

Adsorption studies for the simultaneous removal of arsenic and selenium using naturally prepared adsorbent materials

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Abstract The adsorption properties of eggshell membranes (ESM), eggshells (ES) and orange peels (OP) were studied for the removal of arsenic (total As) and selenium (total Se). The effect of chemical treatment of these adsorbents by HNO_3 and NaOH was also investigated using Fourier transform infrared spectroscopy (FT-IR). Analysis of the FT-IR spectra showed that treatment with NaOH and HNO_3 had an effect on the functional groups present in the materials and also on the adsorption by extension. Thermal analysis showed that ES were more thermally stable than the others with no water molecules in their matrix, which could have caused a substantial weight loss at around 70 °C. In terms of adsorption capacities, chemical treatment increased the adsorption capacities of ESM and OP achieving up to $170 \mu\text{g g}^{-1}$ (As) and $160 \mu\text{g g}^{-1}$ (Se), and $120 \mu\text{g g}^{-1}$ (As) and $70 \mu\text{g g}^{-1}$ (Se), respectively, with not much activity for ES in terms of adsorption. The two adsorbents (NaOH -treated OP and ESM) were then tested in environmental water samples and the results showed that 68.9 % of As and 74.8 % of Se, and 54.1 % of As and 47.3 % of Se were removed from domestic wastewater samples investigated using OP and ESM, respectively. Moreover, better selectivities towards the compounds of interest were achieved.

Keywords Eggshell · Eggshell membranes · Orange peels · Oxyanions

Introduction

Trace metal contamination of most water sources has intensified the effect of the scarcity of safe/potable water for human consumption (Richardson 2001; Richardson and Ternes 2011; Chen and An 2012; Kamsonlian et al. 2012; Igwe et al. 2008). Arsenic and selenium have been identified as two of the most toxic trace metals and are found in most aqueous environments with deficiencies closely associated with toxic levels (Peak 2006; Li et al. 2012; Jain and Ali 2000; Hamilton 2004). Through various mechanisms, these trace metals tend to leach into groundwater environments and they also find their way into wastewater treatment systems where they receive minimal attention in terms of treatment (Haque and Johannesson 2006; Mistry et al. 2012). Their toxicity increases from the bottom to the top of the food chain, due to their ability to bio-magnify in organisms and up along the various trophic levels of the food chain. The World Health Organisation (WHO) has recommended the maximum contaminant level (MCL) of $10 \mu\text{g l}^{-1}$ for total arsenic and $40 \mu\text{g l}^{-1}$ for total selenium in drinking water (World Health Organisation 2008). However, for wastewater effluents, the recommended MCL is $100 \mu\text{g l}^{-1}$ for both As and Se (Jain and Ali 2000).

Adsorption is one of the methods that has been recommended for the removal of metals present in water matrices (Li et al. 2012; Babel and Kurniawan 2003; Chen and An 2012). However, though it may be perceived as the easiest process, challenges such as low adsorption capacities, high capital costs, possibility of back-contamination by the adsorbent and the generation of highly contaminated sludge still call for more research to be done to improve the water treatment technologies (Li et al. 2012; Banerjee et al. 2008; Manna and Ghosh 2007; Feng et al. 2009).

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Arsenic and selenium adsorption has been well studied (Jain and Ali 2000; Ladeira and Ciminelli 2004; Bleiman and Mishael 2010; Liu et al. 2012; González et al. 2011; Tian et al. 2011; Yigit et al. 2012; Chen and An 2012); however, the use of low-cost materials in these studies has been minimal, thus making the treatment procedures too expensive or inapplicable to environmental water treatment systems, especially in the developing communities (Zhang et al. 2010). The adsorbents that have been used include activated alumina (Hung et al. 2004), hydrous cerium oxide nanoparticles (Li et al. 2012), magnetic wheat straw (Tian et al. 2011), granular ferric hydroxide (Banerjee et al. 2008) and hydrous stannic oxide (Manna and Ghosh 2007). However, some other remediation techniques such as coagulation and filtration, lime softening and ion-exchange resins amongst others have also been studied (Litter et al. 2010).

Low-cost adsorbents such as agricultural wastes and other plant materials have the potential of removing different types of pollutants present in water. Adsorbents such as peanut husks (Ngah and Hanafiah 2008), orange peels (Feng et al. 2009; Dhakal et al. 2005; Lasheen et al. 2012; Yigit et al. 2012) and eggshell membranes (Cheng et al. 2011; Zhang et al. 2010) can be used for the adsorption of toxic materials from water, such as copper, cadmium, lead, nickel and zinc, amongst others. Eggshell membranes and orange peels are abundantly available with the eggshell membranes being available throughout the year whilst the orange peels are seasonal, yet the output when in season is too high to ignore. Latest studies showed that dehydrated aquatic plants (Deng et al. 2013) and spent coffee grains (Cerino-Córdova et al. 2013) could also be used as low-cost adsorbents. Utilising such materials is desirable for providing cheap techniques suitable for the removal of contaminants present in water (Abdel et al. 2011; Love and Thatcher 1953).

Eggshells (ES), eggshell membranes (ESM) and orange peels (OP) have been found to have various functional groups, which would possibly favour the adsorption of negatively charged species (Feng and Guo 2012; Tsai et al. 2006). Eggshells have been found to have mainly carbonyl functionality, whilst eggshell membranes have $-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$ and a high surface area to boost their adsorption abilities in addition to the carbonyl functional group (Tsai et al. 2006). On the other hand, orange peels are mainly composed of hemicellulose, pectin and lignin, and contain the functional groups $-\text{COOH}$, $-\text{COOCH}_3$, $-\text{COO}-$, $-\text{OH}$ (Feng et al. 2009; Feng et al. 2011). All these functional groups play a part in the shaping of the adsorption sites to suit the 'needs' of the adsorbate under study.

The work presented here was conducted at the Department of Applied Chemistry, University of Johannesburg, between the period covering February to July 2012 and it

investigates the simultaneous adsorption of the highly toxic arsenic and selenium trace metals using ES, ESM and OP as low-cost adsorbents. The work also focuses on the effect of chemical treatment on the adsorption using only HNO_3 and NaOH . To the best of our knowledge, no such study has been carried out and reported elsewhere with regard to the use of these adsorbents for the simultaneous removal of As and Se.

Materials and methods

Chemicals

Nitric acid (65 %), hydrochloric acid (32 %), sodium hydroxide, arsenic powder and selenium metal were supplied by Merck (Darmstadt, Germany), and they were all of analytical grade (AR) and were used as supplied without any further purification. Deionised water ($18.4 \text{ M}\Omega$ conductivity) was obtained from an in-house reverse osmosis system and was used for most dilutions and the preparation of standards.

Instrumentation

The determination of metal concentrations was performed with inductively coupled plasma optical emission spectroscopy (ICP-OES) (Wirsam Scientific, GBC Quantima Series ICP connected to a GBC SDS 720 autosampler). Scanning electron microscope (SEM) analyses were carried out using SEM (Tescan) to determine the surface morphology of the materials, whilst Thermo Scientific (Nicolet IS 10) Fourier transform infrared (FT-IR) spectroscopy was used for functional group characterisation. The thermogravimetric analysis was performed using a PerkinElmer TGA 400.

Chemical modification of adsorbents

Eggs and oranges were bought from local supermarkets around the City of Johannesburg, South Africa. Albumin (egg white) and egg yolk were removed from the eggs, and then the shells were rinsed 5 times with deionised water. The eggshell and eggshell membranes were separated by hand, and thereafter dried in an oven at 80°C , and then ground and sieved through a 45 mesh. The oranges were peeled, diced and oven-dried at 80°C overnight, and then ground and sieved through a 45 mesh. These adsorbents were then sonicated in 0.1 M HNO_3 to remove any As and Se that could be present, and rinsed with deionised water until a pH of 7 was attained.

The adsorbents were further treated with 0.05 M HNO_3 and 0.05 M NaOH overnight, filtered and repeatedly rinsed with deionised water until a pH of 7 was attained. To

ascertain the quality of adsorbents after chemical modification, these adsorbents were then analysed by FT-IR to track the functional group changes in the treated and untreated adsorbents.

Batch adsorption experiments

Batch adsorption experiments were carried out by mixing 0.5 g of adsorbent in a 100 ml solution containing As and Se in the desired concentration at a temperature of 25 °C for 2 h, and shaking the mixture. The effects of pH on desorption were investigated in the pH range of 4–11. Adsorption isotherm experiments were performed at 25 °C by using 0.5 g of adsorbent in 100 ml solution of varying concentrations of As and Se (150 and 800 $\mu\text{g l}^{-1}$). The effect of contact time on the adsorption capacity was studied by varying the exposure time from 10 min to 300 min and kinetic modelling was then used to evaluate the generated data. After every adsorption or desorption experiment, the solutions were filtered using 0.45- μm porous membrane filters and the residue was analysed for As and Se using ICP-OES, and adsorption capacity (AC) was calculated using:

$$AC = (C_0 - C_f) \frac{V}{m}$$

where C_0 is the initial concentration; C_f is the final concentration after adsorption; V is the sample volume (l); m is the mass of adsorbent (g).

All adsorption and desorption experiments were done in triplicate and the average values were reported.

Desorption and regeneration tests

To study the possible reuse of these adsorbents, desorption studies and regeneration tests were performed. Two desorption reagents, NaOH and HNO_3 , were investigated. The As/Se-loaded adsorbents were filtered and transferred to a stoppered conical flask with 100 ml of 0.1 M NaOH and HNO_3 , then sonicated, and filtered again and the residue determined for the amount of As and Se present. For reuse, the adsorbents were washed using deionised water until a constant pH of 7 was reached.

Results and discussion

Materials characterisation

Surface characterisation

In adsorption, either batch or column, the surface morphology of the adsorbent plays a significant role in the

adsorption process. The surface texture and morphology of ESM, ES and OP were found to differ from one another, as shown in Fig. 1, with OPs showing a more fibrous surface than ESM, whilst ES shows a more uniform fibre-free surface. Although the surface areas of OPs were very fibrous, their structure was found to be more regular than the highly irregular yet fibrous surface structure of the ESM. This could either enhance the surface area for adsorption or have an effect on the adsorption sites for As and Se.

Fourier transform infrared (FT-IR)

The presence or absence of certain functional groups in adsorbents does play a major role in the adsorption of different adsorbates (Abdel et al. 2011). In this study, FT-IR spectroscopy was used to determine the type of functional groups present in each adsorbent used and also to follow the chemical modification of the adsorbents using both NaOH and HNO_3 as presented in Fig. 2. The untreated adsorbents showed a constitution of functional groups with distinct differences amongst the three adsorbents. OPs showed a broad peak at 3 309 cm^{-1} , which could be associated with the highly dense –OH functionality of the hemicellulose, pectin and water molecules. The peak at 2,919 cm^{-1} could be a result of the C–H stretching vibrations of –CH₃, –CH₂ and –CH, and the peak at 1,737 cm^{-1} shows the presence of C=O of ketones or aldehydes and amides. The peaks at 1,607 and 1,418 cm^{-1} are as a result of the presence of C=C of arenes possibly from the presence of limonene and $\alpha\text{-CH}_3$, respectively. However, the ES only showed a broad band at 1,500 cm^{-1} signifying the presence of carbonates and amides, and a few other peaks in the fingerprint region. ESM has amides, amines, carbonates and carboxylic acids as evidenced by the presence of peaks at 3,285, 2,352, 1,631 and 1,418 cm^{-1} .

The modifications of these adsorbents were also evident from the emergence of new peaks or the disappearance of old peaks signifying the modification of functional groups, and hence a possibility of an improvement in the adsorption kinetics or capacity. Treatment of OPs with NaOH mainly resulted in the shift in infrared absorbance of these materials. The peaks at 746, 1,005, 1,418, 1,607 and 1,737 cm^{-1} disappeared and shifted to 766, 1,002, 1,414, 1,614 and 1,732 cm^{-1} , respectively. The peak at 1,645 cm^{-1} disappeared and the peak at 1,605 cm^{-1} appeared instead. This shows the modification of C=O into C=C or the modification of the amides to amines. In addition, it was observed that the peak at 1,229 cm^{-1} due to C–N disappeared. When treated with HNO_3 , OPs showed a shift in the peak position, from 1,606 to 1,645 cm^{-1} and the peak at 1,732 cm^{-1} due to C=O was



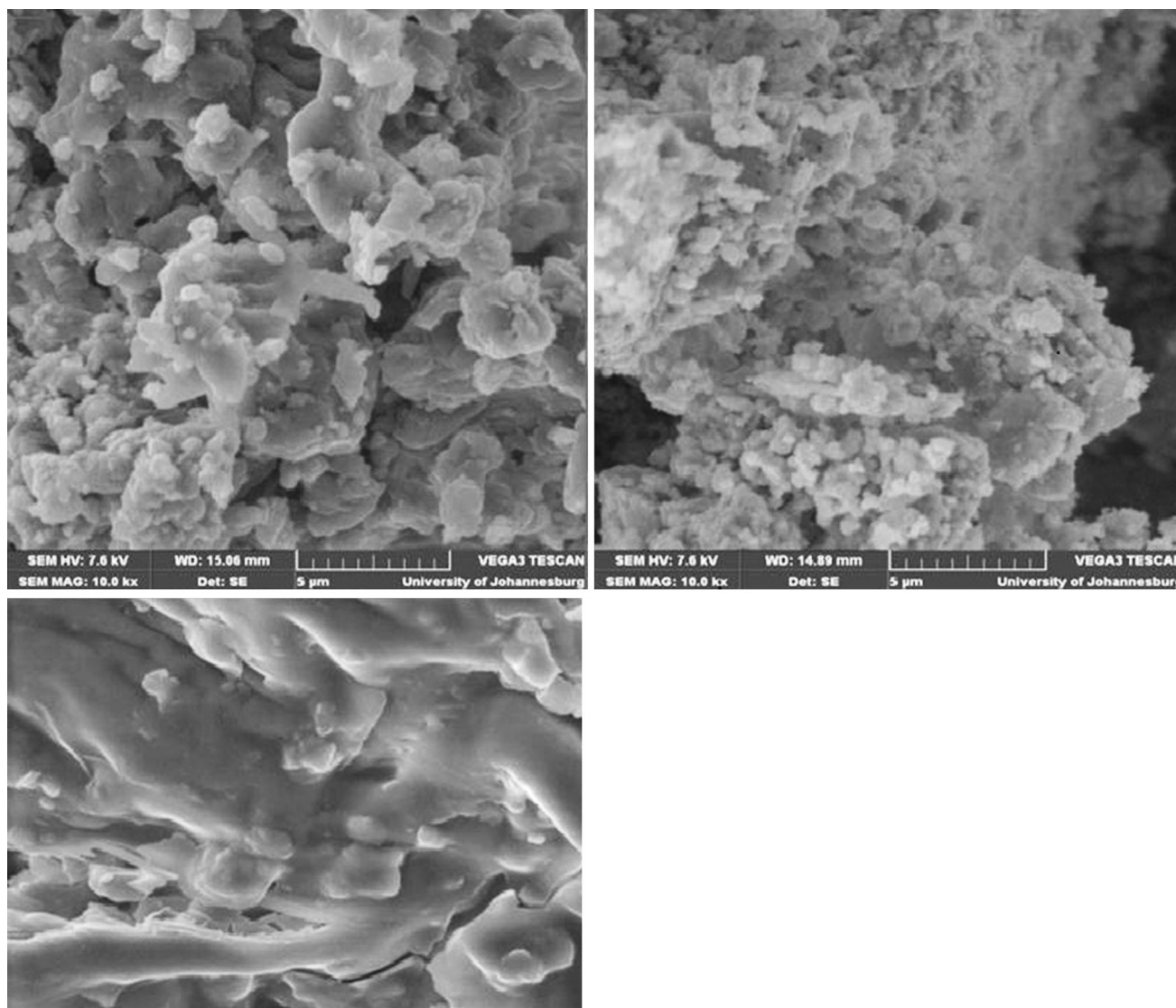


Fig. 1 Scanning electron: micrographs showing the surface texture and morphology of ESM, ES and OP

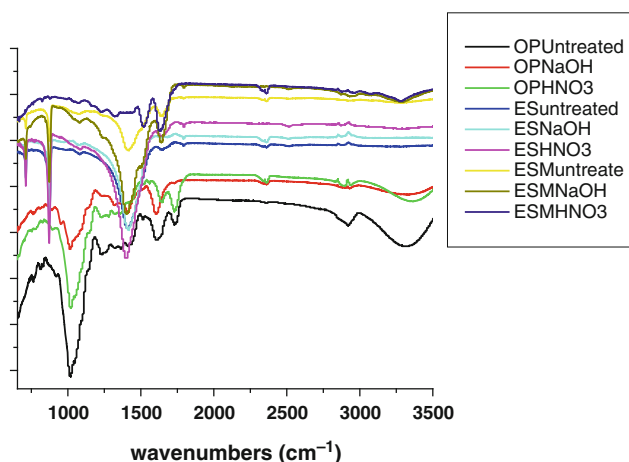
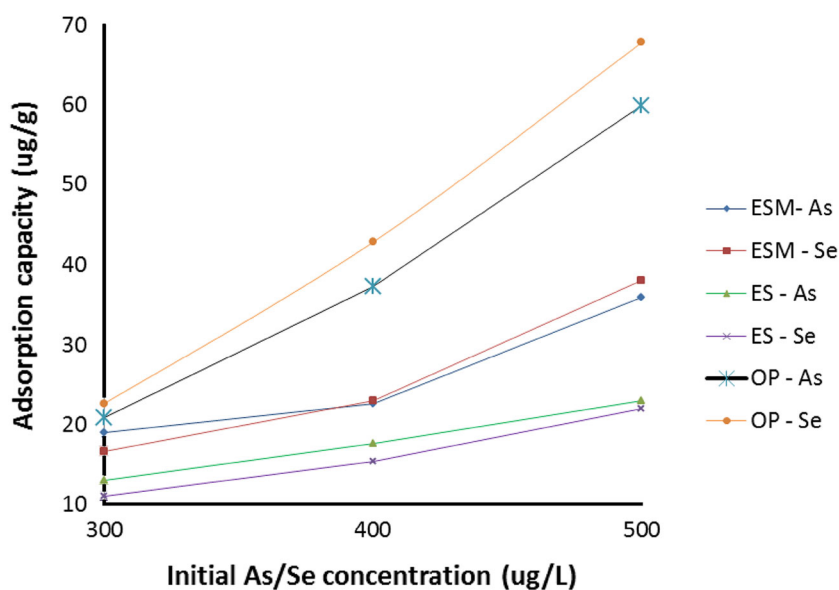


Fig. 2 IR spectra for untreated and treated low-cost adsorbents

retained. There was a new peak at $1,024, 2,357 \text{ cm}^{-1}$ and a shift in the peak position from $2,919$ to $2,887 \text{ cm}^{-1}$ and from $3,309$ to $3,346 \text{ cm}^{-1}$ signifying the formation of isocyanates from the parent C=O , CN and C=C bonds.

ES did not show much activity in terms of functional group modification on chemical treatment with both NaOH and HNO_3 . However, of note is the presence of the peaks at $3,314\text{--}3,334 \text{ cm}^{-1}$ and $2,361 \text{ cm}^{-1}$ for ES treated with both NaOH and HNO_3 signifying the presence of -OH and isocyanates or alkynes, respectively. Treatment with HNO_3 introduces a peak at $3,315 \text{ cm}^{-1}$ because of the C-H stretching vibrations of alkanes. Looking at the ESM before and after chemical treatment reveals that treatment with NaOH introduces the isocyanates, nitriles, O-C of acids and the C=O amide bands as evidenced by the peaks at $2,360, 1,235$, and $1,080 \text{ cm}^{-1}$, respectively. However,



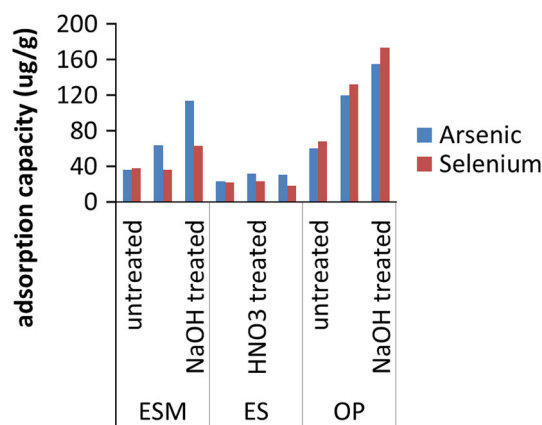
Fig. 3 Adsorption profile of As and Se

treatment with HNO_3 introduces O–H of carboxylic acids, C–O–H bending vibrations, isocyanates, O–C of acids and O–H bending vibrations at 2,964, 1,386, 2,360 and 1,226 cm^{-1} , respectively. From all the data collected using FT-IR, it can be concluded that NaOH and HNO_3 had different effects on OP, ESM and ES.

Adsorption studies

Adsorption behaviour

To ascertain whether it is adsorption that takes place, an adsorption–breakthrough curve was generated from monitoring the adsorption of both As and Se at different initial concentrations fixing the adsorbent mass. The resultant responses are presented in Fig. 3. It was observed that there was a difference in adsorption capacities for the different materials with OP adsorbing more than ESM, which in turn adsorbs more than ES at all the initial As and Se concentrations studied. For example, at an initial concentration of 400 $\mu\text{g l}^{-1}$, ES adsorbed around 12 $\mu\text{g g}^{-1}$ of Se and 15 $\mu\text{g g}^{-1}$ of As whilst ESM adsorbed 18 and 20 $\mu\text{g g}^{-1}$ of Se and As, respectively, and OP achieved 32 and 39 $\mu\text{g g}^{-1}$ of As and Se, respectively. This could be as a result of the difference in the surface orientation and the presence or absence of certain functional groups in the respective adsorbents. This suggests that functional groups and surface orientation play an important role in the adsorption of both As and Se. As shown in Fig. 3, an increase in the adsorption capacity was observed with increasing initial concentration, suggesting that adsorption is taking place rather than precipitation or masking of the adsorbates.

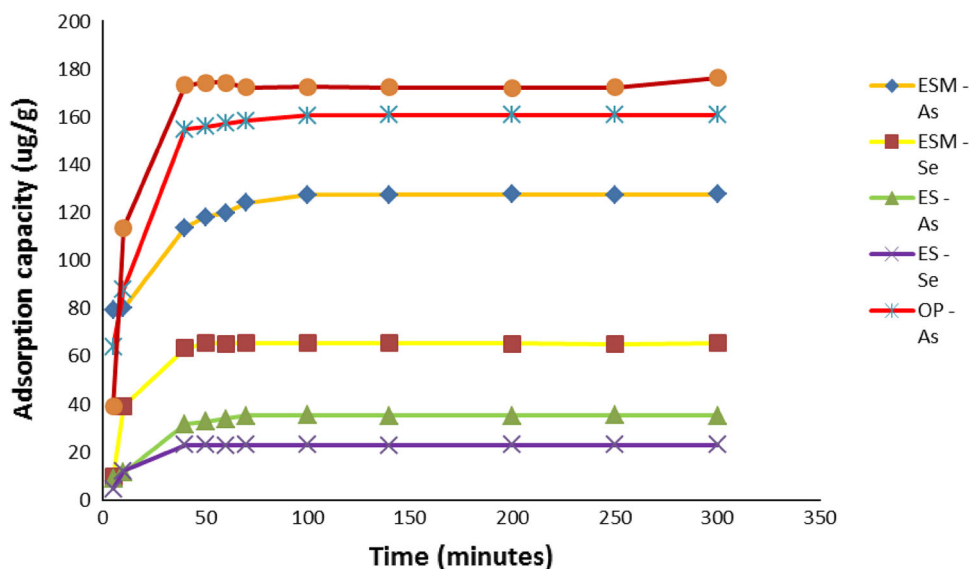
**Fig. 4** Effect of chemical modification on the adsorption capacities

Effect of adsorbent chemical treatment on the adsorption

After successful modification of the adsorbents, as confirmed by FT-IR spectroscopy, these adsorbents were then tested for any improvement or decline in terms of the adsorption and the results are depicted in Fig. 4. Untreated ESM and ES showed no difference in the adsorption of As and Se, even though ESM adsorbed As and Se more than ES. This could be a result of the presence of amines, amides and carboxylic acids in ESM, which are not present in ES. After chemical treatment with HNO_3 , an increase in As adsorption was evident possibly because of the introduction of positive O–C of acids, O–H bending and C–O–H bending vibrations, which could promote the adsorption of As. With NaOH modification, a further increase is observed probably because of the addition of nitriles and



Fig. 5 Effect of contact time on the adsorption



C=O bending vibrations to the functional groups already present in HNO₃-treated ESM.

Untreated OP showed a slight difference in the adsorption of As and Se with As adsorbed more, suggesting that the functional groups present in OP are better suited to As than Se adsorption. In addition, the surface morphology could play a part here because the overall adsorption of As and Se by OP is better than that of ESM and ES. The adsorption increases uniformly with HNO₃ treatment and reaches a peak with NaOH treatment from which a conclusion may be drawn that the presence of C=O stalls the adsorption of both As and Se, yet the C=C is better oriented to adsorb the adsorbates. Amines, amides, isocyanates and arenes improve the adsorption of both As and Se because of their unsaturation and hence they can form fairly strong interactions with the adsorbates, consequently promoting adsorption.

Effect of contact time on the adsorption

“Effect of adsorbent chemical treatment on the adsorption” of this communication showed that ESM and OP treated with NaOH and ES treated with HNO₃ performed better in terms of adsorption. In order to investigate the effect of contact time, only these three were studied and the results are presented in Fig. 5. Generally, the adsorption seemed to be adsorbate-dependent rather than adsorbent-dependent, with Se adsorption reaching a maximum at around 50 min whilst As adsorption reached a maximum just after 100 min. This could be attributed to the size of these toxins and further the stability of the interactions formed between adsorbent and adsorbate, without disregarding the dynamics of the compounds under study. Either the As takes some time to form a strong interaction with the adsorbents or the

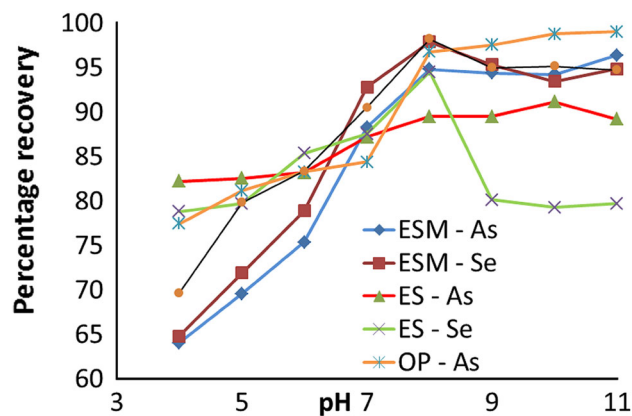


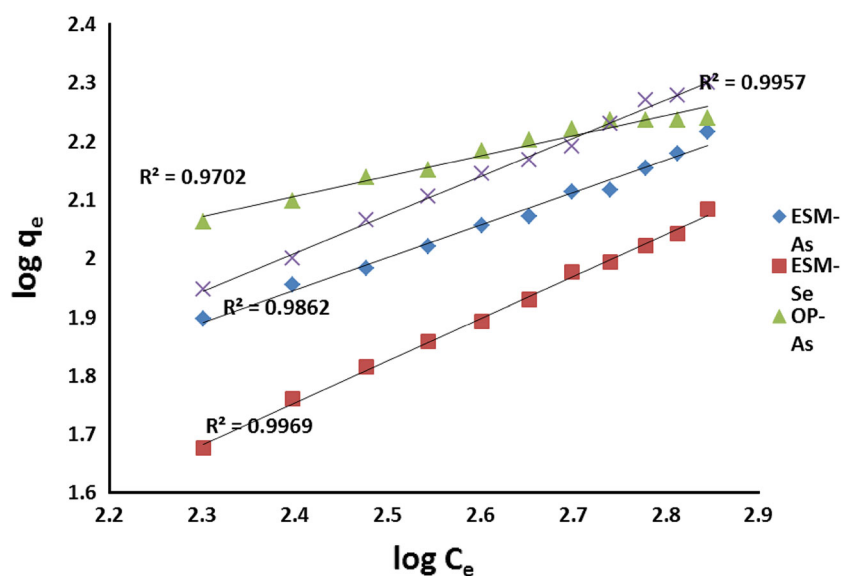
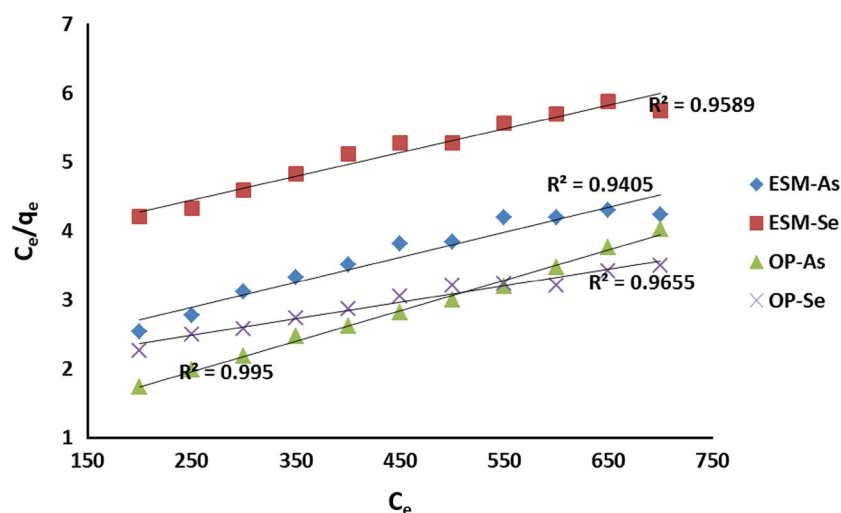
Fig. 6 Effect of the pH on desorption

Se reaction kinetics are faster, hence they exhaust their adsorption sites faster than As does. As shown in Fig. 5, the results of the adsorption follow the pattern OP > ESM > ES and there is not much difference in the adsorption of As and Se by OP and also by ES, yet there was a difference in the adsorption of As and Se by ESM.

Effect of the pH on As/Se desorption

The ability to desorb adsorbates after adsorption is important because it allows the adsorbent to be reused over and over again and again. The desorption is known to be highly dependent on the pH of the sample solution (Li et al. 2012; Feng et al. 2009; Liu et al. 2012). With most adsorptions well documented to successfully take place at pH 7 and above, a desorption pH of above pH 7 would be desirable because it would not compromise the adsorption capacity. The desorption pattern was investigated from pH 4–11 with pH adjustments achieved with concentrated



Fig. 7 Freundlich adsorption isotherm analysis**Fig. 8** Langmuir isotherm analysis

NaOH and HNO₃ to avoid altering the initial concentration of both As and Se. The resulting trends are shown in Fig. 6 and they show that, in general, the desorption is adsorbate-dependent as maximal desorption of Se is observed at pH 8 whilst for As, it is constant at pH 10 for all adsorbents. Throughout the entire pH range studied, the desorption percentage was above 60 % and improved with an increase in pH peaking at pH 8 for Se and at pH 10 for As. Beyond the acidic range, the overall desorption was above 85 % probably because of the semi-rigid interactions formed between adsorbent and adsorbate, which could have been more rigid in the acidic pH range. Worth noting is the desorption path of Se using ES; beyond pH 8, there was a gradual decline in the desorption percentage probably because at pH levels higher than pH 8, the adsorbed Se forms mostly permanent bonds with the ES restricting the reusability of ES for Se removal to only one successful run.

For subsequent adsorption studies, the sample pH was kept constant at pH 8.5 to accommodate both the adsorption of As and Se.

Adsorption profile

Figures 7 and 8 show the adsorption isotherms for both As and Se, whereby two adsorption models, namely Langmuir and Freundlich, were used to fully describe the data at equilibrium. Adsorption behaviour was investigated using 0.5 g of adsorbent in 100 ml of metal solutions in the range 200–700 µg l⁻¹ at a temperature of 22 °C. Langmuir isotherms are postulated using the modified Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}$$



Table 1 Analysis of real wastewater effluent samples

Element	C_i ($\mu\text{g l}^{-1}$)	Orange peels			Eggshell membranes		
		AC ($\mu\text{g g}^{-1}$)	%R	%RC	AC ($\mu\text{g g}^{-1}$)	%R	%RC
As	245.1	84.4	68.9	96.7	66.3	54.1	97.8
Se	197.3	73.7	74.8	93.9	46.75	47.3	95.1
Pb	301.8	35.4	23.4	90.7	35.05	23.22	93.3
Cd	84.2	11.5	27.3	94.1	14.7	34.9	94.6
Hg	72.1	8.7	24.1	93.3	6.25	17.3	97.5

Table 2 Results for Langmuir and Freundlich models

	Langmuir		Freundlich		Best model
	R^2	Adsorption capacity	R^2	Adsorption capacity	
ESM-As	0.9405	0.036	0.9862	0.5562	Freundlich
ESM-Se	0.9589	0.034	0.9969	0.7071	Freundlich
OP-As	0.9950	0.044	0.9702	0.3450	Langmuir
OP-Se	0.9655	0.024	0.9957	0.655	Langmuir

where q_e is the amount of metals adsorbed in $\mu\text{g g}^{-1}$; C_e is the metal concentration at equilibrium in $\mu\text{g l}^{-1}$; Q_0 is the monolayer maximum adsorption capacity of adsorbent ($\mu\text{g g}^{-1}$); b is the adsorption constant ($\text{l } \mu\text{g}^{-1}$).

A plot of C_e/q_e against C_e should give a straight line with $1/Q_0$ the slope and the intercept given by $1/Q_0b$.

Apart from Langmuir plots which only account for monolayer coverage of the adsorbent surface, the Freundlich isotherm has been used to incorporate the role of substrate–substrate interaction on the surface of the adsorbent. The linear form of the Freundlich equation is given by

$$\log q_e = \log k_f + \frac{1}{n} \log C_e$$

where k_f and n are related to the adsorption capacity and extent of adsorption, respectively.

A plot of $\log q_e$ against $\log C_e$ gives a straight line with $\log k_f$ the intercept and the slope given by $1/n$.

From the analysis of both the Langmuir and Freundlich plots, it can be concluded that the adsorption of As and Se by ESM treated with NaOH follows the Freundlich adsorption model whilst for the NaOH-treated OP, adsorption of As follows the Langmuir adsorption model, yet adsorption of Se follows the Freundlich adsorption isotherm. This suggests that even though adsorption patterns are known to be adsorbate-dependent, they are partly adsorbent-dependent.

Moreover, for the adsorption of the two metals with ESM and OP, the experimental data obtained were analysed with Langmuir and Freundlich isotherms and the results are recorded as shown in Table 2.

The results reveal that the adsorption of both arsenic and selenium on the ESM prescribed to the Freundlich model. This implies that the interaction was a multi-site adsorption for heterogeneous surfaces especially for organic compounds and highly interactive species (Freundlich 1906). Physical adsorption due to van der Waals forces of attraction could also have contributed to the interaction phenomenon (Bayrak 2003). The ESM is a membrane to selectively permeate a flow of fluids by osmosis, which is basically a physical process. The adsorption of both arsenic and selenium on OP was by monolayer adsorption. Langmuir (1918) model describes a monolayer adsorption and it indicates a chemisorption mechanism (Deng et al. 2003). The existence of functional groups on OP created sites for metal attachment.

Analysis of actual water samples

After successful optimisation of the contact time, sample pH and the effects of chemical treatment on the adsorption, NaOH-treated OP and ESM were then selected for the adsorption from actual domestic wastewater effluent samples. The results are shown in Table 1 where AC is the adsorption capacity, %R is the percentage of pollutants removed and %RC is the percentage amount of pollutants recovered. These samples were found to contain As, Se, Pb, Cd and Hg, with As and Se levels above the maximum permissible limit for wastewater effluents, at concentrations of 245.1 and 197.4 $\mu\text{g l}^{-1}$, respectively. On adsorption with N-treated OP, adsorption capacities of 84.4, 73.7, 35.4, 11.5 and 72.1 $\mu\text{g g}^{-1}$ were achieved for As, Se, Pb, Cd, and Hg, respectively, with per cent recoveries of more than 90 % for all the compounds. With NaOH-treated ESM, removal efficiencies of only 66.3, 46.75, 35.05, 14.7 and 6.25 $\mu\text{g g}^{-1}$ were achieved for As, Se, Pb, Cd and Hg, respectively, with recoveries greater than 90 %. Although the ESM also performed well, the adsorption by OP



Table 3 Analysis of CRM-CA615

Element	Certified value ($\mu\text{g l}^{-1}$)	Our value ($\mu\text{g l}^{-1}$)	Relative error (%)
As	9.9	9.76 ± 0.362	1.4
Fe	5.11	4.98 ± 0.513	2.5
Pb	7.1	7.078 ± 0.196	0.3

reduced the amount of As and Se in solution to the admissible levels of 100 and $150 \mu\text{g l}^{-1}$, respectively.

Data validation

Apart from performing statistical data analysis and achieving per cent relative standard deviation (%RSD) of <5 %, and calibration curves with correlation coefficients of 0.9995 and 0.9991 for arsenic and selenium, respectively, it was important to complement these data with the analysis of certified reference materials. Certified reference materials are sold with certificate values; they are used for method validation and to verify the correct use of a method. The certified reference material (ERM-CA615) was analysed and the results are presented in Table 3. The results showed agreement with the certified values of the reference material (ERM-CA 615) with a relative error of 2.5 %.

Conclusion

ESM, ES and OP have been successfully modified using HNO_3 and NaOH, and the results of the FT-IR spectra confirmed the modification of the functional groups present. Furthermore, the difference in functional groups of the untreated adsorbents has been confirmed by FT-IR results and scanning electron microscope images showed the differences in surface morphology between the adsorbents. Both the functional groups and the surface orientation were observed to be linked to the performance of the adsorbents in the remediation of both As and Se. TGA studies showed that even though ES were the least adsorbing and dense in terms of the availability of functional groups, they are thermally stable as they only decomposed beyond 700°C ; yet the ESM and OP, which performed better than ES, degraded only after 300°C , which is still acceptable because the actual temperatures in an adsorption process would not be that high. Better performance of NaOH-treated OP and ESM was experienced at contact times of 100 min and a sample pH of 8.5 with OP being able to reduce the amount of both As and Se to acceptable levels with selectivities towards As and Se is greater than 1.

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