



# Simultaneous removal of heavy metals from drinking water by banana, orange and potato peel beads: a study of biosorption kinetics

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## Abstract

Banana, orange and potato peels (BP, OP and PP, respectively) were immobilised to produce biosorbent beads that were employed for the biosorption of heavy metals from a cocktail solution containing As(V), Cd(II), Cr(VI), Cu(II), Hg(II) and Ni(II) ions. Drinking water conditions were maintained with neutral initial pH and low concentration of the ions. Batch experiments were performed for evaluating the effect of pH in the drinking water range (6.5–8.5). Results showed a significant increase in the biosorption capacity of the beads with respect to the uptake of As and Pb, whereas it decreased significantly for Cd, Cu, Hg and Ni ions at basic pH values. Approximate equilibrium biosorption of Cd, Cu, Hg and Ni was 89–92%, 79–87%, 84% and 71–80% by BP, OP and PP beads. The physisorption-based PFO model was the most suitable for the ions with biosorption capacities closer to the experimental values. BP and OP beads had better biosorption efficiencies relative to PP bead due to the higher surface heterogeneity observed by scanning electron microscopy coupled with energy-dispersive spectroscopy. An increase in the biosorbent concentration from one to ten BP beads significantly increased the biosorption percentage of the ions. The biosorption capacities of Cd, Hg and Ni uptake by one BP bead from a 1 mgL<sup>-1</sup> cocktail solution were 3.4 ± 0.0, 5.3 ± 0.1 and 3.0 ± 0.0 mgg<sup>-1</sup>, respectively. Thus, BP beads were the most effective than for the simultaneous removal of heavy metals from drinking water.

**Keywords** Banana peel · Orange peel · Potato peel · Sodium alginate bead · Biosorption · Heavy metals

## Abbreviations

As Arsenic  
AP Apple peel  
BP Banana peel

$c_{ad}$  Concentration adsorbed  
Cd Cadmium  
CP Cucumber peel  
 $c_o$  Initial concentration  
Cr Chromium  
 $c_t$  Concentration at time 't'  
Cu Copper  
EDS Energy-dispersive spectroscopy  
FD Film diffusion  
Hg Mercury  
ICP-MS Inductively coupled plasma-mass spectrometry  
 $k_1$  Rate constant for PFO  
 $k_2$  Rate constant for PSO  
 $k_{FD}$  Rate constant for film diffusion  
 $k_{PD}$  Rate constant for pore diffusion  
m Weight of biosorbent  
Ni Nickel ion  
OP Orange peel  
Pb Lead  
PD Pore diffusion  
PFO Pseudo-first order

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PP	Potato peel
PSO	Pseudo-second order
$q_e$	Equilibrium biosorption capacity
$q_t$	Biosorption capacity at time 't'
$R^2$	Correlation coefficient
SA	Sodium alginate
SE	Standard error of the mean
SEM	Scanning electron microscopy
$T$	Contact time
$V$	Volume of solution

## Introduction

Contamination of drinking water and water quality issues are serious environmental concerns that presently affect 2.1 billion or more people globally according to United Nations Water Facts (UNESCO World Water Assessment Programme 2019). Among the major pollutants of drinking water, a range of metals and metalloids may be found at concentrations in the nanogram to microgram per litre range (Schwarzenbach et al. 2010). Biosorption methods for removal of metal and metalloid ions from drinking water have gained interest over the past few decades due to their lower costs, flexible design and ease of operation relative to traditional methods. Some of the most efficient biomolecules with the ability to complex metals in aqueous solutions include polysaccharides such as cellulose, starch, pectin and alginate (Crini 2005; Krishnani and Ayyappan 2006). The most abundant natural polysaccharides are found in plants (Lesmana et al. 2009; Schiewer and Iqbal 2010; Schiewer and Patil 2008b), and peel wastes from fruits and vegetables are a significant source of methane production when dumped in landfills (Chand and Pakade 2013). Therefore, a range of FVP wastes have been used as biosorbents for the removal of toxic ions from aqueous solutions (Jain 2015; Malik et al. 2016).

Alginate is an acidic polysaccharide that is found naturally in edible brown seaweeds (Phaeophyceae) and is used

in various food industries as a thickener, gel producer and for stabilising emulsions (King 1983). The anionic nature of the alginate enables it to bind metal ions from solution and is a good option for use as a biosorbent because of its large availability, biodegradability, mechanical stability and low density (Banerjee et al. 2018; Wang et al. 2016a). Alginate may also be used for immobilising fine peel particles which are otherwise difficult to separate from water post biosorption (Jakóbk-Kolon et al. 2017; Wang et al. 2019).

Biosorption is complicated in the presence of multiple ions as there are ion–ion interactions taking place in addition to the surface interactions with the biosorbent (Mohan and Chander 2001). In this study, we have explored the biosorption potential of peels from banana (BP), orange (OP) and potato (PP) immobilised on sodium alginate (SA) beads to simultaneously remove seven toxic ions (As, Cd, Cr, Cu, Hg, Pb and Ni) at concentrations close to those found in contaminated drinking water. The chemical composition of three peels is given in Table 1. The advantage of using these peels is the utilisation of waste products from the food and agricultural industry. Such by-products of agricultural production have immense potential to be used in sustainable water treatment projects. On the other hand, the small requirement of FVPs in the manufacture of biosorbent beads may not be able to balance the huge amount of peels generated which is a major concern. Nonetheless, efforts have been made to study the biosorption potential of these FVPs.

In the present work, scanning electron microscopy coupled with energy-dispersive spectroscopy (SEM–EDS) was used to visualise the variation in surface structures of the beads that may affect their biosorption efficiencies. Experiments were performed at various drinking water pH values, and biosorption kinetic data were assessed using five standard models, namely film diffusion (FD), pore diffusion (PD), pseudo-first order (PFO), pseudo-second order (PSO) and Elovich equation. The performance of the SA bead with and without immobilised peel was studied, and the effect of increasing biosorbent concentration was investigated using FVP beads.

**Table 1** Chemical composition of FVPs

Composition	Banana peel	Orange peel	Potato peel
Cellulose, %	8.4	9.2	12
Fat, %	1.7	0.8	0
Proteins, %	8.3	8.1	8.3
Starch, %	1.2	3.8	7.8
Total sugar, %	29	46.2	17
Vitamin C, %	1.9	0.1	5
Reference	Emaga et al. (2007) Mohapatra et al. (2010) Mosa and Khalil (2015)	López, (2010) M'hiri, (2015) Witczak et al. (2017)	Augustin et al. (1979) Camire et al. (1997) Sepelev and Galoburda (2015) Toma et al. (1979)

## Materials and methods

### Cocktail solution

A cocktail solution of seven ions was prepared by spiking standard solutions of As(V), Cd(II), Cr(VI), Cu(II), Hg(II), Pb(II) and Ni(II) each at the same initial ion concentration 0.1 mgL<sup>-1</sup> for surface imaging, pH and kinetic studies. For studying the effect of bead number on biosorption, cocktail solutions were prepared by spiking all seven ions at initial concentration of 1 mgL<sup>-1</sup>. The pH of the solution was adjusted using 0.1 M nitric acid and 0.1 M sodium hydroxide.

### Biosorbent preparation

Biosorbent beads were prepared from BP, OP and PP according to the methods published in our earlier work with apple and cucumber peel beads (AP and CP, respectively) (Singh et al. 2019a, 2019b). BP, OP and PP were washed once with hot water, twice with tap water and twice with deionised distilled water, dried, pulverised and sieved to particle size < 240 µm. The peel particles were mixed with SA slurry and dropped in 0.1 M calcium chloride solution. The beads formed were cured in the solution overnight, washed with deionised water to remove excess solution and dried. The dried beads were stored in a desiccator.

### Surface imaging

The beads were analysed for changes in surface morphology before and after biosorption using SEM–EDS. The samples were mounted on an aluminium stub using double-sided carbon tape and sputter coated with 10 nm of gold palladium

using an Emitech K575x sputter coater (EM Technologies Ltd, Kent, England). The surface morphology was examined using a JEOL 6700F Field emission SEM (JSM-6700F, JEOL Ltd., Japan) at 3.0 kV. Samples for EDS were coated with 10 nm of carbon using an Emitech 250X carbon coater attachment on the sputter coater. EDS analysis was performed using a JEOL 2300F EDS system (JEOL Ltd, Tokyo, Japan) at 20.0 kV.

### Experimental procedure

Batch biosorption experiments were performed for all three bead types under identical conditions. One biosorbent bead was added to 25 mL of cocktail solution incubated at 25 °C in an orbital shaker set at 250 rpm. To examine the effect of changes in pH, initial pH ranges of 6.5–8.5 were incubated for 24 h. For kinetic studies, the cocktail solutions at pH 7.0 were incubated over the time-frame of 15 min–72 h.

### Concentration measurement, calculations and statistics

At the end of each experiment, the beads were removed and the solutions were acidified and diluted with 2% nitric acid before injecting in an Agilent 7900 quadrupole inductively coupled plasma coupled with mass spectrometry (ICP-MS). A general purpose tune was selected for robust conditions to minimise interferences and instrumental drift. A multi-ion of six reference elements was added online to compensate for any drift or possible matrix effects. The instrument was calibrated using NIST traceable ICP-MS standards.

All experiments were performed in triplicate and the mean of the results along with the standard errors of the mean was used for calculations using the equations given in Table 2. For statistical analysis of the data, a one-way analysis of

**Table 2** Equations used for calculations

Concentration biosorbed:	$c_{ad} = c_0 - c_t$	(Singh et al. 2019b)
Biosorption percentage:	Biosorption % = $\frac{c_{ad}}{c_0} \times 100$	(Singh et al. 2019b)
Biosorption capacity:	$q_t = \frac{c_{ad}}{m} \cdot \frac{V}{1000}$	(Singh et al. 2019b)
Film diffusion (FD) kinetics:	$\ln(-F) = -k_{FD} t$	(Gupta and Bhattacharyya 2011)
Pore diffusion (PD)-Weber–Morris kinetics:	$q_t = k_{PD} t^{0.5}$	(Gupta and Bhattacharyya 2011)
Pseudo-first-order (PFO) kinetics:	$\ln(q_e - q_t) = \ln q_e - k_1 t$	(Gupta and Bhattacharyya 2011)
Pseudo-second-order (PSO) kinetics:	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	(Tan and Hameed 2017)
Initial biosorption rate:	$h = \frac{dq}{dt} = k_2 (q_e)^2$	(Tan and Hameed 2017)
Elovich equation kinetics:	$q_t = a + b \ln t$	(Schwantes 2016)

$c_0$  = initial concentration (mgL<sup>-1</sup>),  $c_t$  = concentration at time ‘ $t$ ’ (mgL<sup>-1</sup>),  $q_t$  = biosorption capacity at time ‘ $t$ ’ (mgg<sup>-1</sup>),  $m$  = mass of biosorbent (g),  $V$  = volume of solution (mL),  $K_{FD}$  = film diffusion rate constant (min<sup>-1</sup>);  $q_e$  = Biosorption capacity (mg g<sup>-1</sup>) at equilibrium;  $K_{PD}$  = pore diffusion rate constant (mgg<sup>-1</sup> min<sup>-0.5</sup>);  $K_1$  = pseudo-first-order rate constant (min<sup>-1</sup>);  $K_2$  = pseudo-second-order rate constant (mgg<sup>-1</sup> min<sup>-1</sup>);  $h$  = initial biosorption rate (mgg<sup>-1</sup> min<sup>-1</sup>);  $a$  = Elovich constant indicating chemisorption initial rate (mgg<sup>-1</sup> min<sup>-1</sup>);  $b$  = number of adsorption surface sites related to the coverage extension and the activation energy of chemisorption (gmg<sup>-1</sup>)

variance (ANOVA) coupled with a Bonferroni post hoc test was used and  $p < 0.05$  was the minimum requirement for statistical difference. All results are expressed as the mean  $\pm$  SE of three experiments.

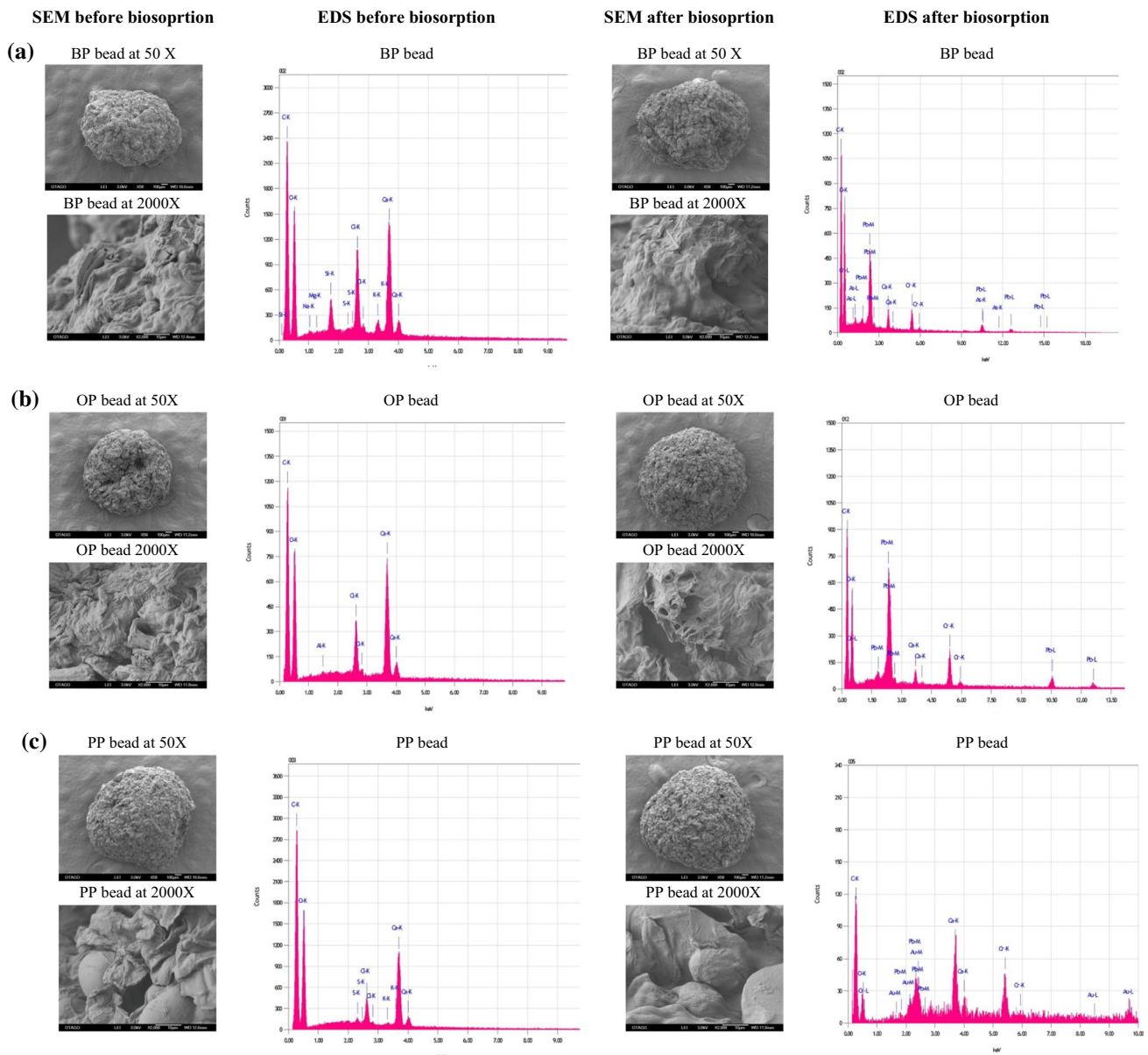
## Results and discussion

### Surface imaging

SEM–EDS was used to identify the morphological and topographical changes on the bead surface following biosorption.

The beads were spherical in shape with an approximate diameter 1.5 mm and had a heterogeneous distribution of folds throughout the surface. Similar observations were made in case of hydrous zirconium oxide immobilised alginate beads which had an average bead diameter was  $\sim 2$  mm (Kumar et al. 2018), and activated lemon peel immobilised alginate beads that had an average diameter of  $\sim 3$  mm (Aichour et al. 2018). However, the beads differed in weight and size and therefore, their biosorption capacities were non-comparable.

SEM results at 50X and 2000X before biosorption revealed the presence of hills and valleys (Fig. 1). Among



**Fig. 1** SEM–EDS of FVP beads before and after biosorption. One bead was incubated in a cocktail solution containing all seven ions each at 0.1 mgL<sup>-1</sup>, pH 7.0, 25 °C with continuous shaking at 250 rpm for 10 h. **a** BP bead, **b** OP bead and **c** PP bead

the three beads, the surface of BP bead appeared to be most highly folded followed by OP bead. These folds formed cracks and pores of various sizes throughout the entire surface. The surface of PP bead on the other hand was the smoothest and was made of smooth ball-like structures that were embedded among the folds forming few or no gaps on the surface. EDS analysis did not show the presence of the spiked ions on the surface of any of the beads (Table 3).

The beads were incubated in a cocktail solution of seven ions for 10 h, removed from solution and dried again. Zhang et al. have reported that the presence of a heterogeneous surface can be advantageous as it can expand to accommodate more ions (Zhang et al. 2018) and this has been demonstrated in the biosorption of Cd and Pb by waste tea leaves (Shrestha et al. 2013). This was also observed at 50 X, where the beads appeared swollen and were larger. While BP and OP beads were swollen by ~20%, there was negligible swelling (<5%) in PP bead (Table 3). A closer view at 2000X revealed the surface was more compact with partially or completely closed pores due to the relaxing of folds (Fig. 1). Similar observation was made in the biosorption of Cu by alga (Pouya and Behnam 2017) and methylene blue by carbon–alginate beads (Nasrullah et al. 2018) where the surface became more compact post biosorption. The surface of the beads became smoother after coming in contact with the ions. This was also reported in the biosorption of Cr by modified banana peel (Ali et al. 2016a) and multiple ions by tea wastes, maple leaves and mandarin peels (Abdolali, 2016) where the biosorbent surfaces became smoother as a result of entrapping of the ions in the pores. Similarly, BP and OP beads had a higher biosorption of ions compared to the smoother PP bead (Fig. 2). This may be because a

highly folded surface is associated with higher biosorption capacity due to the increase in surface area (Wang et al. 2016b). This was also reported by Gerola et al. and Feng and Guo, where chemical modification of passion-fruit skin and orange peel, respectively, resulted in a rougher surface that yielded enhanced biosorption (Feng and Guo 2012; Gerola et al. 2013).

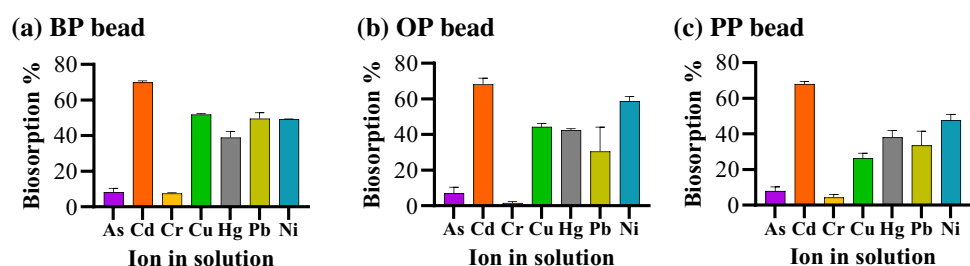
Sodium alginate has a unique property to form cross-linkages in the presence of multivalent cations such as calcium ions (Mohammadabadi and Javanbakht, 2020). In a study on alginate nanoparticles, the presence of calcium ions in the EDS spectra indicated the formation of cross-linkages between carboxylate ions in the polysaccharide and the divalent calcium ions (Geetha et al. 2015). In the present work, cross-linkages between polymeric chains by electrostatic interaction were evident in all the three FVP beads as indicated by their respective EDS spectra (Fig. 1, Table 3). Additionally, it is well known that the degree of cross-linking controls the level of water absorption by hydrogels and their capacity to take up and hold water (Pavithra et al. 2021). This swelling of hydrogels is because of the hydration of the hydrophilic groups of alginate (Ivánová et al. 2010). Among the three FVP beads studied, BP and OP beads had higher swelling than PP beads (Table 3). This is consistent with the ability of BP and OP beads to biosorb higher amount of heavy metals from cocktail solution (Fig. 2). Similar observations were made in the study of dry and gel calcium alginate beads where the gel beads demonstrated a higher amount of swelling by accommodating more water molecules and showed a faster removal of copper ions from solution (Ivánová et al. 2010). Thus, both a highly folded structure and the degree of cross-linkages in the polymeric

**Table 3** Summary of SEM–EDS analysis of the beads

Bead	Weight of bead before biosorption (mg)	Size before biosorption (µm × µm)	Size after biosorption (µm × µm)	EDS elements before biosorption	Additional EDS elements after biosorption
BP	2.50 ± 0.05	1522 × 1282	1658 × 1564	C, O, K, Na, Ca, Mg, Si, P, S, Cl	As, Cr, Hg, Pb
OP	1.00 ± 0.02	1395 × 1339	1699 × 1609	C, O, K, Na, Ca, Al, Cl	Cr, Cu, Pb
PP	2.00 ± 0.05	1699 × 1612	1778 × 1642	C, O, K, Ca, Al, S, Cl	Cr, Pb

One bead was incubated in a cocktail solution containing all seven ions each at 0.1 mgL<sup>-1</sup>, pH 7.0, 25 °C with continuous shaking at 250 rpm for 10 h

**Fig. 2** Biosorption of ions. One bead was incubated in a cocktail solution containing all seven ions each at 0.1 mgL<sup>-1</sup>, pH 7.0, 25 °C with continuous shaking at 250 rpm for 10 h. **a** BP bead, **b** OP bead and **c** PP bead





alginate complex are responsible for the increased ability of FVP beads to take up metal ions from solution.

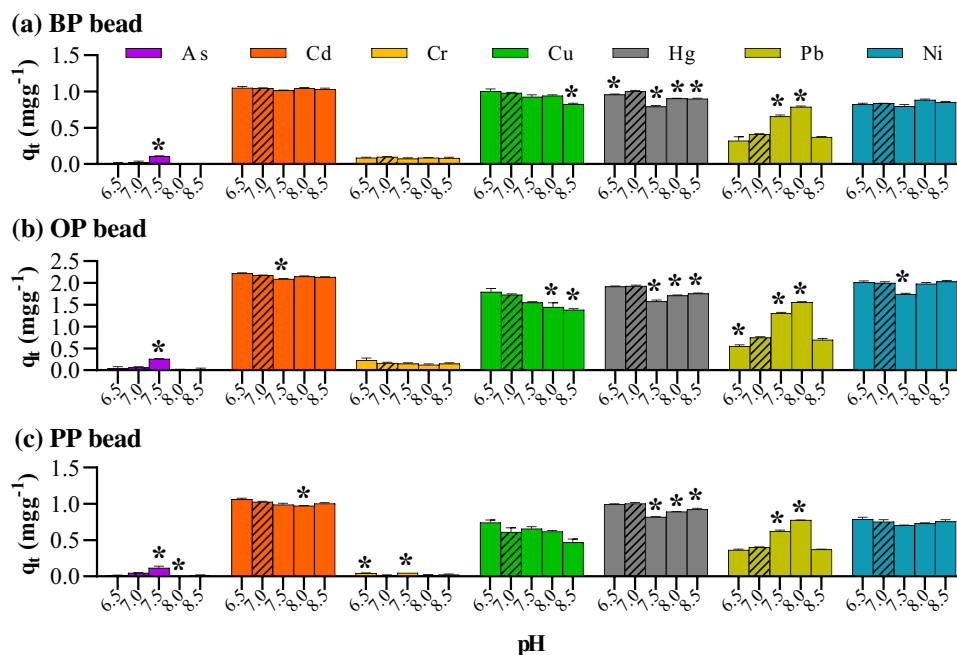
The simultaneous removal of ions from solution by the three beads was compared and the ICP-MS results (Fig. 2) were compared with the EDS results. While the EDS spectra showed prominent peaks of As, Cr, Cu, Hg and Pb post biosorption (Table 3), Cd was missing from the EDS spectra even though the biosorption of Cd was among the highest for all beads (Fig. 2). Cu was found in the spectra of only OP beads, although BP had a higher biosorption of this ion. Similarly, Hg was absent from the spectra of OP and PP beads although the biosorption of Hg by these beads was similar. Ni was absent from all the three beads although there was significant biosorption of this ion. In contrast, As and Cr anions had significantly smaller biosorption but were identified in the spectra of the beads. This suggests that these may have stacked on the previously biosorbed divalent ions such as Cu, Hg and Pb because of the unsuitability of the biosorbent surface for the binding of these anions. In contrast, the ions with high biosorption such as Cd and Ni may have penetrated the biosorbent surface through the pores present. Similar findings were reported in our earlier work with AP and CP beads (Singh et al. 2019a, 2019b).

### Effect of initial pH

The pH of the solution is an important parameter that influences the biosorption of ions. To determine the effect of water pH, but still remain in the acceptable range for drinking water, BP, OP and PP beads were incubated in cocktail solutions at pH values between 6.5 and 8.5. The

results showed that the biosorption capacity of Pb was most significantly affected among all the seven ions. It increased significantly at pH 7.5 and 8.0 for all three bead types compared to a pH of 7.0 (Fig. 3). We reported a similar significant pH-dependent effect for Pb with AP beads (Singh et al. 2019a). Optimal biosorption of Pb at pH 8.0 was also demonstrated for potato peel biomass by Kajjumba et al. (2018). In contrast, the biosorption capacity of Cd and Ni significantly decreased at pH 7.5 for OP beads, and of Cd at pH 8.0 for PP beads (Fig. 3b and c). In contrast, Kajjumba et al. (2018) also reported that pH 8.0 was ideal for the biosorption of Cd by potato peel biomass. This may be because of the increased complexity of multi-ion biosorption where the ions were competing for the same binding sites on the surface of the beads. A decrease in the biosorption of Cd and Ni may have occurred due to the formation of hydroxyl complexes (Beidokhti et al. 2019; Boparai et al. 2013; Ciesielczyk et al. 2013; Mohamed et al. 2019; Park et al. 2017; Van Thuan et al. 2017) at more basic pH. Additionally, the mobility of these ion complexes may be limited thus lowering their diffusion through the liquid film and/or pores of the beads (Cozmuta et al. 2012). Similarly, a significant decrease in the biosorption capacity of BP and OP beads was observed for Cu and Hg ions at pH 8.0 and 8.5 (Fig. 3a and b). This could also be the result of precipitation of  $\text{Cu}(\text{OH})_2$  and  $\text{Hg}(\text{OH})_2$  that has been reported when water pH is greater than 5.0 (Deng et al. 2015; Raza et al. 2015). In fact, neutral pH has been reported as optimum for Cu biosorption by *Pinus* sawdust (Semerjian 2018). Overall, the results for Cu, Hg, Pb and Ni biosorption by BP, OP and PP beads are

**Fig. 3** Effect of pH on bead biosorption capacity. One bead was incubated in a cocktail solution of all seven ions each at 0.1 mgL<sup>-1</sup>, 25 °C with continuous shaking at 250 rpm for 24 h. The initial pH of each solution was adjusted to the specified pH at the start of the experiment. The points represent mean  $\pm$  SE for  $N=3$ . Statistical significance was calculated based on a one-way ANOVA with Bonferroni post hoc test, \*Significantly different compared to pH 7.0,  $p < 0.05$ . **a** BP bead, **b** OP bead and **c** PP bead



similar to our results for CP bead biosorption of these ions from an identical cocktail solution (Singh et al. 2019b).

The ions with the lowest biosorption were As and Cr. This was expected because As adsorption is high in strongly acidic pH where the biosorbent surface is more protonated thus allowing feasible uptake of arsenate anion from solution. In contrast, at higher pH values the biosorbent becomes more negatively charged and therefore repels the negatively charged species (Jung et al. 2017; Vu et al. 2017). In contrast, since Cr is an amphoteric metal (Thakur et al. 2015), there was no variation in the biosorption capacity with changes in pH for Cr, except for PP bead where it significantly increased at 6.5 and 8.5 compared to neutral pH (Fig. 3c). In contrast to the biosorption capacity of these anions, that of the metal ions was low at acidic pH, due to the higher availability of hydrogen ions that compete for binding to surface functional groups (Kakalanga et al. 2012). Additionally, deprotonation of surface functional groups at acidic pH impairs the ability of the biosorbent surface to bind metal cations (Romero-González et al. 2001). Thus, the simultaneous removal of both cations and anions from drinking water is challenging and requires more research.

### Effect of contact time and biosorption kinetics

To study the biosorption trend with time and determine the equilibrium time for the various ions, BP, OP and PP beads were incubated with a cocktail solution of 7 ions for 15 min–72 h. The results showed that there was a faster initial biosorption phase followed by a slower rate of removal of the ions (Fig. 4). This is directly related to the availability of the binding sites on the bead surface that were rapidly occupied by the ions in the initial phase. As the reaction approached equilibrium, biosorption slowed and biosorption percentage decreased due to the decrease in the ion concentration in solution (Akkaya and Güzel 2013; Iqbal et al. 2009b; Iqbal et al. 2009c). The ion with the shortest equilibrium time and the highest biosorption percentage was Cd, followed by Cu, Hg and Ni (Table 4). PP bead was

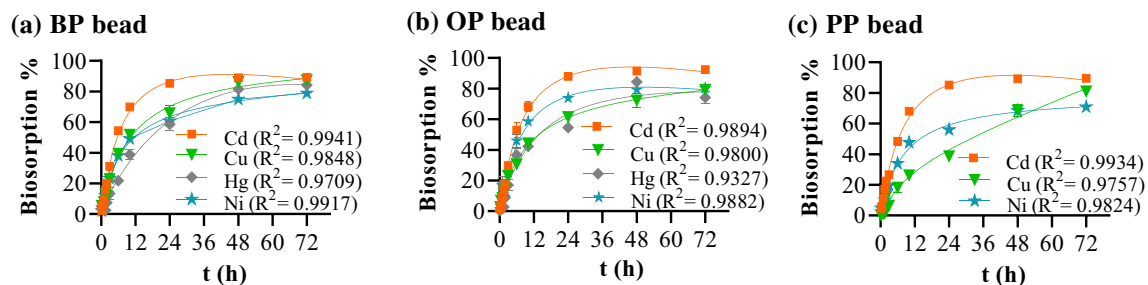
the slowest in the uptake of Cu which did not reach equilibrium within 72 h (Fig. 4). Similar behaviour of Cu ions was observed with CP bead in our previous work, where the ion had not reached equilibrium within 72 h (Singh et al. 2019b). This suggests that surfaces of CP and PP beads were not suitable for the competitive binding of Cu relative to the other ions.

A deeper investigation into the kinetics of biosorption by BP, OP and PP immobilised beads was made at four time points and a comparison was made with SA beads. A significantly enhanced biosorption was observed with FVP beads especially in the initial phase of biosorption (Fig. 5). By 24 h, biosorption by SA bead became closer to the uptake of ions by FVP beads. Similar results were obtained with identical experiments comparing AP beads and SA beads (Singh et al. 2019a). Thus, immobilising AP, BP, OP and PP beads on SA shortened the equilibrium time and significantly increased the biosorption percentage of ions from a cocktail solution.

Biosorption kinetics determine the rate at which the process occurs and are influenced by the properties of the bead and the ions in solution. Among the most popular are linearised diffusion models such as FD and PD, and surface attachment models such as PFO, PSO and Elovich equation. (Kajjumba et al. 2018). Data generated with BP, OP and PP beads were modelled using these models and the suitability of each model was determined by the goodness of fit calculated by  $R^2$  values.

### Film and pore diffusion kinetics

According to the FD model, the ions must overcome the hydrodynamic layer resistance in order to penetrate the liquid film surrounding the bead and the rate of reaction is determined by the distance the ions need to travel to reach the bead surface, the thickness of the boundary layer and the velocity of the bulk solution (Sahmoune 2018). Among the ions that fit this model well, the diffusion of Cd was the highest on BP and PP beads, whereas Hg was the fastest on



**Fig. 4** Effect of contact time on biosorption. One bead was incubated in a cocktail solution containing all seven ions each at 0.1 mgL<sup>-1</sup>, pH 7.0, 25 °C with continuous shaking at 250 rpm for 15 min–72 h. The

points represent mean  $\pm$  SE for  $N=3$  with data analysis by nonlinear regression where  $R^2 > 0.93$ . **a** BP bead, **b** OP bead and **c** PP bead

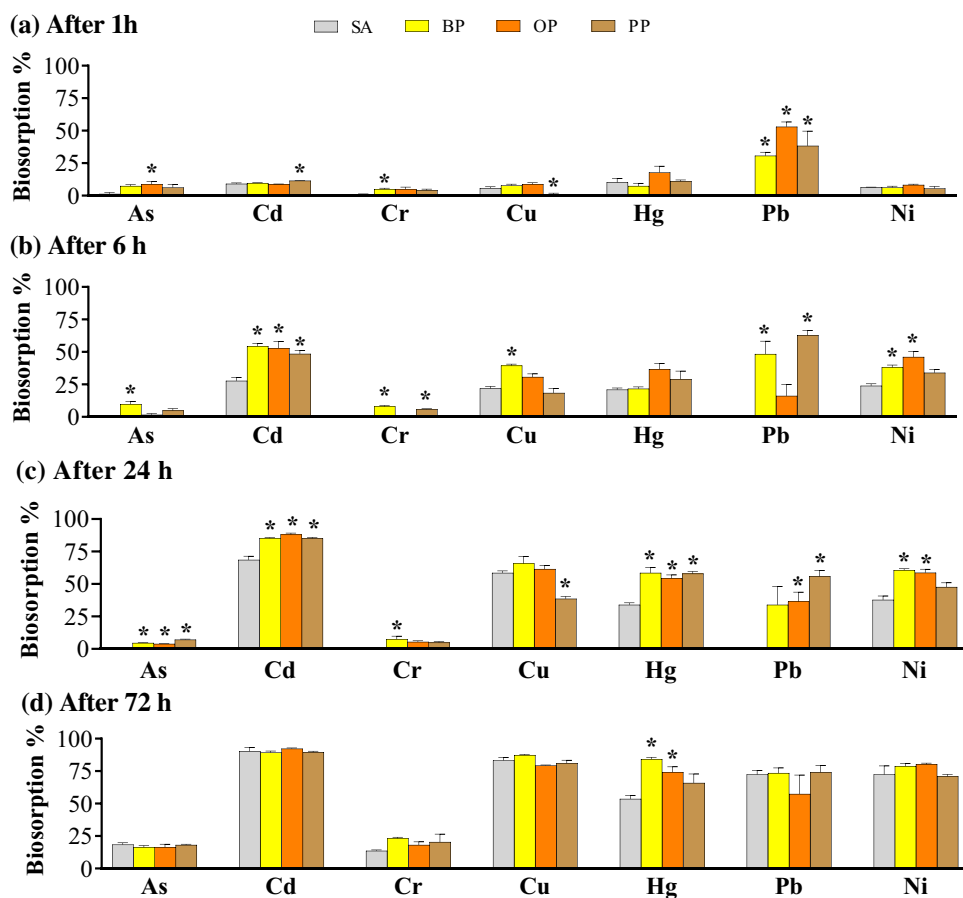
**Table 4** Biosorption kinetic parameters

Ion/ Parameter	Cd	Cu	Hg	Ni
<i>BP bead</i>				
Eq. time (h)	24	48	48	48
Max eq. bios%	89.3±1.2	87.3±0.7	84.2±1.5	78.9±0.2
Max eq. bios. capacity (mgg <sup>-1</sup> )	1.02±0.01	1.15±0.01	0.39±0.01	0.90±0.02
<i>OP bead</i>				
Eq. time (h)	24	48	48	24
Max eq. bios%	92.4±0.4	79.3±0.4	84.4±1.0	80.3±0.9
Max eq. bios. capacity (mgg <sup>-1</sup> )	2.11±0.01	2.09±0.01	0.78±0.01	1.84±0.02
<i>PP bead</i>				
Eq. time (h)	24	**	–	48
Max eq. bios%	89.6±0.7	81.1±2.2	–	70.9±1.7
Max eq. bios. capacity (mgg <sup>-1</sup> )	1.02±0.01	1.07±0.03	–	0.81±0.02

One bead was incubated in a cocktail solution containing all seven ions each at 0.1 mgL<sup>-1</sup>, pH 7.0, 25 °C with continuous shaking at 250 rpm for 15 min–72 h. Data presented for N=3. Only ions with R<sup>2</sup>>0.93 are shown

\*\*Did not reach equilibrium, data presented for the last time point in the experiment

**Fig. 5** Temporal biosorption of FVP and SA beads. One bead was incubated in a cocktail solution containing all seven ions each at 0.1 mgL<sup>-1</sup>, pH 7.0, 25 °C with continuous shaking at 250 rpm for 15 min–72 h. \*Significantly different biosorption compared to the corresponding SA bead, p<0.05. The bars represent mean ± SE for N=3; data analysis by one-way ANOVA with a Bonferroni post hoc test. **a** 1 h, **b** 6 h, **c** 24 h and **d** 72 h

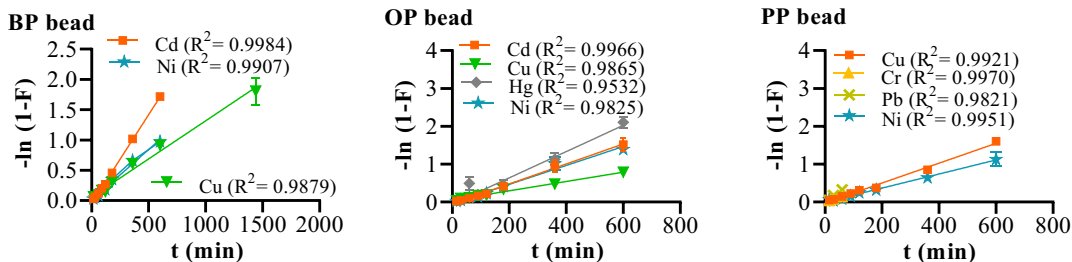


OP bead (Fig. 6, Table 5). In contrast, the PD-Weber–Morris model is based on the assumption that diffusion through the pores of the bead is the sole rate determining step in the reaction and thus, the straight line graph of the equation

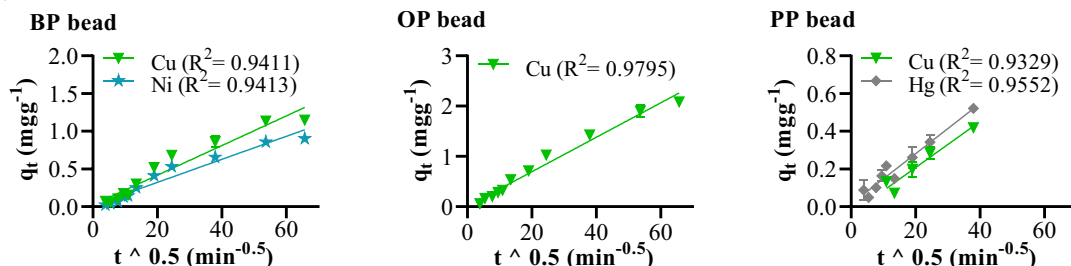
(Table 2) must pass through the origin. Any deviation from this indicates that the biosorption reaction is also controlled by FD (Stavrinou et al. 2018). Cu and Ni biosorption by BP and OP beads fit both FD and PD models, thereby indicating



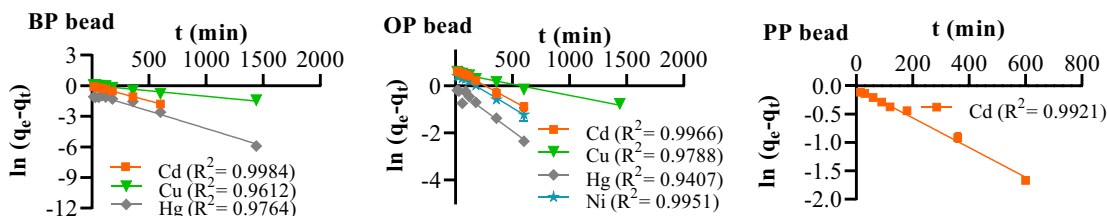
(a) Film diffusion



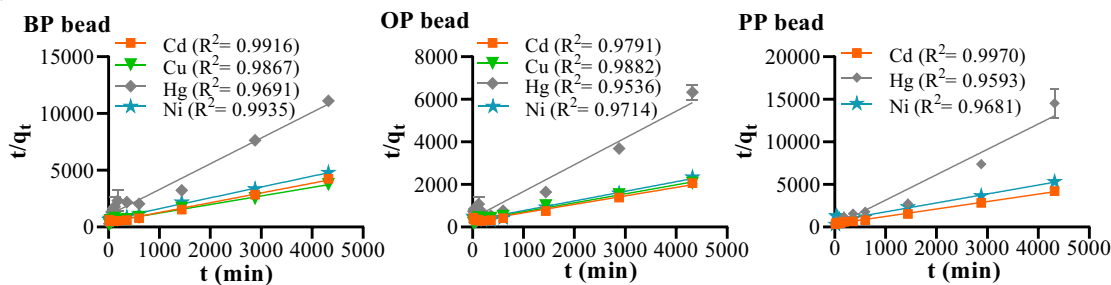
(b) Pore diffusion



(c) Pseudo-first order



(d) Pseudo-second order



(e) Elovich equation

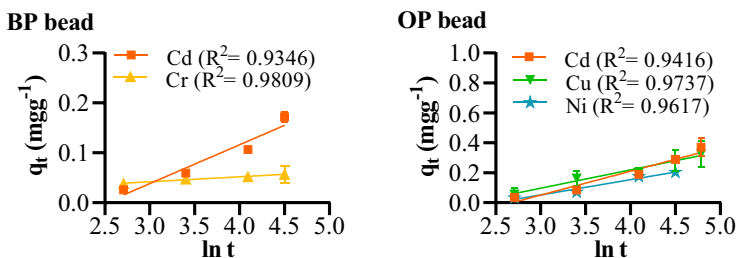


Fig. 6 Biosorption kinetic models. One bead was incubated in a cocktail solution containing all seven ions each at 0.1 mgL<sup>-1</sup>, pH 7.0, 25 °C with continuous shaking at 250 rpm for 15 min–72 h.

The points represent mean ± SE for  $N=3$  with data analysis by linear regression. Only ions with an  $R^2 > 0.93$  are shown. **a** FD, **b** PD, **c** PFO, **d** PSO and **e** Elovich equation

**Table 5** Biosorption kinetic model constants

Bead-metal	Exp $q_e$	Film diffusion (FD)			Pore diffusion (PD)			Pseudo-first order (PFO)			Pseudo-second order (PSO)			Elovich equation					
		up to time (h)	$k_{FD} \times 10^{-4}$	$R^2$	up to time (h)	$k_{PD} \times 10^{-4}$	$R^2$	up to time (h)	$k_1 \times 10^{-4}$	$R^2$	up to time (h)	$k_2 \times 10^{-4}$	$R^2$	up to time (h)	$a \times 10^{-2}$	$b \times 10^{-2}$	$R^2$		
<i>Banana peel (BP) bead</i>																			
Cd	0.9 ± 0.0	10	29.3	0.9984	-	-	24	29.3	0.9984	1.0	72	17.5	23.7	0.9916	1.2	1.5	19.5	7.8	0.9346
Cr	0.3 ± 0.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.5	-1.2	1.0	0.9809
Cu	1.1 ± 0.0	24	12.6	0.9879	72	196.6	48	10.7	0.9612	1.0	72	11.9	20.9	0.9867	1.3	-	-	-	-
Hg	0.4 ± 0.0	-	-	-	-	-	48	34.3	0.9764	0.4	72	49.4	9.6	0.9691	0.4	-	-	-	-
Ni	0.9 ± 0.0	10	16.7	0.9907	72	152.6	-	-	-	0.8	72	13.6	15.0	0.9935	1.0	-	-	-	-
<i>Orange peel (OP) bead</i>																			
Cd	1.9 ± 0.0	10	26.4	0.9966	-	-	24	26.4	0.9966	2.0	72	5.9	37.0	0.9791	2.5	2	42.8	15.9	0.9416
Cu	1.9 ± 0.1	10	12.3	0.9865	72	342.6	48	9.5	0.9788	1.7	72	6.2	34.8	0.9882	2.4	2	27.0	12.2	0.9737
Hg	0.8 ± 0.0	10	34.7	0.9532	-	-	48	35.9	0.9407	0.9	72	38.3	24.2	0.9536	0.8	-	-	-	-
Ni	1.6 ± 0.0	10	25.0	0.9825	-	-	24	28.8	0.9951	1.7	72	6.4	32.5	0.9714	2.2	1.5	25.5	10.2	0.9617
<i>Potato peel (PP) bead</i>																			
Cd	0.9 ± 0.0	10	26.2	0.9921	-	-	24	26.2	0.9921	1.0	72	20.6	26.9	0.9970	1.1	-	-	-	-
Cr	0.1 ± 0.0	1	22.2	0.9970	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Cu	0.9 ± 0.0	-	-	-	24	122.3	-	-	-	-	-	-	-	-	-	-	-	-	-
Hg	0.4 ± 0.0	-	-	-	24	133.1	-	-	-	-	72	505.3	56.8	0.9593	0.3	-	-	-	-
Pb	1.0 ± 0.0	1	59.9	0.9821	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Ni	0.8 ± 0.0	10	18.6	0.9951	-	-	-	-	-	-	72	15.0	13.6	0.9681	1.0	-	-	-	-

One bead was incubated in a cocktail solution containing all seven ions each at 0.1 mgL<sup>-1</sup>, pH 7.0, 25 °C with continuous shaking at 250 rpm for 15 min–72 h. Linear regression data presented for N=3 and only for ions that fit the models with an R<sup>2</sup> > 0.93.  $k_{FD}$  = Film diffusion rate constant (min<sup>-1</sup>);  $k_{PD}$  = Pore diffusion rate constant (mg g<sup>-1</sup> min<sup>-0.5</sup>);  $k_1$  = Pseudo-first-order rate constant (min<sup>-1</sup>);  $k_2$  = Pseudo-second-order rate constant (mgg<sup>-1</sup> min<sup>-1</sup>);  $h$  = initial biosorption rate (mgg<sup>-1</sup> min<sup>-1</sup>);  $a$  = Elovich constant indicating chemisorption initial rate (mgg<sup>-1</sup> min<sup>-1</sup>);  $b$  = number of adsorption surface sites related to the coverage extension and the activation energy of chemisorption (mgg<sup>-1</sup>). -Data could not be fit with any kinetic model. Exp  $q_e$  = experimental equilibrium biosorption capacity (mgg<sup>-1</sup>); PFO  $q_e$  = equilibrium biosorption capacity (mgg<sup>-1</sup>) calculated from pseudo-first-order model; PSO  $q_e$  = equilibrium biosorption capacity (mgg<sup>-1</sup>) calculated from pseudo-second-order model

that both film and pore diffusions were contributing factors in determining the rate of the biosorption reaction. In contrast, Cu and Hg biosorption rate on PP bead was controlled by PD for up to 24 h (Fig. 6, Table 5). This confirms the assumption that heterogeneity of the surface is directly related to the performance of the biosorbent. The surface of the PP bead was the smoothest and appeared to be least porous, thus limiting the diffusion of the ions through its surface and increasing the equilibrium time (Fig. 1, Table 4).

### Pseudo-first and pseudo-second-order kinetics

The PFO model given by Lagergren assumes that the rate of the biosorption reaction is directly proportional to the number of vacant binding sites on the surface of the biosorbent and is usually valid only for time periods where biosorption is fast (Ali et al. 2016b). However, it has been shown to be valid for both the initial phases as well as for longer biosorption times near equilibrium when the biosorbate is present at high enough concentrations (Mashkour and Nasar 2019; Tan and Hameed 2017; Wang, 2018). This contradiction is a result of the uniqueness of the various biosorption systems used to test the validity of the model. While data for Cd and Ni were valid for 24 h, that for Cu and Hg fit for up to 48 h in the PFO model (Table 5). In contrast, the PSO model given by Ho and McKay, assumes that the rate of reaction is proportional to the square of the number of vacant sites (Ali et al. 2016b).

While the PFO model considers mass transfer resistance and incorporates the role of both film and pore diffusions (Deng et al. 2015; Plazinski 2010), the PSO model assumes that surface attachment is the slowest step in the biosorption reaction and includes PD for explaining the rate determining mechanism (Deng et al. 2015; Plazinski et al. 2013). The FD model was only valid in the initial phase for all of three beads, whereas the PD, PFO and PSO models fit until equilibrium was reached. This suggests that while diffusion of ions was still occurring through the pores of the bead, surface attachment mechanisms also took over as the reaction progressed towards equilibrium. A good fitting to both PFO and PSO models also indicates the possibility of simultaneously occurring physisorption and chemisorption which has been reported in the biosorption of Orange 16 dye on activated carbon prepared from hemp stalks (Rehman 2017). This may be due to the stacking of ions physically on top of the first layer chemisorbed on the biosorbent surface. Similar observations were made for the uptake of Cd, Cu, Pb and Ni by modified Chitosan nanofiber membrane, where both PFO and PSO models were valid (Aliabadi et al. 2013). Similar to our findings with AP and CP beads (Singh et al. 2019a, 2019b), the experimental  $q_e$  values were closer to PFO  $q_e$  than PSO  $q_e$  (Table 5), thus confirming the better fit to the physisorption-based PFO model. The physisorption

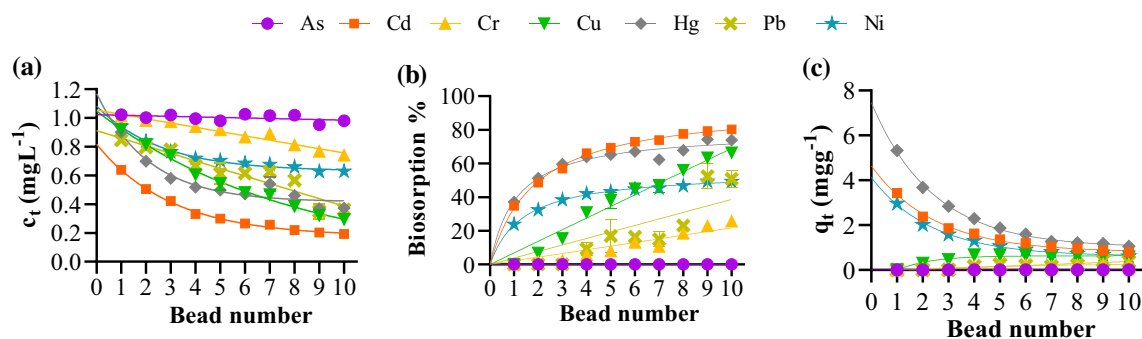
rate of Cu was the slowest, while that of Hg was the highest among all ions (Fig. 6c) and similar results were reported from our work with AP and CP beads.

### Elovich equation kinetics

This is a chemisorption-based model that ignores the possibility of desorption or any interaction among ions (Gupta and Bhattacharyya 2011). Results from the modelling showed that the biosorption of Cr by BP bead was valid for the first 1.5 h with the highest  $R^2$  value for this model (Table 5). Cr biosorption data were also reported to fit the Elovich equation with kaolinite (Gupta and Bhattacharyya 2011), suggesting the formation of chemical bonds between Cr and the biosorbent surface. However, similar to our previously reported work with AP and CP beads (Singh et al. 2019a, 2019b), relatively low  $R^2$  values were calculated for the biosorption of the other ions by BP, OP and PP beads. This validates the physical nature of ion interactions on the bead surface.

### Effect of biosorbent concentration

To determine the change in biosorption with increase in bead number, one to ten BP beads were incubated in a cocktail solution of seven ions. BP beads were chosen for this study because they were more versatile and performed better overall, as compared to OP and PP. Since the number of binding sites is proportional to the number of beads, the concentration of the ions in solution decreased exponentially with an increase in bead number, with a corresponding logarithmic increase in the biosorption percentage (Fig. 7a and b). This is explained by the saturation of the binding sites at low biosorbent concentration because of the excessive number of ions present in solution (Paul et al. 2018). Furthermore, the bead to ion ratio decreases, thus decreasing the overall biosorption capacity at higher bead numbers. Additionally, with an increase in bead number, although the amount of biosorbed ions increased, the biosorbed ion-to-bead ratio actually decreased, due to the corresponding increase in total bead weight leading to an exponential decrease in biosorption capacity of Cd, Hg and Ni ions (Fig. 7c). The curves tended to plateau at concentrations of 5–6 beads due to the saturation of the binding sites. A similar exponential decrease in ion concentration was previously demonstrated for AP bead (Singh et al. 2019a). Therefore, we compared the biosorption of AP and BP beads and the results indicated a significantly higher biosorption of Cd, Hg and Ni ions even though the weight of BP bead was more than AP bead (Table 6). Thus, under identical environmental conditions, the simultaneous biosorption of heavy metals by BP bead was superior to AP bead.



**Fig. 7** Effect of an increase in bead number. One to ten beads were incubated in a cocktail solution containing all seven ions each at  $1 \text{ mgL}^{-1}$  at pH 7.0,  $25^\circ \text{C}$  with continuous shaking at 250 rpm for 10 h.

The points represent the mean  $\pm$  SE for  $N=3$  with data analysis by nonlinear regression. **a** ion concentration, **b** biosorption percentage and **c** biosorption capacity

**Table 6** FVP bead biosorbent concentration parameters

Parameters	Weight of one bead (mg)	Cd	Hg	Ni
AP bead	$2.20 \pm 0.05$			
Bios%		$27.4 \pm 0.7$	$31.9 \pm 1.4$	$20.0 \pm 0.7$
$q_t$ ( $\text{mgg}^{-1}$ )		$3.06 \pm 0.08$	$5.20 \pm 0.23$	$2.82 \pm 0.09$
BP bead	$2.50 \pm 0.05$			
Bios%		$34.9 \pm 0.1^*$	$37.2 \pm 0.9^*$	$23.9 \pm 0.3^*$
$q_t$ ( $\text{mgg}^{-1}$ )		$3.43 \pm 0.01$	$5.33 \pm 0.13$	$2.96 \pm 0.04$

One bead in cocktail solution containing all seven ions each at  $1 \text{ mgL}^{-1}$  at pH 7.0,  $25^\circ \text{C}$  with continuous shaking at 250 rpm for 10 h. Values represent the mean  $\pm$  SE for  $N=3$ . \*Significantly different to the corresponding value for AP bead,  $p < 0.05$

In our study with CP bead, we had established that biosorption was suppressed in the presence of multi-ion solutions compared to single ion solutions, and suppression was enhanced as the number of competing ions increased (Singh et al. 2019b). Additionally, low initial ion concentrations used in our experiments yielded significantly small biosorption capacities and this was also reported by Kurniawan et al. (2006). Unfavourable biosorption at low concentrations was demonstrated by El-Azazy et al. in their work on the biosorption of heavy metals by potato peel (El-Azazy et al. 2019). Lastly, while drinking water pH is not ideal for the optimum removal of toxic ions from solution, the biosorption capacities presented in our work are lower than those published by others.

## Conclusion

Examination of bead surface morphology indicated that the degree of roughness and heterogeneity of the surface was directly related to the biosorption performance. Additionally,

the degree of cross-linkages formed in the alginate polymeric complex indicated by the amount of swelling by the intake of water molecules in the FVP beads is also responsible for the increased assimilation of metal ions by the beads. PP bead was slower in the uptake of Cu and Hg ions as it was smoother and had the least amount of swelling among the three FVP beads. This limited the diffusion of these ions through the pores on the bead. The binding of the ions on the surface of BP, OP and PP beads was physical in nature and thus can potentially be recovered through desorption methods requiring low energy. Biosorption of the ions was pH-dependent but the beads were effective at all drinking water pH values for the removal of divalent cations. Although an increase in the number of BP beads in cocktail solution significantly increased the percentage of ions, it also significantly decreased their biosorption capacity. Thus, optimum values of biosorbent concentration must be determined for each biosorbent for cost-effective water treatment.

The physical and chemical properties of the beads, ions to be removed, solution matrix and the environmental conditions significantly influence biosorption, and each of these parameters is unique in the various published studies. Therefore, an accurate comparison of the biosorption kinetics can only be made when experiments are performed under identical conditions. Even though the biosorption capacities of BP, OP and PP beads are non-comparable with other biosorbents, the overall usefulness of these beads is shown by their ability to remove a high percentage of metals from solution. Furthermore, the advantage of immobilising the peels was the ability to easily remove them from water by decantation, as well as their significantly higher biosorption and smaller equilibrium times relative to SA beads. Thus, FVP beads have the potential to ultimately revolutionise the treatment of drinking water in developing countries.

The aim of this research was to highlight the usefulness of a waste product such as FVP to be employed as a potential biosorbent for the removal of heavy metals from

drinking water. For this purpose, peels were collected from banana, orange and potato and immobilised on to alginate beads. A comparison of their structures and biosorption properties revealed the difference in their ability to take up heavy metals from solution under similar environmental conditions. The results of this experiment show that careful study of FVP bead surface characteristics can save both time and resources. The less useful biosorbent beads can be removed in the initial stages of screening as valuable information can be collected just by studying the structure of the biosorbents before batch biosorption experiments are performed. In this study, unmodified peels from potato have proven to be the least useful as biosorbent beads and thus modifications must be done to increase their biosorption ability.

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## Declarations

**Conflict of interest** The authors have no competing interests.

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