Biosorption of Cadmium from Water using Surfactant Impregnated Eggshell

Elvis Fosso-Kankeu*, Gerhard Steenekamp, Enoch Akinpelu and Frans Waanders

***Abstract*—Cadmium (Cd) is regarded as one of the most toxic elements and it causes water pollution when it exceeds the permissible limit. It is currently present in the Mooi River above these permitted levels, and must therefore be removed using effective methods. In this study, egg shell adsorbent was prepared through physico-chemical treatment including impregnation with an anionic surfactant, namely sodium dodecyl sulphate; the resulting adsorbents were characterized using FTIR spectroscopy. The prepared adsorbents were then used for the removal of cadmium from solution. The results showed that there were additional binding groups on the egg shell following impregnation, this contributed to increase the adsorption capacity of the adsorbent. The adsorption of cadmium by the pristine egg shell membrane (ESM) and the impregnated egg shell membrane (SDS-ESM) fitted the pseudo second order kinetic model which allowed to predict adsorption capacities of 16.56 mg/g and 20.4 mg/g, respectively. In can therefore be concluded that the impregnation of the ESM is a suitable approach to improve its adsorption capacity.**

***Keywords*—** Water pollution, cadmium, adsorption, eggshell, surfactant impregnation

I. Introduction

A significant amount of pressure is currently exerted on arid and semi-arid countries due to a lack of safe, usable water resources [1]. Water is an essential necessity for all humans, vegetation and animals throughout the world [2]. However, water scarcity and pollution have become worldwide concerns due to an increase in human population, industrial and agricultural production as well as domestic activities [3].

Water scarcity is expanding in too many regions throughout the world due to the impact of water usage on available resources and the existing water quality [4-12]. Water scarcity poses a threat on biodiversity and human welfare [5].

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Humans, animals and vegetation can be harmed when exposed to an excess amount of heavy metals, such as cadmium, chromium arsenic, mercury, zinc and lead [13]. Serious and painful symptoms can be experienced when exposed to a critical amount of heavy metals. These symptoms include fatigue, high blood pressure, speech disorders, vascular occlusion, sleep disabilities, poor concentration, increased allergic reactions, autoimmune diseases and even memory loss [1, 14].

The contamination of drinking water by means of heavy metals is a significant problem that can be seen in South Africa as well as many other countries throughout the world [4, 15]. South Africa has a substantial amount of semi-arid regions and experiences an uneven distribution of seasonal rainfall. Floods, droughts and high rates of evaporation are also serious problems experienced in South Africa [16]. Therefore, South Africa faces water scarcity on a regular basis and thus, the quality and quantity of every possible water resource must be maintained.

Conventional methods used for the removal of heavy metals from surface water, consist of different physico-chemical processes [17-22]. These methods include mechanical screening, hydrodynamic classification, gravity concentration, filtration, reverse osmosis, scrubbing, chemical precipitation, coagulation and flocculation, ion exchange, electrodialysis as well as adsorption [18, 23, 24].

However, toxic heavy metals can also be removed by the use of agricultural by-products as adsorbents through the unconventional biosorption process [4,25-29]. Organic material such as eggshell membranes, hazelnut shell, orange peels, pecan shells, maize cob and coconut shell can be used as adsorbents in the biosorption process [18, 30]. These adsorbents can be pretreated with chemical or physical methods to improve their adsorption capacities.

The scope of this study is to prepare an eggshell-based biosorbent for the removal of cadmium from the surface water of the Mooi River. Eggshell membranes have a very high surface area with functional groups such as hydroxyl, thiol, carboxyl, amino and amide. These functional groups have the ability to bind effectively to heavy metal ions [31]. Therefore, these membranes have the ability to be utilized as biosorbents for the removal of toxic heavy metal ions [32].

The adsorption capacity of natural eggshell membranes as well as eggshell membranes modified with surfactant impregnation will be investigated. Sodium dodecyl sulphate (SDS) is an anionic surfactant that will be used for modification to increase the membranes' affinity to the adsorption of cations, such as heavy metal ions [33, 34].

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The characteristics of the two biosorbents will be investigated to establish the behavior and adsorption mechanism of each biosorbent. This investigation will then also be used to make educated conclusions regarding the adsorption process. Lastly, the kinetics and isotherms of each biosorbent will be utilized to quantify the method of biosorption. Thus, the purpose of this study is to analyze and evaluate the adsorption mechanism of cadmium (II) ions onto natural and SDS impregnated eggshell membranes.

II. Experimental

A. Materials

Egg shell membranes which are abundant biological waste materials in the study area were used as biosorbents. The eggshells were collected at a hatchery near Potchefstroom, South Africa. Two different pathways were followed when using the biosorption materials during the experimental procedure, namely the use of non-treated eggshell membranes and surfactant impregnated eggshell membranes.

Sodium dodecyl sulphate (SDS) was used as surfactant to impregnate the eggshell membranes. It was bought from ACE chemicals. By impregnating the membranes, the structure of the membranes is altered, which will cause an increase in its adsorption efficiency.

Cadmium chloride ($CdCl_2$. 2, 5 H_2O) was used as the initial salt for cadmium adsorbate and it was supplied by the School of Chemical- and Mineral Engineering of the North-West University. Deionized water was used for the preparation of the heavy metal solutions.

B. Preparation of eggshell membranes

To prepare the adsorbent, the membranes were then separated from the eggshells, then rinsed with tap water to remove any unwanted materials. Thereafter, the eggshell membranes were dried in an oven at 105°C for 45 minutes. After drying has taken place, eggshell membranes were grinded in the mortar. The grinded membranes were then pulverized by using a mechanical pulverizer. The membranes were pulverized for 5 minutes at 200 rpm and then for 5 minutes at 250 rpm. The powdered materials were then sieved to obtain particles at the desired uniform particle size, namely 100 µm. Finally, the materials were stored in the refrigerator at 4°C.

C. Surfactant impregnation of eggshell membranes

Firstly, 10 grams of sodium dodecyl sulphate (SDS) was dissolved in 1 liter of deionized water. Then, 10 grams of the biosorbent was added to the SDS solution. The solution was then shaken at 160 rpm and 50°C for 24 hours by using a shaking incubator. After shaking has taken place, the solution was filtered by using a Buchner funnel (vacuum filter). Finally, the residue on the filter paper was oven dried at 60°C for 12 hours. The surfactant impregnated adsorbent was then used for the removal of cadmium from aqueous solutions.

D. Characteristics of biosorbents

The non-impregnated and impregnated biosorbents were characterise using Fourier Transform Infrared Spectroscopy (FTIR). Characterization was done before and after biosorption has taken place.

FTIR analyses were carried out to identify the functional groups of the non-impregnated and impregnated biosorbents. Thus, the purpose of these FTIR analyses was to establish the degree of surface activation and to determine which functional groups were available to bind to the cadmium ions.

E. Adsorption studies

To determine the equilibrium concentration of each cadmium solution, an Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used.

The effects of adsorbent dosage (0.01–0.5 g), initial metal concentration (20–100 mg/L) and contact time (15–300 min) were tested, keeping constant the following parameters: temperature at 25°C, adsorbent particle size at 100 µm, rotation speed at 150 rpm and a cadmium solution volume of 50 mL. The adsorption of cadmium from Mooi River surface water was done at a temperature of 25°C, rotation speed of 150 rpm and aliquots of 50 mL by using the optimal adsorbent dosages of each biosorbent.

F. Isotherm and kinetic models

The cadmium adsorption of natural eggshell membranes (ESM) and SDS impregnated eggshell membranes (SDS-ESM) were investigated by using the Langmuir and Freundlich isotherm models [35].

The Langmuir isotherm assumes a monolayer surface coverage and homogeneous adsorption [36-38]. The linear form of the Langmuir model is given as follow:

$$\frac{C_e}{q_e} = \frac{1}{k \cdot q_m} + \frac{C_e}{q_m} \quad (1)$$

The Freundlich model is not limited to monolayer adsorption and assumes a heterogeneous system [38]. The linear form of the Freundlich model is given as follow:

$$\log q_e = log k_f + \frac{1}{n} \cdot \log C_e \quad (2)$$

In the two isotherm models given, Ce is the cadmium concentration at equilibrium in (mg/L), q_e is the amount of cadmium adsorbed per unit mass of adsorbent at equilibrium in (mg/g), q_m is a Langmuir constant associated with the adsorption capacity in (mg/g), k is a Langmuir constant related to energy released during adsorption in (L/mg), k_f is the Freundlich adsorption capacity parameter in (mg/g) and n indicates the deviation of adsorption from linearity.

The pseudo-kinetic models were also used to identify the adsorption affinity of the different biosorbents [35, 39]. The pseudo-first-order kinetic model is as follow:

$$\ln(q_e - q_t) = q_e - \frac{k_1}{2.303} t \quad (3)$$

The pseudo-second-order kinetic model is as follow [40, 41]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

In the two kinetic models given, q_e is the amount of cadmium adsorbed per unit mass of adsorbent at equilibrium in (mg/g), q_t is the amount of cadmium adsorbed at time t in (mg/g), k1 is the first-order rate constant in (min−1), k2 is the second-order rate constant in (g/mg/min) and t is the time in (min).

III. Results and discussion

3.1 FTIR analyses

3.1.1 Natural eggshell membranes

A peak could be observed between 3500 cm^{-1} and 3100 cm^{-1}, indicating a vibrational stretch of N-H groups and the presence of amines and amides.

Between 3300 cm^{-1} and 3200 cm^{-1} a peak emerged in the spectral region, implying symmetric and asymmetric vibrational stretch of C-H functional groups.

Between 3000 cm^{-1} and 2800 cm^{-1} a peak was observed in the spectral region, which may represent a symmetric and asymmetric stretch of H-C-H groups.

Between 1750 cm^{-1} and 1625 cm^{-1} there is a vibrational stretch of the C=O functional groups as depicted by the peak formed in this spectral region. This can be related to aldehyde and ketone.

The presence of peaks between 1300 cm^{-1} and 1000 cm^{-1} indicates the presence of a vibrational stretch of the C-O functional groups.

3.1.2 SDS impregnated eggshell membranes

A peak was also observed between 3500 cm^{-1} and 3100 cm^{-1}, and could represent a vibrational stretch of N-H groups.

Between 3300 cm^{-1} and 3200 cm^{-1} a peak was present in the spectral region, and could be ascribed to a symmetric and asymmetric vibrational stretch of ≡C-H functional groups.

The presence of a peak between 3100 cm^{-1} and 3000 cm^{-1} indicates the presence of a vibrational asymmetric stretch of the C=C-H functional groups of alkenes and aromatic rings.

Hydrogen-bonded O-H groups could be responsible of the broad peak between 3600 cm^{-1} and 3100 cm^{-1}.Between 3000 cm^{-1} and 2800 cm^{-1}, there are peaks in the spectral region, which represent a symmetric and asymmetric stretch of H-C-H groups.

Between 1750 cm^{-1} and 1625 cm^{-1} there is a vibrational stretch of the C=O functional groups as depicted by the peak formed in this spectral region.

Between 1600 cm^{-1} and 1500 cm^{-1}, there is a peak in the spectral region representing a vibrational stretch of N=O groups.

The presence of peaks between 1300 cm^{-1} and 1000 cm^{-1} relates to a vibrational stretch of the C-O functional groups.

3.2 Adsorption behavior of ESM and SDS-ESM

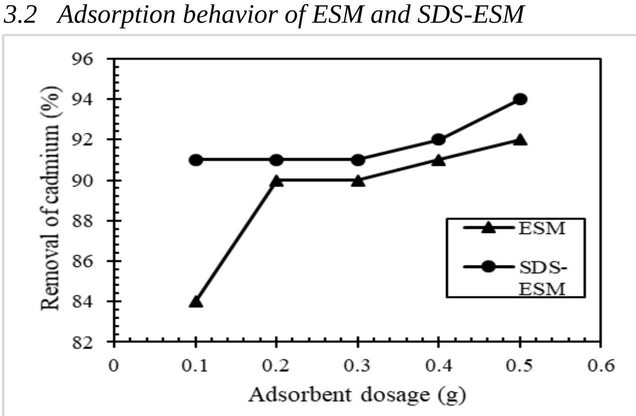

Fig. 1. Adsorption of cadmium at various adsorbents dosages.

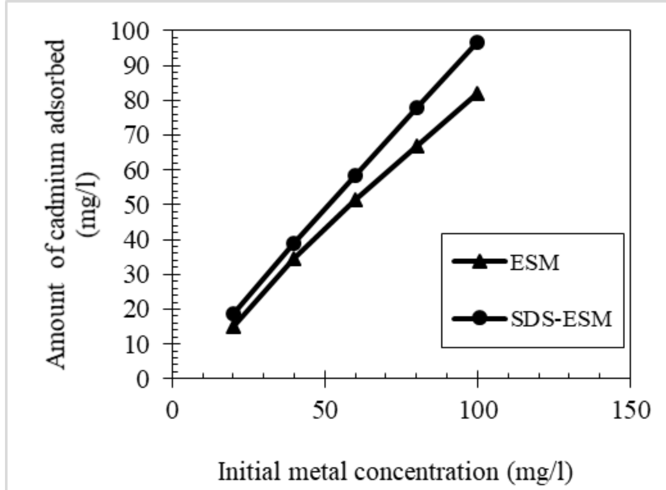

Fig. 2. Adsorption pattern at various initial cadmium concentrations

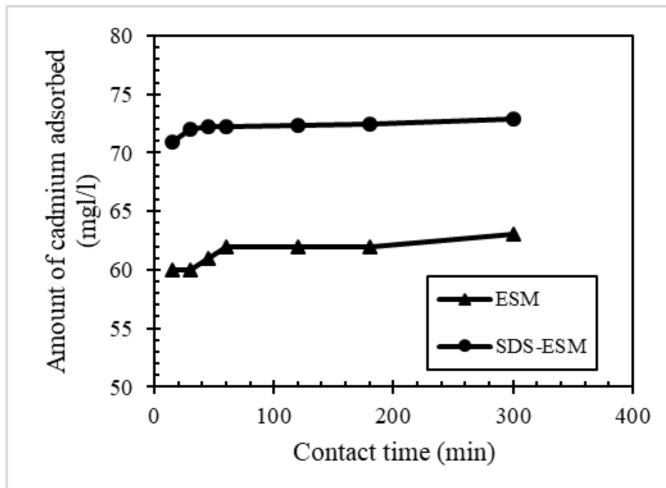

Fig. 3. Adsorption of cadmium at various exposure times

The percentage of cadmium adsorbed is plotted as a function of the amount of adsorbent dosage, as shown in Figure 1. When the biosorbent was impregnated with SDS, less biosorbent was required to remove an efficient amount of cadmium. The optimal adsorbent dosage of ESM was therefore chosen as 0.2 g and the optimal dosage of SDS-ESM was chosen as 0.1 g.

The amount of cadmium adsorbed is plotted against the initial cadmium concentration of the metal solutions, as shown in Figure 2. There exists a linear increase in the adsorption of cadmium ions when the initial cadmium concentration was increased. The maximum amount of cadmium was adsorbed at 100 mg/L using ESM and SDS-ESM. Furthermore, the SDS-ESM delivered a higher adsorption affinity to cadmium ions than the ESM, as shown in Figure 2.

The amount of cadmium adsorbed is plotted against the contact time of adsorption in the metal solutions, as shown in Figure 3. Impregnated eggshell membranes displayed a higher adsorption affinity than that of the non-treated eggshell membranes. The equilibrium concentration of cadmium ions

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was reached at 62 mg/L after 60 minutes, when ESM was used as the biosorbent. The equilibrium concentration was therefore reached after 60 min ESM dosage of 0.2 g. Furthermore, the equilibrium concentration of cadmium ions was reached at 72 mg/L after 30 minutes, when SDS-ESM was used as the biosorbent. The equilibrium concentration was reached faster using SDS-ESM.

The coefficient of determination (R^2) of the different SDS-ESM models, as shown in Tables 1 and 2, indicates that the Freundlich isotherm model describes the adsorption behaviour the best. The Freundlich model is not limited to monolayer adsorption and assumes a heterogeneous system [37, 42-49].

After comparing the correlation coefficient of the different ESM models, it was found that the Langmuir isotherm model describes the adsorption behaviour of ESM the best. The Langmuir isotherm assumes a monolayer surface coverage and homogeneous adsorption [38, 42-49]. Whereas the Freundlich adsorption capacity constant (kf) is significantly higher for the SDS-ESM impregnated eggshell membranes.

The coefficient of determination (R^2) of the different kinetic models, as shown in Tables 3 and 4, indicates that the pseudo-second-order model describes the kinetic data of both biosorbents the best.

TABLE I
PARAMETERS OF THE LANGMUIR ISOTHERM MODEL

Isotherm Model	Parameters	Cd(II)	
		ESM	SDS-ESM
Langmuir	q_m (mg/g)	50.25126	250
	k_L (l/mg)	0.038521	0.075901
	R^2	0.9946	0.2092

TABLE II
PARAMETERS OF THE FREUNDLICH ISOTHERM MODEL

Isotherm Model	Parameters	Cd(II)	
		ESM	SDS-ESM
Freundlich	k_f (mg/g)	2.583449639	17.74598
	n	1.380834024	1.126761
	R^2	0.9943	0.9058

TABLE III PARAMETERS OF THE PSEUDO-FIRST-ORDER KINETIC MODEL

Kinetic Model	Parameters	Cd(II)	
		ESM	SDS-ESM
Pseudo First Order	q_e (mg/g)	15.5	36
	k_1 (min^{-1})	0.0006909	0.0006909
	R^2	0.7241	0.5677

TABLE IV PARAMETERS OF THE PSEUDO-SECOND-ORDER KINETIC MODEL

Kinetic Model	Parameters	Cd(II)	
		ESM	SDS-ESM
Pseudo Second Order	q_e (mg/g)	16.55629	20.40816
	k_2 (g/mg.min-1)	0.010131	0.022932
	R^2	0.9997	0.9999

The surface water of the Mooi River contains many essential trace elements. As shown in Figure 4, both ESM and SDS-ESM had the ability to adsorb cadmium in the presence of other heavy metals. Again, SDS-ESM delivered a higher adsorption efficiency for cadmium than ESM. SDS-ESM removed 83.45% of cadmium, while ESM removed 62.10% of cadmium.

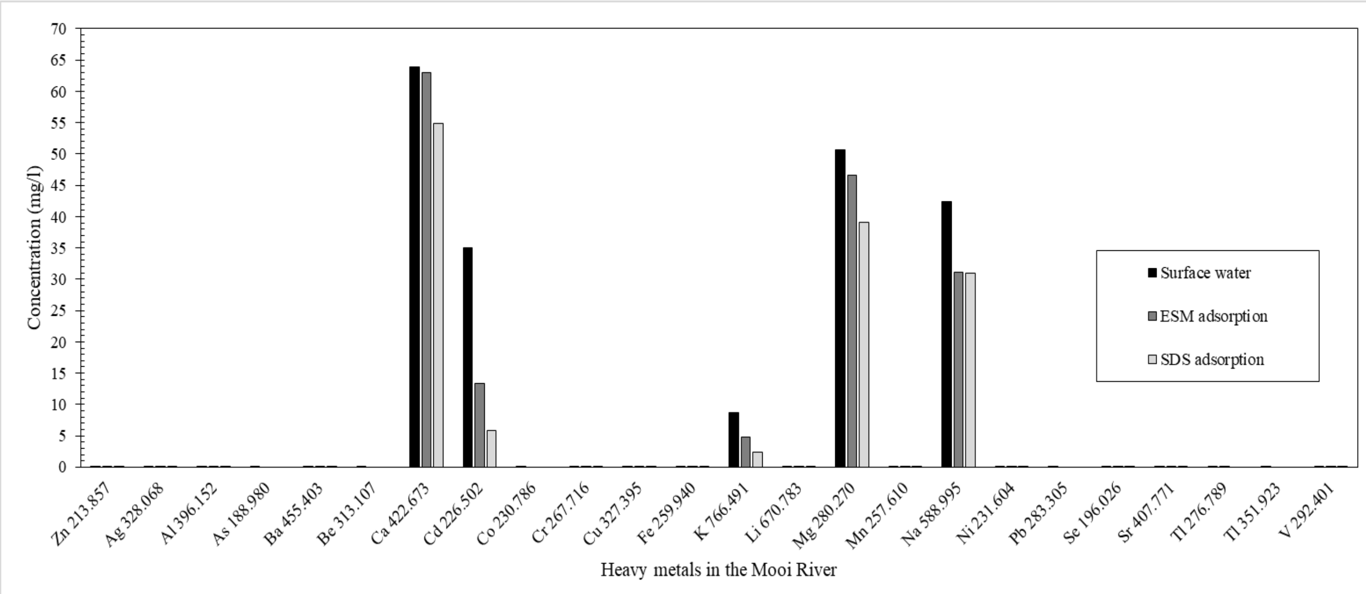

Fig. 4. Trace element concentrations in the Mooi River

IV. Conclusion

Successful surfactant impregnation of the eggshell membranes was established after comparing the FTIR results and characteristics of the different biosorbents.

After comparing the variation in adsorbent dosage, it was evident that the SDS-ESM delivered a higher cadmium removal efficiency than ESM. The optimal dosage for ESM and SDS-ESM was 0.2 g and 0.1 g, respectively.

The equilibrium concentration of cadmium (II) ions was reached at 62 mg/L after 60 minutes, when ESM was used as biosorbent, and the equilibrium concentration of cadmium ions was reached at 72 mg/L after 30 minutes, when SDS-ESM was used as the biosorbent. Thus, the equilibrium concentration was reached faster when SDS-ESM was used.

Both ESM and SDS-ESM had the ability to adsorb cadmium, in the presence of other heavy metals, from the surface water of the Mooi River. SDS-ESM had a higher adsorption efficiency than ESM.

The Langmuir isotherm model describes the adsorption behaviour of ESM and therefore, ESM has a monolayer surface coverage and applied homogeneous adsorption.

The Freundlich isotherm model describes the adsorption behaviour of SDS-ESM and therefore, SDS-ESM applied multilayer adsorption that occurred on a heterogeneous surface and it was not limited to monolayer adsorption.

The pseudo-second order kinetic was found to fit best the adsorption of cadmium by both ESM and SDS-ESM implying that the adsorption occurred mainly through chemisorption process.

It is thus clear that natural and SDS impregnated eggshell membranes have the ability of serving as adsorbents during the adsorption of heavy metals such as cadmium. These biosorbents, especially SDS-ESM, can therefore be used in the purification of surface water of essential water resources.

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