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Regeneration of a chemically improved peat moss for the removal and recovery of Cu(II) and Pb(II) from aqueous solution

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ABSTRACT

Unabated research into biosorption technology is fueled by the prospect of a low-cost solution to the unrestrained discharge of heavy metal effluents. However, the resulting spent biosorbents can become an environmental burden, and thus, the ability to remove and recover metal contaminants from spent biosorbents can reduce disposal risk. A suitable desorption process should, therefore, generate a rapid sorbate release, a high metal concentrated effluent, provide minimal physico-chemical damage to the biosorbent, as well as, produce little or no change in biosorbent capacity upon re-use. In this study, an improved peat biosorbent produced by hot-alkali pretreatment was subjected to individual and sequential desorption, desorption kinetics, and regeneration studies using various eluents. Elution studies using distilled water, calcium chloride ($CaCl_2$), ethylenediaminetetraacetic acid (EDTA), and hydrochloric acid (HCl) to release Cu(II) and Pb(II) ions exposed the involvement of multi-mechanistic attachment. Cu(II) sorption was attributed to 3% physisorption, 26% ion exchange and 71% complexation while Pb(II) sorption was attributed to 50% ion exchange and 50% complexation. Desorption kinetics was examined to elucidate the rate of release of the metal ions and was best modeled by the pseudo-second-order equation. Regeneration tests revealed after 4 biosorption/desorption cycles, EDTA washes delivered an increased sorbent capacity. However, HCl offered the most rapid release of metal ions, a marginal increase in sorbent capacity and more significant, the greatest release of bound ions, thus producing a safer biosorbent for disposal.

Keywords: Biosorption; Kinetics; Heavy metal; Regeneration; Desorption; Peat moss

1. Introduction

Adsorption is a well-established technology capable of efficiently removing heavy metal contaminants [1] as well as other industrial contaminants [2,3] from wastewaters. However, the high cost of adsorbents has triggered numerous investigations into the development of new cost-effective adsorbents. According to Veglio and Beolchini [4], the search for new technologies involving the removal of these toxic metals has directed attention to biosorption, based on the metal binding capacities of various biological material. To date, biosorption remains an emerging technology that has gained significant momentum in recent years [5]. This is due to the high affinity of natural, low-cost biosorbents for metal ions [6]. However, the safe disposal of the metal loaded biosorbent, sorbate recovery, and regeneration of the biosorbent remains a matter of practical and ecological concern [7]. Biosorption results in transforming the contaminant from a liquid phase onto a solid interface; thus, improper disposal of the spent sorbent can lead to the accrual of contaminants in the environment. Pedersen et al. [8] explained that such

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a practice could create point-sources for metal ion pollution in the future. Consequently, desorption studies aimed at the recovery of sorbed contaminants can avert the discharge of toxic contaminants into the environment [9].

Gardea-Torresdey et al. [10] explained that an eluent or stripping agent is a chemical mediator used in the recovery of the sorbed metal ions from the biosorbent. The authors went on to explain that when determining the optimal stripping agent, one should consider the following: the capacity to recuperate the metal ions in a high percentage by using a small volume of such agent in solution; the "benevolence" of the stripping agent in terms of not causing physical damage to the biomaterial; its potential toxicity; and the possible reduction of the metal uptake capacity that the stripping agent might cause. Several authors including Bernardo and Rene [11] who studied the removal of Cr(III) from afro-waste and Azzaz et al. [12] who studied the removal of cationic dye by orange tree sawdust have demonstrated that the type of eluent used to leach sorbed ions can provide significant insight into the mechanism of biosorption. If the adsorbed metal ion can be desorbed using neutral pH water or by very dilute acids, then the attachment of the metal ion to the sorbent is by weak bonds [13]. Such weak bonds are often associated with physical adsorption [14]. The presence of a secondary ion exchange cation such as Ca^{2+} ions competes most effectively with sorbed divalent metal ions [15]. Compounds such as ethylenediaminetetraacetic acid (EDTA), infer the mechanism of complexation as such eluents can complex heavy metals and put them back into the solution [10]. Strong mineral acids such as hydrochloric acid (HCl) is reported to destroy binding sites and alter the morphology of the biomass surface [16], as well as destroy surface functional groups [6].

The exact mechanism of metal ion binding to peat is not well understood [17]. Peat moss has been reported to comprise a rich array of polar functional groups such as alcohol, aldehydes, carboxylic acids, ketones, and phenolic hydroxides, which are suitable for sorption or ion-exchange processes [18]. Though without consensus, some researchers have suggested that the attachment mechanisms of metal ions binding to peat may include ion exchange and complexation [17,19,20]. Further, relatively few studies have attempted to address the issue of biosorbent reusability. Sharma and Forster [20,21] reported that the regeneration of Irish peat was uneconomical because little desorption occurs in low molarity caustic solutions while in high molarity caustic solutions, the peat becomes unstable. In this study, hot-alkali pretreatment of peat moss was conducted to stabilize the peat and subsequently used in regeneration studies. Hot-alkali treated peat was previously reported to possess an exceptional affinity for heavy metal ions [22]. The authors went on to describe the major rate-limiting transport mechanisms to be initially film diffusion followed by intraparticle diffusion. However, the ability to regenerate this novel modified biosorbent and fully elucidate the attachment mechanisms has not been explored and therefore provides sufficient interest to undertake this study, which can advance its applicability.

The foregoing study was initiated to (i) investigate the attachment mechanisms and by extension the nature and reversibility of biosorption of Cu(II) and Pb(II) from hot-alkali modified peat, (ii) study the regeneration and re-usability of this modified peat, and (iii) model the desorption kinetic process to expound the efficiency of each tested eluent.

2. Materials and methods

2.1. Preparation of the biosorbent

Biosorption experiments were conducted with *Canadian sphagnum* peat moss manufactured by Acadian Limited of Canada. In preparation for batch experiments, the peat samples were dried at 90°C for 1 h. It was subsequently washed with distilled water and sieved to obtain a geometric mean size (GMS) expressed as (diameter of upper sieve *x* diameter of lower sieve)$^{0.5}$ [23] of 1.05 mm. Peat moss samples were chemically treated using the hot alkali pre-treatment procedure previously reported by Muraleedharan and Venkobachar [22,24]. 40 g of the biosorbent was treated with 100 ml of 40% NaOH at 128°C for 4 h. The residue was separated, washed with distilled water and then dried at 40°C for 24 h. Scanning electron microscopy revealed that subsequent to hot-alkali treatment, the peat possessed a porous morphology with the removal of constituents that may have occluded the pores [22]. Further, the authors reported that energy-dispersive X-ray spectroscopy analysis of untreated peat revealed the presence of C and O and trace amounts of Al, Si, S, and Ca. After hot-alkali pretreatment, the C, Al, Si, and S peaks diminished while the Ca increased. After biosorption the Ca peak was significantly reduced, which confirmed the occurrence of ion exchange in the biosorption process as one of the operative mechanisms.

2.2. Determination of metal ions concentration

Cu(II) and Pb(II) were selected for these experiments and were analyzed using an atomic absorption spectrophotometer (Perkin-Elmer 3030B, United States of America). Stock solutions were prepared from analytical-grade copper(II) sulfate and lead(II) nitrate in distilled water (prepared by Corning Mega-Pure System MP-1, Barnstead, United States of America, of pH approximately 7 and conductivity <5 mS/cm).

2.3. Biosorption and desorption experimental procedure

Biosorption and desorption kinetics were conducted in triplicate and by the parallel method outlined in Environmental Protection Agency, Office of Prevention, Pesticides and Toxic Substances (EPA OPPTS) method 835.1230 [25]. Experiments were performed at room temperature (26°C ± 2°C) in a batch reactor with an adsorbent mass 1.0 g/L and spiked with synthetic metal ion solution. Sorbent masses were accurate to ±0.001 g and solution volumes to ±0.5 ml. The reaction mixture was agitated on a mechanical shaker at 300 rpm up to the point of equilibrium, which occurred after 30 min. The biosorbent was then separated by gravity filtration using Whatman No. 2 qualitative filter paper. The filtrate/supernatant was subsequently tested for residual metal ions. To monitor and control any interference due to leaching during the test period, a blank was prepared, which comprised distilled water and modified peat moss. The separated biosorbent was dried and added to an equivalent volume (50 ml) of desorbing eluent (0.1 M HCl, 0.1 M EDTA, 0.1 M calcium chloride ($CaCl_2$) and distilled water) and agitated for predetermined times until equilibrium. The biosorbent was again separated by gravity filtration using Whatman No. 2 qualitative filter paper. The filtrate/supernatant was subsequently tested for leached metal ions.

2.4. Analytical methods

The biosorption and desorption yield was calculated using Eqs. (1) and (2):

$$\%\text{Biosorption} = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

$$\%\text{Desorption} = \frac{C_f}{C_0 - C_t} \times 100 \tag{2}$$

where C_0 (mg/L) is the initial concentration of metal ions in solution, C_t (mg/L) is the final concentration of metal ions in solution after biosorption, and C_f is the final concentration of metal ions in solution after desorption.

The concentration of metal ions biosorbed was determined using the mass balance equation expressed as Eq. (3):

$$q_t = \frac{\left(C_0 - C_t\right)}{m} \tag{3}$$

where q_t (mg/g) is the mass of the adsorbate adsorbed per mass of biosorbent and m (g) is the mass of the biosorbent.

2.5. Kinetic modelling

2.5.1. Lagergren model

In 1898, Lagergren as cited in [26], developed a first-order rate equation to describe the kinetic process of oxalic acid and malonic acid onto the charcoal. Ho and McKay [26], described the equation as pseudo-first-order (PFO). Table 1 presents the non-linear and linear forms of the pseudo-first-order model represented by Eqs. (4) and (5) respectively, where, K_{PFO} (min^{-1}) is the rate constant of pseudo-first-order adsorption, q_t (mg/g) is the mass of adsorbate sorbed per gram of adsorbent at any time, t (min) and q_e (mg/g) is the mass of adsorbate sorbed per gram of adsorbent at equilibrium.

2.5.2. Pseudo-second-order model

The pseudo-second-order (PSO) equation was developed for the sorption of divalent metal ions onto peat moss [27]. According to Ho and McKay [28], the model is based on pseudo-second-order chemical reaction kinetics. Linear and non-linear forms of the model are presented in Table 1, where K_{PSO} (g/mg min) is the pseudo-second-order rate, q_t (mg/g) is the mass of adsorbate adsorbed per g of adsorbent at any time, t (min), q_e (mg/g) is the mass of adsorbate adsorbed per gram of adsorbent at equilibrium and h (mg/g-t) is the initial rate of adsorption given by $K_{\text{PSO}}\, q_e^2$.

2.5.3. Intraparticle diffusion model

Weber and Morris [29], proposed that the rate of intraparticle diffusion varies proportionally with the half-power of time and is expressed as Eq. (8). According to Ofomaja [30], the model can be linearized to Eq. (9) where q_t (mg/g) is the adsorbate uptake at time, t (min), K_{id} (mg/g $t^{1/2}$) is the rate constant of intraparticle transport and the intercept c (mg/g), is taken to be proportional to the extent of the boundary layer thickness. According to Weber and Morris [29], if the rate-limiting step is intraparticle diffusion, a plot of solute adsorbed against the square root of the contact time should yield a straight line passing through the origin.

2.5.4. Diffusion-chemisorption model

The diffusion-chemisorption kinetic model [31], was developed to simulate sorption of heavy metals onto heterogeneous media. To obtain the derivatives, a correlation is made where the rate of change of concentration of the solid phase q_t (mg/g), is equated as a function of the rate of mass transfer of ions from the fluid phase to the adsorption site

Table 1
Linear and non-linear equations of different kinetic models

Model	Non-linear equation	Equations	Linear equation	Equations
Pseudo-first-order model	$q_t = q_e\left(1 - \exp^{-K_{\text{PFO}}t}\right)$	(4)	$\log\left(q_e - q_t\right) = \log q_e - \frac{K_{\text{PFO}}}{2.303}t$	(5)
Pseudo-second-order model	$q_t = \frac{K_{\text{PSO}} q_e^2 t}{1 + K_2 q_e t}$	(6)	$\frac{t}{q_t} = \frac{1}{K_{\text{PSO}} q_e^2} + \frac{t}{q_e}$	(7)
Intraparticle diffusion model	$q_t = K_{\text{id}}\left(t^{1/2}\right)$	(8)	$q_t = K_{\text{id}}(t^{1/2}) + c$	(9)
Diffusion-chemisorption model	$q_t = \frac{1}{\frac{1}{q_e} + \frac{1}{K_{\text{DC}} \times t^{0.5}}}$	(10)	$\frac{t^{0.5}}{q_t} = \frac{t^{0.5}}{q_e} + \frac{1}{K_{\text{DC}}}$	(11)

K_{DC} (mg/g $t^{0.5}$); the equilibrium sorption capacity q_e (mg/g); and time to the power of n–1, t^{n-1}. Linear and non-linear forms of the model are presented in Table 1 where K_{DC} (g/mg min) is the diffusion–chemisorption constant, q_t (mg/g) is the mass of ions adsorbed per gram of sorbent at any time, t (min), q_e (mg/g) is the adsorption at equilibrium and k_i (mg/g t) is the initial adsorption rate given by K_{DC}^2/q_e.

2.6. Error analysis

The goodness of fit of the kinetic models to the experimental data was evaluated using the coefficient of determination, (R^2), as well as the Marquardt's percent standard deviation (MPSD), hybrid error function (HYBRID), and relative percent error (RPE) which are presented in Table 2.

3. Results and discussion

3.1. Elucidating the attachment mechanism of biosorption

3.1.1. Desorption using various eluents

According to Allard et al. [32], there are three pathways by which sorption may occur onto the surface; (i) physical adsorption which is considered rapid and reversible and is due to non-specific forces of attraction (e.g., Van der Waals forces); (ii) electrostatic adsorption due to Coulombic forces of attraction between charged solute species and the adsorbing phase - this process is usually rapid and largely reversible; and (iii) specific adsorption due to the action of chemical forces of attraction which leads to surface bonding at a specific site on the solid phase. This process can be slow and partly irreversible. The desorption performance of a material is critical in assessing its applicability as a biosorbent and the probability of recovering the metal ions. Additionally, it can provide valuable insight related to the mechanism of biosorption. Researchers have investigated the nature of metal-binding onto peat moss, but there has been no common consensus on the exact mechanisms, further, various pretreatment can influence the mechanisms [7,33]. Chemical washes were used in this study to elucidate the mechanisms of biosorption by hot-alkali modified peat moss.

Subsequent to batch sorption studies, the metal-laden modified peat moss was subjected to chemical washes in an attempt to desorb the metal ions and assess the desorption efficiency of each solution. The desorbing solutions selected were distilled water, 0.1 M EDTA, 0.1 M HCl, and 0.1 M $CaCl_2$. The eluent molarity of 0.1 was selected based on previous work by Gardea-Torresdey et al. [34], Balan et al. [35], and Wankasi et al. [36] in which the authors demonstrated an effective desorption performance involving peat and other types of biosorbents.

As previously stated, a distilled water wash can indicate whether the metal ions are tightly bound to the modified peat moss. Thus, ions released reflect that physical adsorption existed in the removal process [37]. The batch biosorption

Table 2
Error functions for best-fitting model estimation

Error functions	Expression	Equations
Relative percent error (RPE)	$\mathrm{RPE\%}=\frac{1}{N}\sum_{i=1}^{N}\frac{\left[\left\lvert\left(q_{e_i}\right)_{\text{pred}}-\left(q_{e_i}\right)_{\text{exp}}\right\rvert\right]}{\left(q_{e_i}\right)_{\text{exp}}}\times 100$ where N is the number of experimental points.	(12)
Marquardt's percent standard deviation (MPSD)	$\mathrm{MPSD}=100\sqrt{\frac{1}{N-P}\sum_{i=1}\left[\frac{\left(q_{e_i}\right)_{\text{exp}}-\left(q_{e_i}\right)_{\text{pred}}}{\left(q_{e_i}\right)_{\text{exp}}}\right]^2}$ where, N is the number of experimental points and P is the number of parameters in the regression model.	(13)
Hybrid error function (HYBRID)	$\mathrm{HYBRID}=\frac{100}{N-P}\sum_{i=1}^{N}\left[\frac{\left(\left(q_{e_i}\right)_{\text{exp}}-\left(q_{e_i}\right)_{\text{pred}}\right)^2}{\left(q_{e_i}\right)_{\text{pred}}}\right]$ where N is the number of experimental points and P is the number of parameters in the regression model.	(14)
R^2	$R^2=\frac{\sum_{i=1}^{N}\left(\left(q_{e_i}\right)_{\text{exp}}-q_{e_{\text{exp,mean}}}\right)^2-\sum_{i=1}^{N}\left(\left(q_{e_i}\right)_{\text{exp}}-\left(q_{e_i}\right)_{\text{pred}}\right)^2}{\sum_{i=1}^{N}\left(\left(q_{e_i}\right)_{\text{exp}}-\left(q_{e_i}\right)_{\text{pred}}\right)^2}$ where N is the number of experimental points.	(15)

test was first conducted using an initial adsorbate concentration of 75 mg/L and a particle GMS of 1.05 mm. Desorption analysis showed a release of approximately 3% of Cu(II) ions and 0% Pb(II) ions by the distilled water wash (Figs. 1 and 2).

Wolf et al. [15], concluded that in the presence of Ca^{2+} ions in solution as well as in peat, Cu^{2+} ions competed most effectively with the Ca^{2+} ions for the sorption sites. Thus, metal ions bound to the modified peat was investigated to assess the cation exchangeability. A calcium chloride wash released approximately 27% of Cu(II) ions after 30 min and 29% after 90 min of contact. With respect to Pb(II) ions, desorption efficiencies of 36% and 50% were achieved after 30 and 90 min respectively. Consequently, these results imply that ion exchange is an operative mechanism but is not the only attachment mechanism involved.

Chelating agents such as EDTA are known to form soluble complexes with metals ions over the pH range of 2–12 [17,38]. However, Cline and Reed [39] explained that EDTA begins to protonate at pH less than 4. Trémillon, as cited in [40], further clarified that as pH decreases, EDTA, symbolized by letter "Y", passes through a series of complexes of higher coordination index according to the following order: Y^{4-}, HY^{3-}, H_2Y^{2-},…, H_6Y^{2+}. Therefore, at very low pH values, protonation reduces EDTA solubility and practically loses its complexing power. For these experiments, the average pH of reaction solutions was 4.9. EDTA wash to remove Cu(II) achieved 89% release after 30 min and 100% after 60 min. Concerning Pb(II) desorption by EDTA, 95% was desorbed after 30 min and 100% after 60 min.

The hydrochloric acid wash achieved the greatest metal removal efficiency of 100% for both Cu(II) and Pb(II) after 30 min reaction time. A rapid release of both metal ions was observed. This release may be attributed to a preferential selectivity of peat moss surface groups for H^+ over bound metals ions. However, Kanamarlapudi et al. [41] explained that the use of such mineral acids could lead to a loss in capacity, possibly due to the destruction of surface groups that bind metal ions.

3.1.2. Sequential desorption by multiple solutions to validate sorption mechanisms

These studies were conducted by subjecting the same metal-laden peat sample repeatedly to sequential desorption cycles. Each cycle involved a 90 min wash followed by recovery of the biosorbent and then repeating the elution process using a different chemical eluent. The process began with distilled water, followed by $CaCl_2$, EDTA, and finally HCl. The cumulative amount of ions released after each stage was correlated with desorption results by individual solutions that revealed a total of 100% release after all four washes as seen in Figs. 1 and 2. The results show that the $CaCl_2$ solution was capable of releasing ions held by both physisorption and ion exchange while EDTA and HCL were able to release ions held by physisorption, ion exchange, and complexation. According to these figures, after 90 min of agitation, the release by distilled water wash was 3% Cu(II) ions and 0% Pb(II) ions. The calcium chloride wash exchanged 26% Cu(II) ions and 50% Pb(II) ions. The EDTA wash released 71% Cu(II) ions and 50% Pb(II) ions after 90 min. The HCl wash released 0% Cu(II) ions and 0% Pb(II). The mechanism of adsorption of Cu(II) by peat has been elucidated to be 3% physical adsorption, 26% ion exchange and 71% due to complexation; while Pb(II) sorption may be due to 50% ion exchange and 50% complexation.

3.2. Desorption kinetics

Desorption of heavy metals from peat can comprise three steps; the desorption of the metal ions from the binding sites of the biosorbent, diffusion of metal ions from inside to the exterior of the biosorbent, and diffusion of metal ions across the stationary liquid film surrounding the sorbent particles into the bulk liquid [17]. A suitable desorption process should, therefore, generate a rapid sorbate release, a high metal concentrated effluent, provide minimal physico-chemical damage to the adsorbent, as well as, produce little or no change in adsorbent capacity upon re-use. The kinetics of desorption was used principally to assess the overall performance of each desorbing eluents in terms of the initial and overall rates of the process. The following kinetic models were fitted to the experimental data: Lagergren pseudo-first-order model; pseudo-second-order model; Weber and Morris [29] intraparticle model and the diffusion-chemisorption model.

Batch biosorption kinetic experiments were first performed using an adsorbate concentration of 50 mg/L and particle GMS of 1.05 mm. Following desorption, the ability of the kinetic models to simulate the desorption data was first evaluated using linear regression. The coefficients of

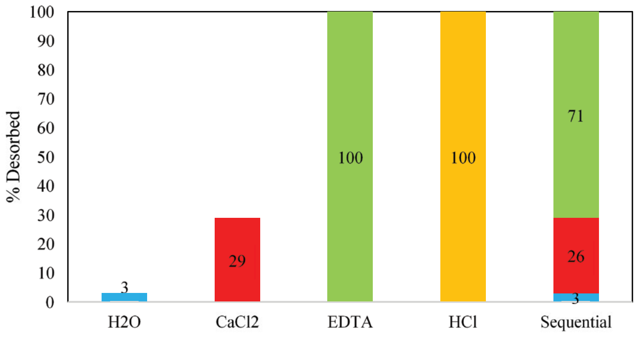

Fig. 1. Cu(II) desorption from hot-alkali modified peat using various eluents.

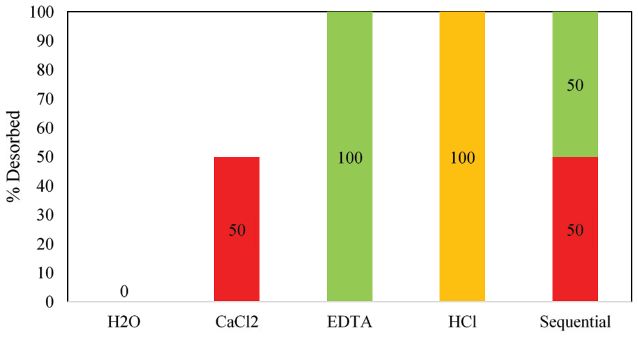

Fig. 2. Pb(II) desorption from hot-alkali modified peat using various eluents.

determination, R^2, obtained from linear plots (Table 3) indicated that the pseudo-second-order model produced the highest correlation for most of the eluents used for both Cu(II) and Pb(II) desorption. A comparison of the non-linear experimental curves to theoretical curves (generated using parameters obtained from linearization) was then performed by calculating the RPE, MPSD, and HYBRID (Table 3). The error values revealed that the diffusion-chemisorption model generally produced the highest correlation for all eluents used for both Cu(II) and Pb(II) desorption. This difference in model performance may be explained by Kinniburgh as cited in [42] whereby the authors highlighted that the transformation of a non-linear model to a linear form could implicitly alter the error functions as well as the error variance and normality assumptions of the least-squares methods.

Consequently, a more robust simulation was performed through non-linear regression by the Levenberg–Marquardt algorithm [43] using the non-linear forms of the pseudo-second-order and the diffusion–chemisorption models (Table 1). Coefficients of determination, R^2, presented in Table 4 suggest the diffusion-chemisorption model produced slightly higher conformity than the pseudo-second-order model. However, analysis of the HYBRID, RPE, and MPSD error functions favored the pseudo-second-order model for all eluents and for both Cu(II) and Pb(II) ions. In light of the overall performance of this model, the pseudo-second-order equation was therefore selected to evaluate desorption performance. In the case of Pb(II), both the overall rate and the initial rate of desorption were highest for HCl, followed by EDTA and finally $CaCl_2$ (Table 5). In the case of Cu(II), the overall rate was highest for distilled water while the initial rate of desorption was highest for EDTA, followed by HCl. Further, HCl wash produced the highest relative desorption capacity for both Cu(II) and Pb(II).

3.3. Optimum concentration of desorbing solution

It was noted previously that the HCl wash achieved equilibrium at a faster rate than that of the other eluents.

Table 3
Comparison of kinetic models using linear regression to simulate Pb(II) and Cu(II) desorption

Adsorbate	Eluent	Model	Error functions			
			Linear	Non-linear		
			R^2	RPE	MPSD	HYBRID
Pb(II)	HCl	Pseudo-first-order	0.5422	77.000	103.441	2193
		Pseudo-second-order	0.9998	3.041	6.200	5.832
		Intraparticle diffusion	0.7243	62.561	84.981	1433
		Diffusion-chemisorption	0.9983	1.842	3.192	1.772
	EDTA	Pseudo-first-order	0.8470	63.245	85.913	1307
		Pseudo-second-order	0.9991	6.351	16.061	26.141
		Intraparticle diffusion	0.7786	52.492	72.554	904.028
		Diffusion-chemisorption	0.9979	2.011	3.640	1.851
	$CaCl_2$	Pseudo-first-order	0.9857	59.233	81.484	434.946
		Pseudo-second-order	0.9861	14.133	30.281	30.737
		Intraparticle diffusion	0.9690	33.811	49.241	135.348
		Diffusion-chemisorption	0.9783	3.591	5.694	1.794
Cu(II)	HCl	Pseudo-first-order	0.0481	101.190	123.923	2420
		Pseudo-second-order	1.000	2.214	5.801	4.394
		Intraparticle diffusion	0.5641	87.552	107.431	1804
		Diffusion-chemisorption	0.9989	2.264	4.250	2.450
	H_2O	Pseudo-first-order	0.4663	1,067	2,299	19,113
		Pseudo-second-order	0.9944	6.601	11.231	0.319
		Intraparticle diffusion	0.7840	43.751	56.462	8.331
		Diffusion-chemisorption	0.9039	7.220	10.181	0.311
	EDTA	Pseudo-first-order	0.9890	90.922	111.511	1919
		Pseudo-second-order	0.9999	2.851	6.970	6.520
		Intraparticle diffusion	0.8226	87.071	106.805	1760
		Diffusion-chemisorption	0.9999	0.550	0.720	0.076
	$CaCl_2$	Pseudo-first-order	0.9756	13.710	30.890	18.518
		Pseudo-second-order	0.9981	6.081	11.831	3.275
		Intraparticle diffusion	0.8535	49.382	62.971	137.178
		Diffusion-chemisorption	0.9792	3.881	4.982	0.976

Table 4
Comparison of kinetic models using non-linear regression to simulate Pb(II) and Cu(II) desorption

Adsorbate	Eluent	Model	Error functions			
			Non-linear			
			R^2	RPE	MPSD	HYBRID
Pb(II)	HCl	Pseudo-second-order	0.9966	1.621	2.790	1.659
		Diffusion-chemisorption	0.9979	11.301	17.141	66.584
	EDTA	Pseudo-second-order	0.9964	1.980	2.981	1.798
		Diffusion-chemisorption	0.9974	19.550	28.330	172.817
	$CaCl_2$	Pseudo-second-order	0.951	13.581	28.420	27.361
		Diffusion-chemisorption	0.9951	46.351	66.712	409.501
Cu(II)	HCl	Pseudo-second-order	0.9995	0.695	1.051	0.179
		Diffusion-chemisorption	0.9972	67.454	88.732	1,280.984
	H_2O	Pseudo-second-order	0.969	74.623	91.653	24.356
		Diffusion-chemisorption	0.9753	23.673	52.101	3.607
	EDTA	Pseudo-second-order	0.9986	1.214	1.733	0.469
		Diffusion-chemisorption	0.9998	80.221	105.414	1,783.871
	$CaCl_2$	Pseudo-second-order	0.9842	5.721	10.030	2.702
		Diffusion-chemisorption	0.9921	50.840	65.574	191.826

Table 5
Pseudo-second-order desorption kinetic parameters obtained by non-linear regression

Adsorbate	Eluent	Initial Rate h (mg/g-t)	Overall Rate K_{PSO} (mg/g-t)	Desorption Capacity q_{des} (mg/g)
Pb(II)	HCl	35.099	0.066	22.991
	EDTA	17.373	0.035	22.408
	$CaCl_2$	1.546	0.013	11.033
Cu(II)	HCl	31.373	0.115	16.539
	H_2O	0.009	0.576	0.128
	EDTA	37.141	0.142	16.196
	$CaCl_2$	1.187	0.048	4.978

Further, together with its higher desorption capacity, the initial and overall rate of desorption compared well to that of EDTA. HCl was therefore selected to determine its optimum concentration. Batch biosorption tests were first conducted using an initial adsorbate concentration of 75 mg/L and a particle GMS of 1.05 mm. Zehra et al. [44] reported a maximum release of Pb(II) from Brunei Darussalam peat using 1 M HCl. In this study, various concentrations of HCl (0.001 M to 0.3 M) were used to desorb Cu(II) and Pb(II) from the hot-alkali pretreated peat. After 30 min of agitation of the spent modified peat in 0.05 M HCl solution, approximately 73% of the adsorbed Cu(II) ions and only 50% Pb(II) ions were released. The 0.1 M HCl solution released 100% of the sorbed Cu(II) ions after 15 min contact and 100% Pb(II) ions after 30 min. The highest desorption rate and capacity for this hot-alkali pretreated peat were observed using a 0.2 M HCl solution that required 10 and 20 min to release 100% of Cu(II) and Pb(II) ions respectively. Beyond 0.2 M HCl, the release of Cu(II) and Pb(II) was insignificant. A change in HCl molarity from 0.1 to 0.2 reduced the time to reach equilibrium by 5 and 10 min for Cu(II) and Pb(II) respectively. As a consequence of this marginal reduction in time, the eluent concentration of 0.1 M HCl was selected for regeneration experiments.

3.4. Batch regeneration studies

A comparative analysis into the regeneration of hot-alkali modified peat for the removal and recovery of Cu(II) ions was performed using 0.1 M HCl and 0.1 M EDTA for a contact time of 30 min. This test involved subjecting the modified peat sample to consecutive cycles of biosorption and desorption.

The results shown in Fig. 3 reveals small changes in biosorption capacity between the 4 successive biosorption/desorption cycles. The study with EDTA showed a slight increase in adsorption capacity after the first biosorption/desorption cycle; the capacity increased by 17%. This might

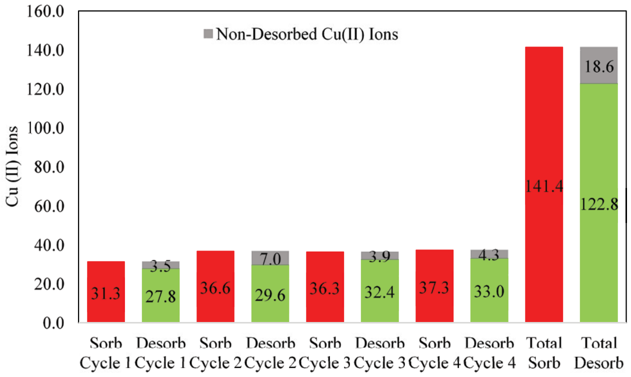

Fig. 3. Effect of multiple adsorption/desorption cycles on the uptake of Cu(II) ions and desorption using EDTA.

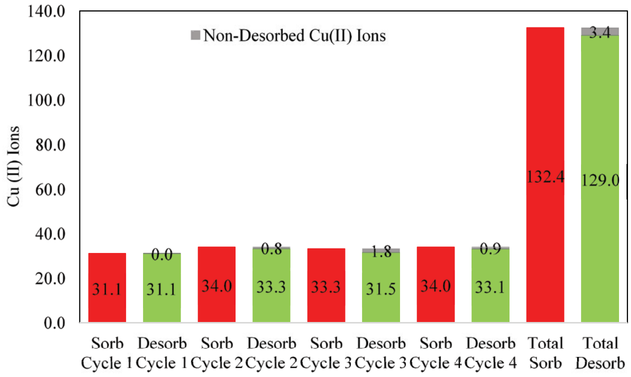

Fig. 4. Effect of multiple adsorption/desorption cycles on the uptake of Cu(II) ions and desorption using HCl.

be attributed to the creation of extra sites due to EDTA coating the peat moss. At the end of the third cycle, biosorption efficiency had increased by 19%. The desorption efficiency was 89% for the first cycle, in the second cycle, this efficiency reduced to 81%, and at the end of the fourth cycle, the efficiency returned to 89%. Samples of modified peat subjected to Cu(II) sorption and HCl desorption also exhibited an increase in sorption capacity after the first cycle (Fig. 4.). This increase may be attributed to increased protonation of peat moss surfaces. Efficiency increased by 7% and eventually climbed to 9% by the fourth cycle. The first desorption stage resulted in 100% Cu(II) desorbed and decreased only slightly throughout the 4 runs. These regeneration studies indicated that after four cycles of sorption and desorption, the biosorption capacity of peat moss increased when EDTA was used as the elution solution. Similarly, an increase in capacity was also observed with HCl desorption; however, this increase was not as significant as that of EDTA. Data revealed that greater desorption efficiencies are obtained by HCl desorption.

Though it was postulated that HCl washes could disrupt the matrix of adsorbents and consequently reduce the adsorption capacity [41], this phenomenon was not observed in these experiments. The chelating agent, EDTA, was successful in extracting the heavy metal ions. However, with EDTA, it is difficult to treat the effluent solution after treatment due to low biodegradability, biological toxicity, and high cost for treatment [45]. The strong inorganic acid, HCl, was a very effective eluent for heavy metal extraction. Further, it has the advantage of reasonable cost and simple handling of the effluent solution [46]. Although the EDTA wash resulted in an improvement in the available capacity of the peat for Cu(II) ions (19%), after 4 cycles the total bound ions retained in the biosorbent was 13%. While, the HCl wash only produced a 9% increase in available capacity, after 4 cycles the total bound ions retained in the biosorbent was 2.5%, which results in a safer spent sorbent for disposal.

The results of this study showed that Cu(II) desorption and the regeneration of the modified peat compared well to other adsorbents reported in the literature. Han et al. [47] reported an 11% decrease in Cu(II) adsorption capacity after 4 cycles using carboxylic acid-functionalized poly porous material. Wang et al. [48] reported that Cu(II) ions could be effectively desorbed from spent organically functionalized silica gel by HNO_3. After 3 adsorption/desorption cycles, the authors also observed minimal change in adsorption capacity (18.3 to 17.9 mg/g) and desorption efficiency (99.3% to 98.2%). Khormaei et al. [49] examined the adsorption/desorption of Cu(II) ions from the natural biosorbent sour orange residue. Using 0.1 M HC1, after 4 cycles, more than 99% of the sorbed Cu(II) ions were released. However, biosorption capacity decreased by 14%. Gupta et al. [17] studied packed-bed columns using Irish peat and reported maximum desorption efficiencies of 55% and 58% when using HCl and EDTA, respectively.

4. Conclusions

Desorption studies were conducted to determine the regeneration and re-usability potential of spent hot-alkali pretreated peat moss in an attempt to avert the discharge of toxic contaminants into the environment, minimize physico-chemical damage to the biosorbent and maintain its biosorption capacity. The mechanism of biosorption was explored through individual and sequential desorption tests while kinetic studies were investigated to generate a rapid sorbate release.

Batch desorption studies revealed that HCl and EDTA wash produced the fastest rate of release of Cu(II) and Pb(II) ions from the biosorbent. Further, equilibrium was attained after 15 and 30 min for Cu(II) and Pb(II) ions respectively using a 0.1 M HCl eluant. Individual and sequential desorption studies revealed that a multi-mechanistic attachment phenomenon controlled the sorption of both Cu (II) and Pb(II) ions whereby 3% of Cu(II) attachment was attributed to physisorption, 26% to ion exchange, and 71% to chemical bonding. Sorption of Pb(II) ions was attributed to 50% ion exchange and 50% chemical bonding. Regeneration studies revealed at least 4 biosorption–desorption cycles were achieved without loss in biosorbent performance. While EDTA washes resulted in a slightly greater increase in biosorbent capacity over that of HCl, the HCl wash produced a safer biosorbent for disposal. Elucidating the biosorption mechanisms and the selection of an effective eluent advances the applicability of this biosorbent for fixed-bed biosorption, regeneration, and the eventual up-scaling of the process.

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