

Adsorption of arsenic from drinking water using natural orange waste: kinetics and fluidized bed column studies

Samra Irem, Ejazul Islam, Qaiser Mahmood Khan,
Muhammad Anwar ul Haq and Amer Jamal Hashmat

ABSTRACT

The biosorption potential of orange waste (OW) was investigated using synthetic solutions of arsenic and contaminated drinking water under different parameters, e.g. biosorbent dose, initial concentrations of solution, contact time, and pH in a batch system. The optimum conditions were identified as a contact time of 30 minutes, pH 6, biosorbent dose of 1 g L^{-1} , and initial arsenic concentration of 250 ppb. A fluidized bed column was used to study the removal of arsenic in the column. The results showed that biosorption of arsenic gave promising results in batch and continuous system, lowering the arsenic concentration down to WHO standards (10 ppb) for drinking water. The Fourier transform infrared spectra indicated that hydroxyl and carboxyl groups were major active sites for biosorption, while the results of scanning electron microscopy showed obvious changes in surface morphology of OW after the biosorption process. With 90% removal efficiency, results indicated that OW is a cost-effective and eco-friendly biosorbent and comparable to current drinking water treatment technologies. Further research is needed to get the optimum conditions for pilot-scale testing of the biosorption process by OW as well as evaluation of treated water for food quality parameters in order to commercialize the process.

Key words | arsenic removal, biosorption, drinking water treatment, fluidized bed column, orange waste

Samra Irem
Ejazul Islam (corresponding author)
Qaiser Mahmood Khan
Muhammad Anwar ul Haq
Amer Jamal Hashmat
Environmental Biotechnology Division,
National Institute for Biotechnology and Genetic
Engineering (NIBGE),
Faisalabad 38000,
Pakistan
E-mail: ejazulislam75@yahoo.com

INTRODUCTION

Around the globe, arsenic is a naturally occurring metalloid (Iriel *et al.* 2015) and being part of the earth's crust, it causes contamination of water resources. Contamination of drinking water with arsenic is a serious issue due to its toxicity and carcinogenicity (Yazdani *et al.* 2016) and it is well known that continuous exposure to low arsenic concentrations can lead to chronic diseases (Zhang *et al.* 2013). Due to its high toxicity and carcinogenicity arsenic is considered a class 1 toxicant and the World Health Organization has set a permissible limit of 10 ppb in drinking water. Arsenic exposure has been linked with a high risk of malignant arsenical skin lesions (Brahman *et al.* 2016), diabetes mellitus, and carcinomas in humans. Chronic exposure can disrupt several biological processes of the

body and can cause severe effects on the body's organs, mainly the liver. Furthermore, alteration of growth factor, suppression of proteins involved in cell cycle checkpoints, and disruption of the DNA methylation and repair system are major pathways that are mainly affected by arsenic toxicity (Kumar *et al.* 2015).

Arsenic contamination of water resources occurs due to natural as well as anthropogenic activities (Islam *et al.* 2015; Yazdani *et al.* 2016) as arsenic is used in different industries. Natural geochemical processes, use of arsenic-containing pesticides, irrigation with contaminated water, and fertilization with municipal solid wastes are major entry points of arsenic into the food chain (Finnegan & Chen 2012). Depending on the redox environment, arsenic mainly

exists in two oxidation states in water known as arsenate(V) and arsenite(III) (Zhang & Gao 2013). In Pakistan, soil and water resources of different regions have substantially high concentrations of arsenic (Brahman *et al.* 2016). In Sindh province, the groundwater arsenic concentration has reached up to 1,100 µg/L against the permissible limit of the World Health Organization (10 µg/L) for drinking water. Moreover, about 20% of the population in Punjab province and 36% of the population in Sindh province is exposed to arsenic contamination above the prescribed limits of the World Health Organization (Haque *et al.* 2007). In order to ensure the use of safe drinking water and to meet water quality standards there is an urgent need to develop a new treatment system that can efficiently remove arsenic from drinking water.

A number of treatment methods are known to eradicate metals from water. For the removal of arsenic from drinking water, adsorption is emerging as a useful technology keeping in considerations the cost, availability, simplicity and operation of the process (Yazdani *et al.* 2016). Different bio-sorbents are used for the removal of toxic compounds from water out of which agricultural wastes are more popular due to their cost effectiveness, availability and efficiency (Paradelo *et al.* 2016). Activated carbon prepared from grape bagasse has been used as a low-cost adsorbent to remove copper from aqueous solution (Demiral & Güngör 2016). Adsorption using cashew nut shell showed 92.55% removal efficiency for the adsorption of arsenic(III) in a three-phase fluidized bed reactor (Dora *et al.* 2013). Pakistan is a citrus-producing country, producing 95% of the *Citrus reticulata* variety (mandarin orange) and orange waste (OW) is freely available in huge quantities (Irem *et al.* 2013; Qureshi *et al.* 2014) having no other use and also causing problems of solid waste management. Therefore using this waste as a bio-sorbent will not only remove arsenic from water but also resolve the issue of waste management. Furthermore use of natural OW is safe for humans as it can be directly used for water treatment without any modifications.

In the last decade several studies were conducted to evaluate the capabilities of OW for the removal of heavy metals from water. Orange juice residue was chemically modified and its biosorption efficiency for removing the arsenic from aqueous media was evaluated at different contact times and pH after loading the gels with iron (Ghimire

et al. 2003). Saponified OW was used to study the effect of adsorbate dose, arsenic(III) concentration and contact time in a batch system (Qureshi *et al.* 2014). Chemically modified orange peel was characterized by Fourier transform infrared (FT-IR) and scanning electron microscopy (SEM) and it showed high efficiency for copper(II) removal from aqueous solution in a batch system (Feng *et al.* 2009). Similarly removal of cadmium by OW revealed that the process is highly dependent on pH and maximum removal was observed at pH 6 (Pérez-Marín *et al.* 2007). In another study Schiewer & Iqbal (2010) reported that the hydroxyl and carboxyl groups of orange peel are responsible for cadmium removal from aqueous media. In adsorption-based water treatment processes, batch and fixed bed column systems are most commonly used. However, in fixed bed columns, the process encounters several problems such as channeling, development of dead zones, improper mixing, temperature gradient and clogging. So, fluidized bed reactors are being widely tested for upscaling of the treatment process to avoid these problems and for the efficient removal of pollutants (Bello *et al.* 2016). In a fluidized bed reactor the static solid particles behave as fluid as they are suspended by the velocity of the passing fluid (Khan *et al.* 2014). Uniform mixing, low operational cost, higher rate for mass transfer and resistance to system upsets are some of the key features of the fluidized bed reactor (Andalib *et al.* 2014; Ahmadi *et al.* 2015). Due to these features researchers are incorporating it in wastewater treatment, especially in biological and advanced oxidation processes. Zou *et al.* (2016) reported the effective use of a fluidized bed reactor for biological processes. Several large-scale fluidized bed bioreactors are being widely used in biological wastewater treatment for the removal of recalcitrant pollutants due to the advantages of efficient mixing and high mass transfer (Bello *et al.* 2016). Micro-grain activated carbon has been used in a fluidized bed reactor as a tertiary treatment process to remove the emerging pollutants from the discharge of a wastewater treatment plant (Mailler *et al.* 2016).

The objectives of the present work were to: (1) evaluate the efficiency of powdered OW in its natural form to remove arsenic from water in batch- and column-scale systems, (2) explain the influence of different experimental conditions such as biosorbent dose, pH, contact time, and initial arsenate concentration on arsenate sorption capacity in

order to optimize the process for treatment of contaminated drinking water, and (3) investigate the mechanism of the biosorption process using FT-IR, electron microscopy and equilibrium as well as kinetic studies.

MATERIALS AND METHODS

Chemicals/reagents

Sodium arsenate was used to prepare the stock solution (1,000 ppm) of arsenic(V) from which dilutions were prepared for working solutions using distilled water. All chemicals and reagents used in the study were of analytical grade and supplied by Merck. The pH of the solutions was maintained using 0.1 M solutions of NaOH and H₂SO₄.

Preparation of the biosorbent

OW (peel along with pulp) was collected from the local juice shop in Faisalabad, Pakistan, and thoroughly washed with tap water to remove dust and adhering particles. After washing with distilled water, the waste was oven dried at 65 °C until it attained a constant weight. Dried OW was crushed and ground by an electric ball mill and sieved through mesh #40 and #80 (corresponding to particle sizes of 425 μm and 180 μm, respectively). The sieved biomass was stored in airtight plastic jars for further use in biosorption experiments.

Characterization of biosorbent

The biosorbent was characterized using a surface area analyzer and porosimeter (ASAP-2020, Germany). The Brunauer–Emmett–Teller (BET) surface area of the OW was 0.2661 m² g⁻¹ with a micropore volume of 0.000044 cm³ g⁻¹ calculated by N₂ adsorption isotherm. Functional group identification was carried out by FT-IR (IR Prestige, SHIMADZU). SEM was used to study the surface morphology of the biosorbent before and after adsorption.

Batch- and column-scale experiments

The biosorption of arsenic was carried out in a laboratory-scale batch system and column under different parameters.

The laboratory-scale biosorption experiments were carried out in batch reactors and all experiments were conducted in triplicate. In a series of experiments, sorption capacity was determined in a batch system, over a pH range of 4–8, using biosorbent dose of 1–3 g/L, at initial arsenic concentrations in the range of 50–500 μg/L (based on our findings during a survey in a well-known arsenic-contaminated area, Manga Mandi, in the Punjab province of Pakistan) and different contact times using 100 mL solutions in Erlenmeyer flasks (250 mL). The mixture was agitated at 120 rpm at room temperature (28 ± 3 °C) for different contact times (0.5–4 h) until equilibrium was achieved. At the end of the adsorption period, samples were filtered and analyzed using atomic absorption spectroscopy (AAS) to measure the concentration of the remaining arsenic in the water. The adsorbed amount of arsenic was calculated from the concentrations in the water before and after adsorption. Water with biosorbent was used as a control while deionized water was used as a blank containing no arsenic in all experiments.

Upscaling for the biosorption of arsenic was carried out in a fluidized bed column of 1.6 cm diameter with bed length of 2.8 cm using 3 g/L of biosorbent (coarse particle size). About 4 L of water with initial arsenic concentration of 50 μg/L was allowed to pass through it at a flow rate of 50 ml/min under the natural pH of water at room temperature, until the complete exhaustion of the column occurred. Breakthrough volume was determined from the plot of volume (L) vs residual arsenic concentration (ppb).

Equilibrium and kinetic studies

The equilibrium sorption capacity of the OW biosorbent was determined using the Langmuir and Freundlich isotherm equations. The amount of solute adsorbed was determined from the following equation:

$$C_e/q_e = 1/(Q_0b) + C_e/Q_0 \quad (1)$$

where C_e is the final concentration of metal after adsorption (mg/g) and q_e is the adsorption capacity at equilibrium (μg/g). Q_0 and b are the Langmuir constants for adsorption capacity and rate of adsorption respectively and were

determined from the slope and intercept. The Freundlich equation can be written as

$$\log q_e = \log K_f + 1/n \log C_e \quad (2)$$

where C_e is the concentration of metal at equilibrium ($\mu\text{g/g}$) and q_e is the adsorption capacity at equilibrium ($\mu\text{g/g}$). K_f and n are the Freundlich constants that describe the surface affinities of the biosorbent. In order to investigate the mechanism of biosorption and influence of parameters like mass transport and chemical reaction, the experimental data have to be tested by kinetic models. The value of constants obtained from kinetic models is required for the upscaling of the process (Ncibi *et al.* 2009). For kinetic studies, the samples were analyzed at different time intervals and the change in sorption capacity was determined. The data were fitted to pseudo-second-order kinetics as expressed in Equation (3):

$$1/q_t = 1/k_2 \cdot q_e^2 + t/q_e \quad (3)$$

The plot of t versus t/q_t gives a linear relationship from which q_e , K and h can be determined from the slope and intercept, respectively. All graphical work was carried out in MS-Excel 2007.

Calculation of sorption capacity and arsenic removal efficiency

The sorption capacity of OW and percentage arsenic removal were calculated using Equations (4) and (5), respectively (Akar *et al.* 2010):

$$q_e = \frac{V(C_i - C_e)}{W} \quad (4)$$

$$\% \text{removal} = \frac{C_i - C_e}{C_i} \times 100 \quad (5)$$

where q_e = uptake capacity ($\mu\text{g g}^{-1}$ of dry weight), C_i = initial concentration ($\mu\text{g L}^{-1}$), C_e = final concentration ($\mu\text{g L}^{-1}$), W = mass of the biosorbent (g), V = volume of the solution (L).

RESULTS AND DISCUSSION

Surface characterization of the biosorbent

OW mainly consists of cellulose, hemi-cellulose, pectin, limonene and many other low molecular weight compounds (Pérez-Marín *et al.* 2008). The presence of cellulose and hydroxyl and carboxyl groups plays an important part in biosorption. Surface area analysis provides the surface properties and pore volume of the material that play an important role in adsorption by banana and orange peel (Thirumavalavan *et al.* 2009). In the present study, the BET surface area and the t-plot pore volume of the biosorbent were found to be in the range of $0.0701 \text{ m}^2/\text{g}$ – $0.2661 \text{ m}^2/\text{g}$, and $-0.000035 \text{ cm}^3/\text{g}$ – $0.000044 \text{ cm}^3/\text{g}$ respectively. The very small pore volume of OW indicates the microporous structure of the biosorbent that causes the surface adsorption of larger adsorbate molecules, making transport limited through the pores (Rodríguez *et al.* 2009). Although the pore size and surface area of the orange peel was very small, it exhibited effective adsorption properties (Thirumavalavan *et al.* 2009).

FT-IR analysis

FT-IR spectroscopy is a technique used for organic structure determination of a material. It is used to get the molecular fingerprints of a sample that help to identify the unknown material and provide information about the major functional groups. FT-IR analysis of orange peel and orange peel carbon was performed by the KBr disk method and used to determine the functional groups involved in the adsorption of dye (Khaled *et al.* 2009). The shift in peaks of orange peel before and after cadmium binding was observed from FT-IR spectra to indicate the involvement of specific functional groups in metal binding (Schiewer & Iqbal 2010). In the present study, FT-IR spectra of OW before and after adsorption of arsenic were obtained using a KBr disk. The presence of absorption peaks at $3,265.49 \text{ cm}^{-1}$ indicates the presence of unsaturated, bonded O-H groups that mainly consist of phenols and alcohols. The peaks at $2,920.23$, $1,737.86$, $1,597.06$, $1,406.11$ and 773.46 cm^{-1} indicate the presence of an aromatic C-H substitution bond. A C-O stretch at

1,240.23–1,055.06 cm^{-1} can be attributed to carboxylic acids, alcohols, esters and ethers (Figure 1(a)). The results are comparable to the findings that the stretch at 3,000–2,800 cm^{-1} shows the vibration of C-H groups while peaks

at 1,130–1,000 cm^{-1} are the indication of C-O groups (Li *et al.* 2008). Peaks in the range of 1,020–1,060 cm^{-1} are due to C-O stretching, while the peaks at 2,940–2,920 cm^{-1} are due to CH_3 , CH_2 , CH , and OH groups (Thirumavalavan

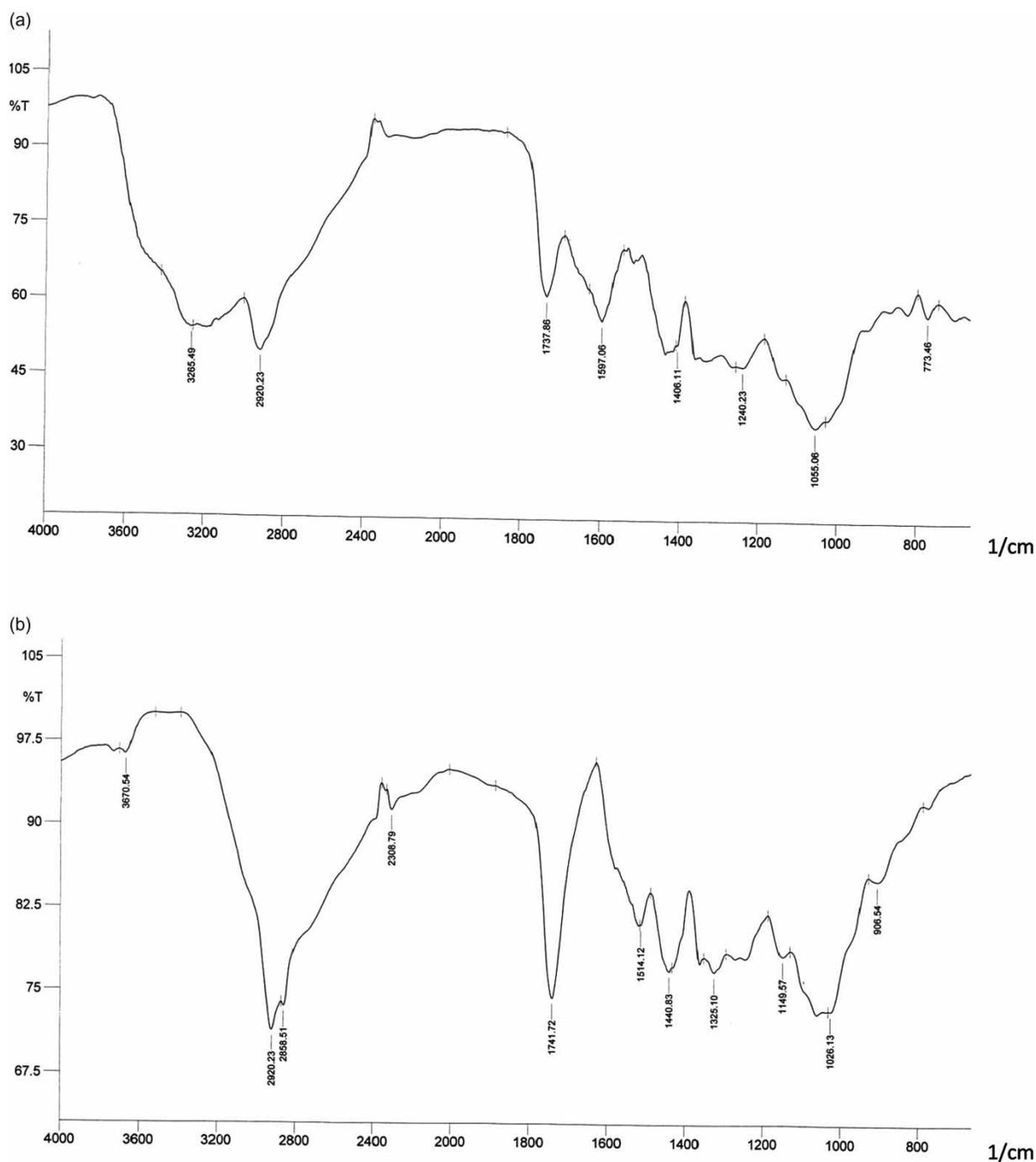


Figure 1 | FT-IR spectra of OW (a) before and (b) after adsorption of arsenic.

et al. 2009). FT-IR of OW gives a broad peak at $2,924\text{ cm}^{-1}$ which indicates the presence of C-H groups (Pérez-Marín *et al.* 2007). The bonded O-H group gives the peak at $3,859\text{--}3,698\text{ cm}^{-1}$ while the peak at $2,696\text{ cm}^{-1}$ is assigned to the C-H group (Khaled *et al.* 2009).

The comparison of OW spectra before and after adsorption of arsenic shows the significant shift in intensity and frequency range of the carboxyl and hydroxyl stretches ($1,537.8$, $1,406.1$, $1,240.2$ and $1,055.1\text{ cm}^{-1}$) and appearance of new peaks ($2,858.51$, $2,308.79$), while some peaks at 773.46 and $3,265.49\text{ cm}^{-1}$ disappeared (Figure 1(b)). The change in intensity and appearance of new peaks can be attributed to the binding of metal ions to the functional groups, while the absence of peaks indicates the involvement of chemical reactions, leading to the decomposition of chemical bonds (Schiewer & Iqbal 2010). Band shifts towards lower frequencies designate the weakening of bonds while a shift towards high frequency

is a sign of strong bonds (Gutha *et al.* 2014). The results indicate that carboxyl and hydroxyl functional groups are mainly involved in arsenic adsorption, while, besides the surface adsorption, chemisorption is also involved in the biosorption process, however, the exact mechanism of chemisorption is not known yet.

SEM analysis

SEM helps to observe the surface morphology of a specimen on micron levels and it is widely used to observe the topographic features of materials. The accumulation of arsenic on the surface of a biosorbent was studied using SEM by Baig *et al.* (2010). In the present study, the surface of the OW shows an irregular pattern with heterogeneous pores, which provides more surface area for arsenic molecules (Figure 2(a) and 2(b)). The surface is covered and looks like a multilayered structure after

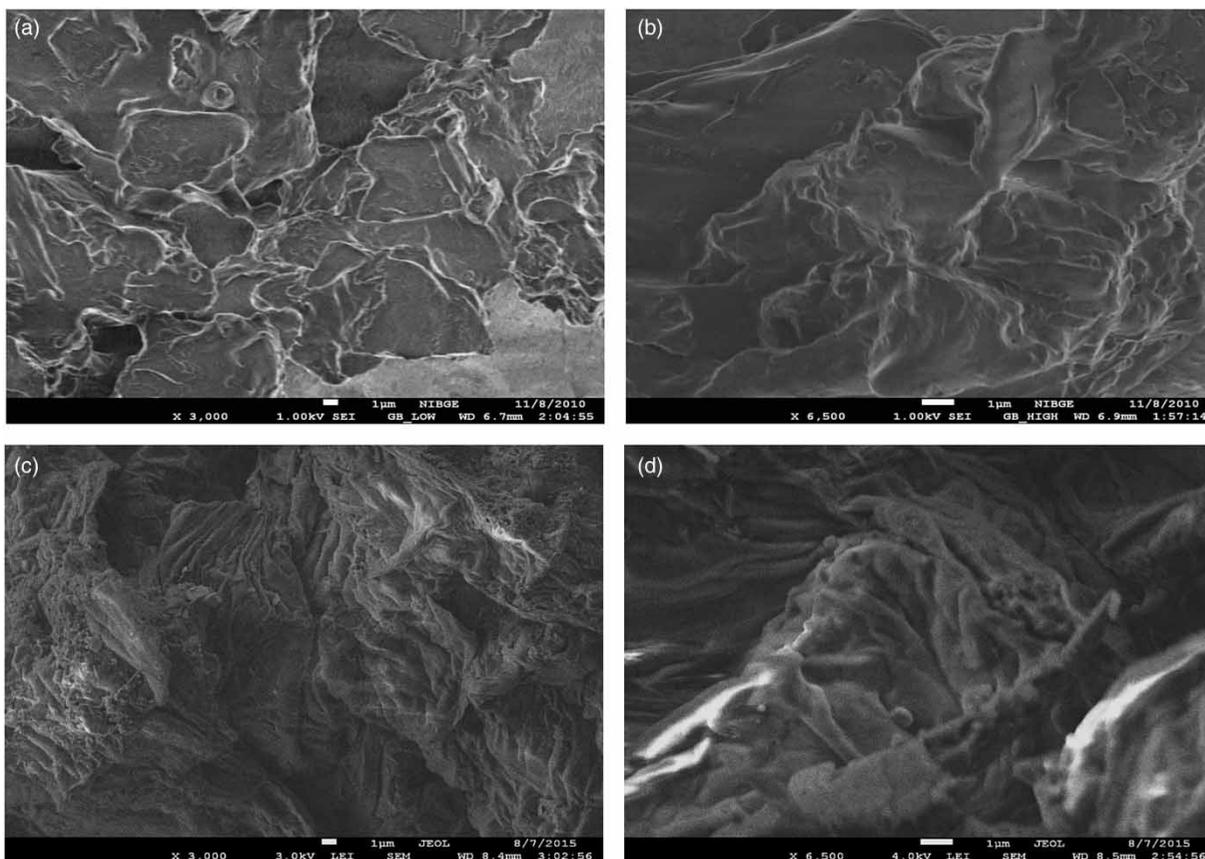


Figure 2 | SEM images of OW ((a) and (b)) before and ((c) and (d)) after biosorption of arsenic.

adsorption, indicating the incorporation of metalloids (Figure 2(c) and 2(d)). The result shows strong agreement with previous research on surface morphology. Distinct change in the surface morphology of *Lycopersicum esculentum* leaf powder has been observed after adsorption of Ni(II) ions (Gutha *et al.* 2014). The pattern of cellular arrangement in orange peel is responsible for the porosity that helps in biosorption (Lugo-Lugo *et al.* 2009). Our results are also in agreement with these findings, indicating that the OW can be used as an effective biosorbent.

Biosorption of arsenic in a batch adsorption system

Biosorption of metal is affected by different parameters such as pH, contact time, initial metal ion concentration and adsorbent dose. Change in removal efficiency at different contact times, pH, initial metal ion concentrations and adsorbent doses were studied for the adsorption of arsenic(III) using

iron oxide-coated sand by Gupta *et al.* (2005). Our preliminary studies for biosorption of arsenic by OW indicated that particle size slightly impacts the removal efficiency of arsenic in a batch system (unpublished results) but it does not exhibit any difference in column-scale experiments, indicating that spontaneous chemisorption is also involved for arsenic uptake.

Effect of contact time and biosorbent dose

Time is also an important parameter that affects the process of biosorption. Sampling at different time intervals gives an idea of how much time the process takes to reach equilibrium (Figure 3(a)). The maximum sorption capacity of OW for arsenic was found after 30 minutes of contact time with a biosorbent dose of 1 g/L (Figure 3(c)) at room temperature and pH 6. There was no difference in sorption capacity ($\mu\text{g/g}$) at contact times of 30 minutes

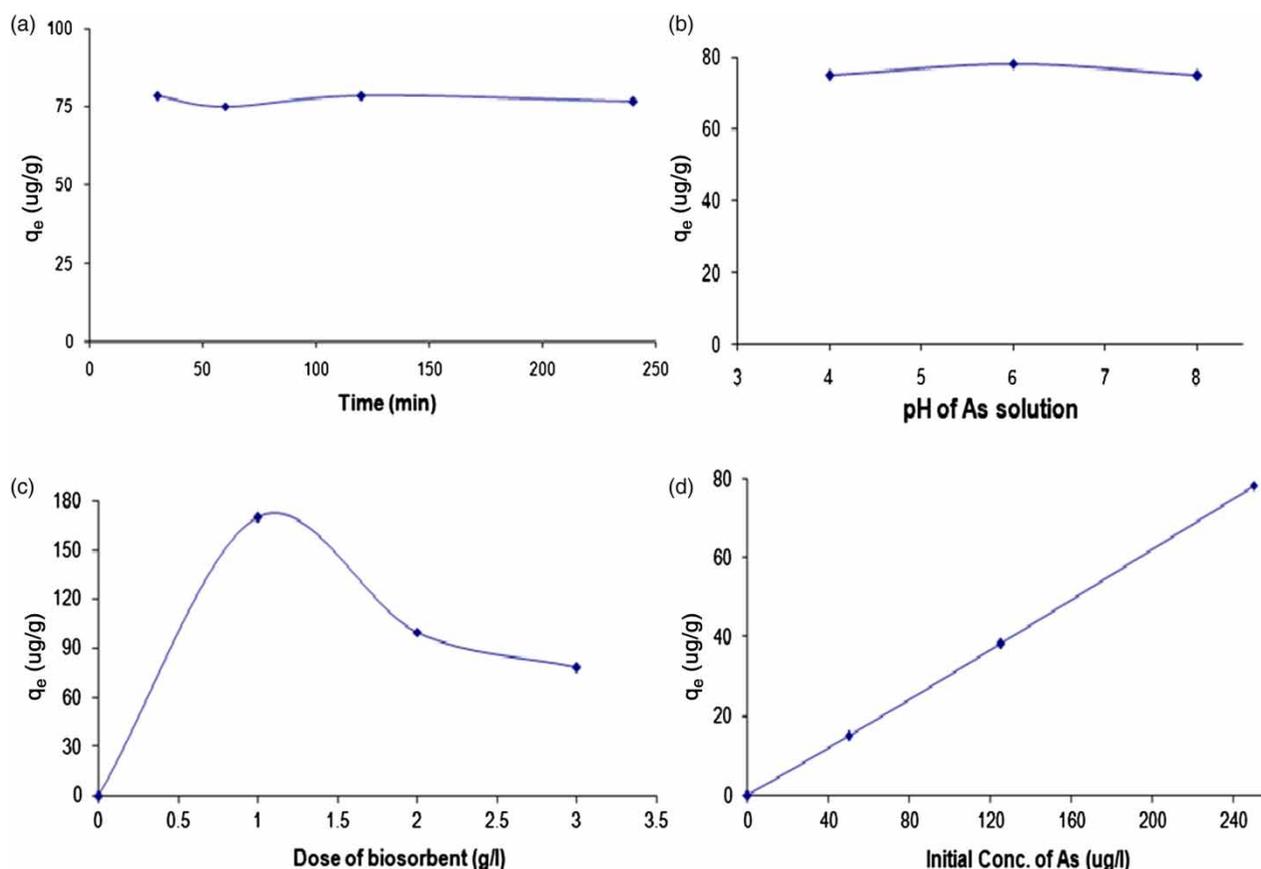


Figure 3 | Effect of (a) contact time, (b) pH, (c) biosorbent dose and (d) initial arsenic concentration on removal of arsenic.

and 120 minutes, indicating that the process attained equilibrium after 30 minutes. The results are in agreement with findings that arsenic adsorption sharply increased with contact time in the initial phase (0–20 min), and attained equilibrium in about 35 min, while negligible effect was observed on adsorption capacity after 35 minutes (Shafique et al. 2012).

Effect of pH

Initial pH of the solution plays an important role in biosorption. A pH-dependent variation in adsorption occurs due to the fact that change in pH modifies the charge of both adsorbent and adsorbate molecules leading to change in interactions among functional groups (Chen et al. 2015). There was a slight difference in the arsenic adsorption capacity of OW when tested under different pH. The optimum pH observed was 6.0 at which maximum sorption capacity was obtained, so further experiments were conducted without changing the pH of the solution as the natural pH of the arsenic solution was 6.0 at room temperature (Figure 3(b)). Furthermore, when tested with drinking water samples, the biosorbent showed similar results as shown with synthetic solutions suggesting that it can be used directly for arsenic removal from drinking water as biosorption of arsenic was less influenced by pH. The results of the present study are similar to those reported by Zhang et al. (2015). FT-IR analysis of the OW has pointed out the presence of –COOH and –OH functional groups that can be considered possible active sites for sorption of arsenic. Arsenic is able to form oxyanions and is also redox sensitive and thus its adsorption is dependent on the pH of the environment. Moreover, under acidic or near-neutral pH, As(V) is more strongly adsorbed than As(III) (Shafique et al. 2012).

Effect of initial arsenic concentration and adsorption isotherms

The initial concentration of contaminant has a strong influence on the percentage removal of the adsorbate and also helps to determine the sorption capacity of the biosorbent. In the present study, the sorption capacity of arsenic on OW showed a linear increasing trend with increase of initial arsenic concentration from 50 µg/L to 500 µg/L

(Figure 3(d)) while a decrease in sorption capacity was observed with increase in biosorbent dose from 1 g/L to 3 g/L (Figure 3(c)). A similar pattern has been observed during the biosorption of lead on modified orange peel (Lugo-Lugo et al. 2009). Adsorption of copper(II) on modified orange peel also increased with increasing initial metal concentration (Feng et al. 2009).

Modeling the behavior of the biosorption system is an important feature of modern engineering for upscaling of the process. In order to develop a good model, experimental observations, understanding of fundamental theoretical parameters and system measurements are prerequisites. For this purpose a number of adsorption isotherms are available and readily implemented to compare adsorption equilibria (Irem et al. 2013). In the present study, Langmuir and Freundlich isotherm models were used to explain the biosorption of arsenic on OW at different initial concentrations of arsenic. Values for R^2 and constants are given in Table 1 while graphical illustration is in Figure 4(c). Experimental data showed a best fit for the Freundlich isotherm and did not favor the Langmuir model, illustrating the fact that the adsorption process was not monolayer and, beside surface adsorption, chemisorption was also involved in the process, and this phenomenon is also supported by FT-IR spectra of OW after biosorption of arsenic where some new peaks appeared and some peaks disappeared (Figure 1(b)). The Freundlich equation explains the exponential expression that expects that the increase in initial concentrations of adsorbate leads to increase in adsorption on the surface of adsorbent molecules that was observed when the adsorption experiment was carried out at different initial concentrations of arsenic (Figure 3(d)). Biosorption of arsenic by *Vallisneria spiralis* plants also followed the Freundlich isotherm (Iriel et al. 2015).

Table 1 | Kinetic and equilibrium model constants for arsenic biosorption by OW

Kinetic and equilibrium models	Parameters	Arsenic
Pseudo-second-order	K_2 (g/mg min)	0.0422
	H	249.68
	q_e (µg/g)	76.92
	R^2	0.9997
Freundlich	R^2	0.998
	K_f	1.3332
	N	0.6719

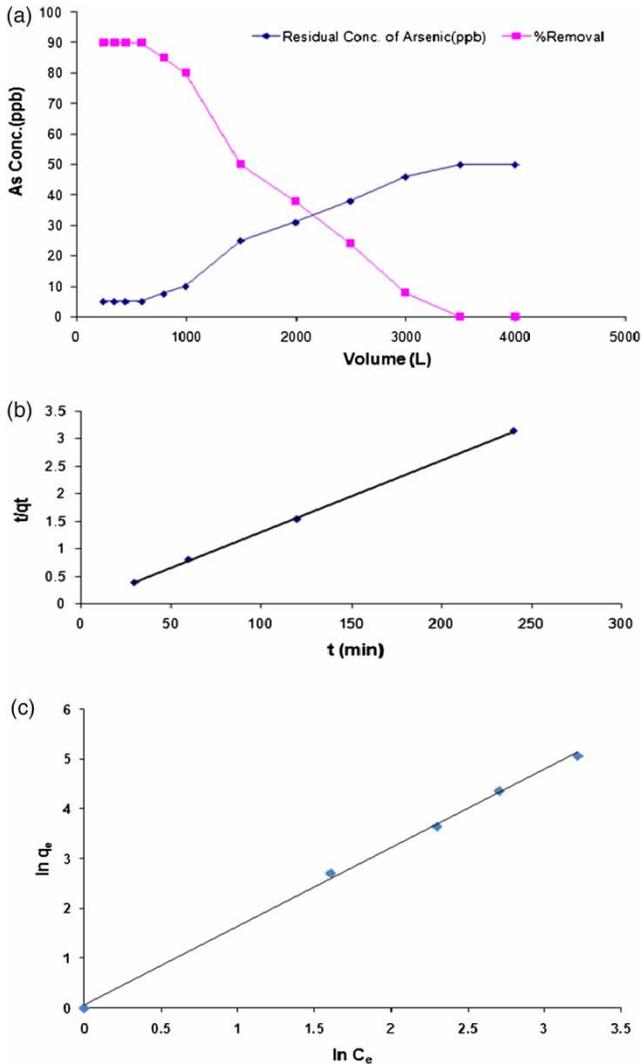


Figure 4 | Equilibrium and kinetic sorption models for arsenic: (a) breakthrough curve and removal efficiency of OW for arsenic, (b) pseudo-second-order kinetics, (c) Freundlich isotherm. C_e = final concentration of arsenic after adsorption ($\mu\text{g/g}$) and q_e = adsorption capacity at equilibrium ($\mu\text{g/g}$).

Kinetic modeling

Kinetic models such as pseudo-first-order and pseudo-second-order kinetics were used to test the experimental data to examine the mass transfer and chemical reactions of the adsorption processes. The data do not show any fit to pseudo-first-order kinetics while they give a straight line for pseudo-second-order kinetics with $R^2 = 0.999$ (Table 1 and Figure 4(b)). The similarity of calculated and experimental adsorption capacities supported the good correlation of the data with the pseudo-second-order model and it implied that chemical

adsorption between As(V) and OW was the rate-limiting step of the process. Similar results have been observed for biosorption of arsenic on pine leaves (Shafique *et al.* 2012; Brahman *et al.* 2016).

Column studies for biosorption of arsenic

Column-scale studies for the biosorption process are required in order to develop a feasible technique for commercial and large-scale application. The column-scale approach has been used for effective removal of arsenic(III) using iron-oxide coated sand as a biosorbent (Gupta *et al.* 2005). Similarly the effect of different parameters on arsenic removal has been investigated in a column study using plant biomass as an adsorbent (Kamala *et al.* 2005). Arsenic removal efficiency and the breakthrough curve for biosorption of arsenic by OW is shown in Figure 4(a).

The fluidized bed column was found to be highly efficient at removing the arsenic and was comparable to that observed in batch experiments (90%) for 0.6 L solutions and reached a breakthrough point at 1 L. The column studies showed promising results giving 50% removal efficiency up to 2 L treated volume and reached exhaustion point after treating 4 L solutions. It could be due to the fact that initially the adsorbent was fresh and all the active sites were available for metal binding and not a single ion escaped from the column. However, as time passed, the functional groups were occupied by metal ions and some of the metal ions started escaping the column leading towards the exhaustion of biosorbent. Being low cost and nontoxic, and having outstanding adsorption capacity and biocompatibility make OW a cost-effective and eco-friendly biosorbent and comparable to the current drinking water treatment technologies. Further research is needed to get the optimum conditions for pilot-scale testing of the biosorption process by OW as well as evaluation of treated water for food quality parameters in order to commercialize the process.

CONCLUSIONS

- OW was found to be a low cost and abundantly available biosorbent for removing arsenic from contaminated water.
- The decrease of arsenic concentrations in water after adsorption in a fluidized bed column met the WHO

standard (10 µg/L) with a flow rate of 50 ml/min under the natural pH of the water at room temperature.

- FT-IR spectra of the biosorbent before and after adsorption indicated that carboxylic and hydroxyl groups are the major active sites involved in metal removal, while SEM confirmed the adsorption process showing obvious changes in surface morphology.
- The removal of arsenic by OW was independent of most of the parameters with the exception of initial arsenic concentration and can be safely used for drinking water treatment.

ACKNOWLEDGEMENTS

The study was financially supported by a grant (No. 1887) from the Higher Education Commission of Pakistan. The authors are greatly thankful to the Institute of Chemical Engineering, University of the Punjab, Pakistan, for FT-IR analysis and the Nano-biotechnology group, National Institute for Biotechnology and Genetic Engineering (NIBGE), Faisalabad, for SEM analysis of the OW samples.

REFERENCES

- Ahmadi, M., Ramavandi, B. & Sahebi, S. 2015 Efficient degradation of a biorecalcitrant pollutant from wastewater using a fluidized catalyst-bed reactor. *Chemical Engineering Communications* **202**, 1118–1129.
- Akar, T., Celik, S. & Akar, S. T. 2010 Biosorption performance of surface modified biomass obtained from *Pyracantha coccinea* for the decolorization of dye contaminated solutions. *Chemical Engineering Journal* **160** (2), 466–472.
- Andalib, M., Elbeshbishy, E., Mustafa, N., Hafez, H., Nakhla, G. & Zhu, J. 2014 Performance of an anaerobic fluidized bed bioreactor (AnFBR) for digestion of primary municipal wastewater treatment biosolids and bioethanol thin stillage. *Renewable Energy* **71**, 276–285.
- Baig, J. A., Kazi, T. G., Shah, A. Q., Kandhro, G. A., Afridi, H. I., Khan, S. & Kolachi, N. F. 2010 Biosorption studies on powder of stem of *Acacia nilotica*: removal of arsenic from surface water. *Journal of Hazardous Materials* **178**, 941–948.
- Bello, M. M., Raman, A. A. A. & Purushothaman, M. 2016 Applications of fluidized bed reactor in wastewater treatment – a review of the major design and operational parameters. *Journal of Cleaner Production* **141**, 1492–1514.
- Brahman, K. D., Kazi, T. G., Baig, J. A., Afridi, H. I., Arain, S. S., Saraj, S., Arain, M. B. & Arain, S. A. 2016 Biosorptive removal of inorganic arsenic species and fluoride from aqueous medium by the stem of *Tecomella undulate*. *Chemosphere* **150**, 320–328.
- Chen, M. L., Sun, Y., Huo, C. B., Liu, C. & Wang, J. H. 2015 Akaganeite decorated graphene oxide composite for arsenic adsorption/removal and its preconcentration at ultra-trace level. *Chemosphere* **130**, 52–58.
- Demiral, H. & Güngör, C. 2016 Adsorption of copper(II) from aqueous solutions on activated carbon prepared from grape bagasse. *Journal of Cleaner Production* **124**, 103–113.
- Dora, T. K., Mohanty, Y. K., Roy, G. K. & Sarangi, B. 2013 Adsorption studies of As(III) from wastewater with a novel adsorbent in a three-phase fluidized bed by using response surface method. *Journal of Environmental Chemical Engineering* **1**, 150–158.
- Feng, N., Guo, X. & Liang, S. 2009 Adsorption study of copper (II) by chemically modified orange peel. *Journal of Hazardous Materials* **164** (2–3), 1286–1292.
- Finnegan, P. & Chen, W. 2012 Arsenic toxicity: the effects on plant metabolism. *Frontiers in Physiology* **3**, article 182.
- Ghimire, K. N., Inoue, K., Yamaguchi, H., Makino, K. & Miyajima, T. 2003 Adsorptive separation of arsenate and arsenite anions from aqueous medium by using orange waste. *Water Research* **37** (20), 4945–4953.
- Gupta, V. K., Saini, V. K. & Jain, N. 2005 Adsorption of As(III) from aqueous solutions by iron oxide-coated sand. *Journal of Colloid and Interface Science* **288** (1), 55–60.
- Gutha, Y., Munagapati, V. S., Naushad, M. & Abburi, K. 2014 Removal of Ni(II) from aqueous solution by *Lycopersicon esculentum* (tomato) leaf powder as a low-cost biosorbent. *Desalination and Water Treatment* **54** (1), 200–208.
- Haque, I., Nabi, D. & Hayat, W. 2007 Groundwater arsenic contamination – a multi directional emerging threat to water scarce areas of Pakistan. In: *6th International IAHS Groundwater Quality Conference, held in Fremantle, Western Australia*, IAHS Publication 324, pp. 24–30.
- Irem, S., Mahmood Khan, Q., Islam, E., Jamal Hashmat, A., Anwar ul Haq, M., Afzal, M. & Mustafa, T. 2013 Enhanced removal of reactive navy blue dye using powdered orange waste. *Ecological Engineering* **58**, 399–405.
- Iriel, A., Lagorio, M. G. & Cirelli, A. F. N. 2015 Biosorption of arsenic from groundwater using *Vallisneria gigantea* plants: kinetics, equilibrium and photophysical considerations. *Chemosphere* **138**, 383–389.
- Islam, E., Khan, M. T. & Irem, S. 2015 Biochemical mechanisms of signaling: perspectives in plants under arsenic stress. *Ecotoxicology and Environmental Safety* **114**, 126–133.
- Kamala, C. T., Chu, K. H., Chary, N. S., Pandey, P. K., Ramesh, S. L., Sastry, A. R. K. & Sekhar, K. C. 2005 Removal of arsenic (III) from aqueous solutions using fresh and immobilized plant biomass. *Water Research* **39**, 2815–2826.
- Khaled, A., El Nemr, A., El-Sikaily, A. & Abdelwahab, O. 2009 Treatment of artificial textile dye effluent containing Direct

- Yellow 12 by orange peel carbon. *Desalination* **238** (1–3), 210–232.
- Khan, M. J. H., Hussain, M. A., Mansourpour, Z., Mostoufi, N., Ghasem, N. M. & Abdullah, E. C. 2014 CFD simulation of fluidized bed reactors for polyolefin production – a review. *Journal of Industrial and Engineering Chemistry* **20**, 3919–3946.
- Kumar, S., Dubey, R. S., Tripathi, R. D., Chakrabarty, D. & Trivedi, P. K. 2015 Omics and biotechnology of arsenic stress and detoxification in plants: current updates and prospective. *Environment International* **74**, 221–230.
- Li, X., Tang, Y., Cao, X., Lu, D., Luo, F. & Shao, W. 2008 Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **317** (1–3), 512–521.
- Lugo-Lugo, V., Hernández-López, S., Barrera-Díaz, C., Ureña-Núñez, F. & Bilyeu, B. 2009 A comparative study of natural, formaldehyde-treated and copolymer-grafted orange peel for Pb(II) adsorption under batch and continuous mode. *Journal of Hazardous Materials* **161** (2–3), 1255–1264.
- Mailler, R., Gasperi, J., Coquet, Y., Buleté, A., Vulliet, E., Deshayes, S., Zedek, S., Mirande-Bret, C., Eudes, V., Bressy, A., Caupos, E., Moilleron, R., Chebbo, G. & Rocher, V. 2016 Removal of a wide range of emerging pollutants from wastewater treatment plant discharges by micro-grain activated carbon in fluidized bed as tertiary treatment at large pilot scale. *Science of the Total Environment* **542** (Part A), 983–996.
- Ncibi, M. C., Mahjoub, B., Seffen, M., Brouers, F. & Gaspard, S. 2009 Sorption dynamic investigation of chromium(VI) onto *Posidonia oceanica* fibres: kinetic modelling using new generalized fractal equation. *Biochemical Engineering Journal* **46** (2), 141–146.
- Paradelo, R., Cutillas-Barreiro, L., Soto-Gómez, D., Nóvoa-Muñoz, J. C., Arias-Estévez, M., Fernández-Sanjurjo, M. J., Álvarez-Rodríguez, E. & Núñez-Delgado, A. 2016 Study of metal transport through pine bark for reutilization as a biosorbent. *Chemosphere* **149**, 146–153.
- Pérez-Marín, A. B., Zapata, V. M., Ortuño, J. F., Aguilar, M., Sáez, J. & Lloréns, M. 2007 Removal of cadmium from aqueous solutions by adsorption onto orange waste. *Journal of Hazardous Materials* **139** (1), 122–131.
- Pérez-Marín, A. B., Ballester, A., González, F., Blázquez, M. L., Muñoz, J. A., Sáez, J. & Zapata, V. M. 2008 Study of cadmium, zinc and lead biosorption by orange wastes using the subsequent addition method. *Bioresource Technology* **99** (17), 8101–8106.
- Qureshi, K., Mangi, Y. H., Mangi, F. H., Mangi, K. H. & Samo, S. R. 2014 Surface adsorption study of saponified orange waste gel for arsenic (III) removal. *Engineering, Science & Technology* **13** (2), 54–58.
- Rodríguez, A., García, J., Ovejero, G. & Mestanza, M. 2009 Adsorption of anionic and cationic dyes on activated carbon from aqueous solutions: equilibrium and kinetics. *Journal of Hazardous Materials* **172** (2–3), 1311–1320.
- Schiewer, S. & Iqbal, M. 2010 The role of pectin in Cd binding by orange peel biosorbents: a comparison of peels, depectinated peels and pectic acid. *Journal of Hazardous Materials* **177** (1–3), 899–907.
- Shafique, U., Ijaz, A., Salman, M., uz Zaman, W., Jamil, N., Rehman, R. & Javaid, A. 2012 Removal of arsenic from water using pine leaves. *Journal of the Taiwan Institute of Chemical Engineers* **43** (2), 256–263.
- Thirumavalavan, M., Lai, Y. L., Lin, L. C. & Lee, J. F. 2009 Cellulose-based native and surface modified fruit peels for the adsorption of heavy metal ions from aqueous solution: Langmuir adsorption isotherms. *Journal of Chemical & Engineering Data* **55** (3), 1186–1192.
- Yazdani, M., Tuutijärvi, T., Bhatnagar, A. & Vahala, R. 2016 Adsorptive removal of arsenic(V) from aqueous phase by feldspars: kinetics, mechanism, and thermodynamic aspects of adsorption. *Journal of Molecular Liquids* **214**, 149–156.
- Zhang, M. & Gao, B. 2013 Removal of arsenic, methylene blue, and phosphate by biochar/AlOOH nanocomposite. *Chemical Engineering Journal* **226**, 286–292.
- Zhang, M., Gao, B., Varnoosfaderani, S., Hebard, A., Yao, Y. & Inyang, M. 2013 Preparation and characterization of a novel magnetic biochar for arsenic removal. *Bioresource Technology* **130**, 457–462.
- Zhang, Z., Liu, J., Cao, X., Luo, X., Hua, R., Liu, Y., Yu, X., He, L. & Liu, Y. 2015 Comparison of U(VI) adsorption onto nanoscale zero-valent iron and red soil in the presence of U(VI)–CO₃/Ca–U(VI)–CO₃ complexes. *Journal of Hazardous Materials* **300**, 633–642.
- Zou, G., Papirio, S., Lakaniemi, A.-M., Ahoranta, S. H. & Puhakka, J. A. 2016 High rate autotrophic denitrification in fluidized-bed biofilm reactors. *Chemical Engineering Journal* **284**, 1287–1294.

First received 4 August 2016; accepted in revised form 4 January 2017. Available online 1 February 2017