.16 and  $0.26 \text{ mg P g}^{-1}$  media respectively. Low removal efficiency was due to the presence of residual phosphorus in the fresh media therefore few adsorption sites making the media to be used in large quantity if used. The pH might also have played a role on low adsorption capacity since the media favours acidic conditions (4–7.5) but since pH values in this study ranged between 6.4 and 7.5 it was close to neutral conditions. In addition point of zero charge of the media was found to be 5.0 suggesting that adsorption was favourable at lower pH values hence the need to adjust pH when using the media. The adsorption

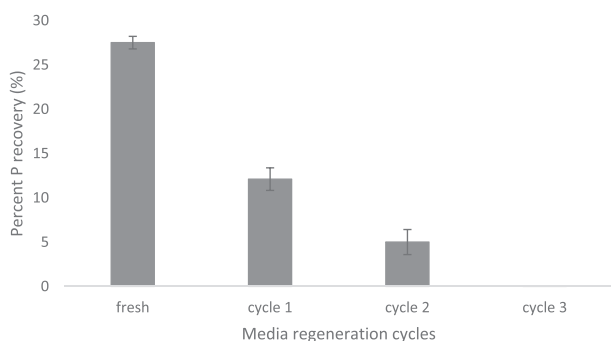


Figure 8. Impact of regeneration cycles on adsorption capacity of smelter slag for phosphorus removal from wastewater.

process was described by Pseudo – second order model suggesting that chemical adsorption might have been one of the mechanisms involved in phosphorus adsorption, the involvement of other mechanisms should be investigated to establish whether chemical or physical bonding were involved. Both intraparticle and film diffusion were controlling the rate of adsorption process as revealed by the different kinetic models. High dosage of smelter slag is needed to achieve high removal efficiency as  $97 \pm 0.42\%$  removal was achieved with a dosage of 16 g/100 mL though this decreased the adsorption capacity of the media. The media also showed a low regeneration potential suggesting frequent replacement of the media which could be costly and reduces economic benefit of the media. Low P removal capacity and less regeneration makes the material to have negative benefits for use in the adsorption process. It can be concluded that copper smelter slag is a poor phosphorus adsorbent under the conditions studied and less phosphorus was recovered from the media during desorption trials. Further studies should be conducted to determine factors that can contribute to improved efficiency of copper smelter slag for phosphorus removal.

## Declarations

### Author contribution statement

Moatlhodi Wise Letshwenyo: Conceived and designed the experiments; Analyzed and interpreted the data; Wrote the paper.

Thandie Veronicah Sima: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

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### Competing interest statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

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