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Adsorption of Pb(II), Hg(II) and Cu(II) ions on Azacrown Ether Grafted Chitosan Films

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ABSTRACT

KEY WORDS

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The adsorption and desorption of Cu(II), Pb(II) and Hg(II) ions from aqueous solutions by porous azacrown ether grafted chitosan films (Ch-DAC) were studied in a batch adsorption system. The porous Ch-DAC films were prepared by hydroamination reaction of azacrown ether activated double bonds with chitosan by changing the proportion of Ch/DAC with 1:0, 1:0.125, 1:0.167, 1:0.25 and 1:0.5 ratios. Characteristics of the films such as pH of aqueous slurry, pH of zero-point charge (pHzpc), surface area and pore volume, energy dispersive X-ray spectroscopy (EDX), Field Emission - Scanning Electron Microscopy (FE-SEM), Fourier transform infrared (FTIR) were investigated. Factors influencing adsorption performance such as pH of the solution, metal ion concentration, adsorbent dosage and the DAC content were studied. Batch studies, investigating film adsorption capacity and adsorption isotherms for Pb(II), Hg(II) and Cu(II) ion adsorption equilibrium correlated well with Langmuir model. The maximum capacity for the adsorption of Pb(II), Hg(II) and Cu(II) ions calculated from the Langmuir isotherm was 256, 200 and 143 mg/g respectively. Compared with the pure non-grafted chitosan films, the azacrown ether films were proved to have better sorption performance for the Pb(II), Hg(II) and Cu(II) ions at pH 5 to 6.

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Introduction

A great number of chitosan derivatives have been obtained with the aim of adsorbing pollutant or precious metal ions by grafting new functional groups on the chitosan backbone. The new functional groups are incorporated with chitosan to increase the density of sorption sites, to change the pH range for metal sorption and to change the sorption sites to increase sorption selectivity for the target pollutant. They may increase the chemical stability of the sorbent in acid media, and especially decrease the solubility in mineral and organic acids, and increase its resistance to biochemical and microbiological degradation (Zhikuan Yang, 2001).

In the case of crown ether modified chitosan derivatives, the complexing properties exhibited towards metal ions is regarded as an interesting process for increasing the sorption properties of chitosan. More interesting are the nitrogen rich azacrown ether macrocyclic polyethers known for their prevalence for soft-metal ions over the all-oxygen crown ethers (Izatt et al., 1985; Yang, Wang, & Tang, 1999). Previously, we have reported on the synthesis, physical, chemical and structural properties of N,N′-diallyl-7,16-diaza-1,4,10,13-tetraoxa-dibenzo-18-crown-6 (DAC) and DAC modified chitosan (Ch) films (Toeri & Laborie, 2016; Toeri, Osorio-Madrazo, & Laborie, 2016, 2017). Composition, structure, and morphology of a series of the azacrown ether crosslinked Ch films were systematically characterized. The crosslinking of Ch with the azacrown ether effectively generated a solid film that could not disintegrate in water and thus is suitable for water remediation. Application of these azacrown ether crosslinked films have not been systematically investigated to establish their performance against adsorption of lead, mercury, and copper ions with respect to variable pH conditions, adsorption dosage, and rate of adsorption. We expect that the modification of Ch with azacrown ether could improve the adsorption capacity for the metal ions due to the nitrogen rich domains contributed by the crown ether cavities. In the present study, we investigate the performance of these derivatives in adsorption of Pb(II), Hg(II) and Cu(II) ions from aqueous solutions of varying pH values ranging from 2 to 7 in a batch adsorption system.

Experimental Procedures

Reagents

Medium-molecular-weight chitosan (77% deacetylated) was supplied by the Sigma-Aldrich Company (Germany) as pale-white powder. The detailed characteristics of the starting chitosan was reported in detail elsewhere (Toeri et al., 2016, 2017). The azacrown ether (DAC) used in this study was synthesized and characterized according Toeri and Laborie (Toeri & Laborie, 2016). All chemical reagents were analytical-grade and were thus used without further purification.

Preparation of azacrown ether crosslinked chitosan films

All chitosan/azacrown ether films used in this study were prepared by solvent casting onto glass plates from reaction mixtures formulated to contain a total solid content of 2 wt% following the procedure by Toeri et al. (Toeri et al., 2016). Five different film formulations were prepared by mixing chitosan (DA 23%) and DAC in molar ratios: Ch:DAC = 1:0, 1:0.125, 1:0.167, 1:0.25 and 1:0.5. In a typical preparation procedure, purified Ch (1.0 g) was first dissolved in deionized water containing 2% (v/v) acetic acid and heated to 40 °C. 5mL of iron(III) chloride hexahydrate solution was added and the mixture was stirred for 15 minutes under nitrogen flow. A required amount of N,N-diallyl-dibenzo-18-crown-6 dissolved in ethanol was slowly dropped into the mixture so that at the end a 2 wt% solid content was achieved. The resulting mixture was then refluxed at 40 °C under continuous stirring for 24 h, followed by addition of 5 mL H_2O_2 solution. After the reaction was completed, 10 mL aliquots were transferred onto cylindrical glass Petri dishes (50mm W × 10mm H, Pyrex, USA) and dried in air for two days followed by oven drying at 60 °C for 24 h. The films were peeled off the glass plates and neutralized by immersion in a $NaHCO_3$ solution. Then, they were washed to pH 7 to give pale white products. The wet films were extracted with ethanol in a Soxhlet extractor for 4 h to eliminate any unreacted crown ether before drying. Five formulations designated as Ch-DAC(0), Ch-DAC(0.125), Ch-DAC(0.167), Ch-DAC(0.25) and Ch-DAC(0.5) based on increasing DAC mole ratio to one mole of Ch, were manufactured.

Characterization techniques

The pH of the zero point of charge (pH_{zpc}) of chitosan and modified chitosan films was determined by the immersion technique, also called pH drift method (Noh & Schwarz, 1989), which is defined as the pH at which the net surface charge becomes zero (Balistrieri & Murray, 1981). An electrolyte solution of 0.01 M $NaNO_3$ was boiled to remove CO_2 and then cooled to room temperature. A series of 50 mL of the solution was placed in closed Erlenmeyer flasks and the pH adjusted to a value between 2 and 12 by adding a solution of 0.5 M HNO_3 or 0.5 M NaOH solution. Then 0.1 g of each Ch-DAC sample was added and agitated at 150 rpm for 24 h under N_2 gas. The final pH was measured by a pH electrode after 24 h. The results were plotted as ΔpH against initial pH (Wan Ngah & Hanafiah, 2008).

Energy dispersive X-ray spectroscopy (EDX) and Field Emission - Scanning Electron Microscopy (FE-SEM) was used to determine the existence of metal ions in the films and their surface condition after adsorption. Several film samples were removed from their solutions and gently rinsed with DI water. They were dried at 60 °C for 12h before measurements to obtain the EDX spectra and FE-SEM micrographs.

IR spectra analysis was employed to confirm changing of functional groups for the free and modified chitosan films. Infrared spectra were recorded with a Spectrum 65 Instrument (Perkin Elmer, Waltham, MA, USA) using 32 scans at a resolution of 2 cm^{-1}.

Adsorption procedures

The batch method was used to perform the adsorption experimental studies in 250-mL LDPE bottles at 22 – 23 °C. A batch of 24 – 36 sample bottles were settled on a VWR ADV 3500 Advanced Digital Shaker (Darmstadt, Germany) in an "Orbital shaking-tank process" with a shaking speed of 150 rpm for several contact hours as mentioned in section 2.4.1. Stock solutions (1000 mg/L) of Hg(II), Pb(II) and Cu(II) metal ions were obtained using analytical grade copper(II) nitrate trihydrate; $Cu(NO_3)_2 \bullet 3H_2O$, lead(II) nitrate; $Pb(NO_3)_2$ and mercury(II) nitrate monohydrate; $Hg(NO_3)_2 \bullet H_2O$ as purchased from Sigma-Aldrich, Germany. All glassware was rinsed in 0.1 M HCl before each experiment to avoid the ions binding to glass walls. To determine the optimum adsorption values for pH of solution, contact time, solution concentration and sorbent dosage, several preliminary experiments were performed.

Effects of pH and contact time

To study the effect of pH and contact time on the adsorption characteristics of the films, two experiments were conducted. The first was to investigate natural pH change of the metal ion solutions contacting the films with time during adsorption and the adsorption capacity under uncontrolled solution pH. The initial pH of the solutions remained uncontrolled during this adsorption process. After adsorption, the solution equilibrium pH (pH_{eq}) was measured with a pH electrode. The second was to investigate the effect of fixed pH of the metal ion solution on the adsorption capacity. The acidity level of the solutions was adjusted to pH values of 2 – 7 using drops of 1.0 M HNO_3 and NaOH solutions and monitored with a pH electrode. In each experiment, a dosage of 2g/L adsorbent was mixed with 100 mg/L metal ion solution of 100 mL. The bottles were settled on a shaker and agitated at 150 rpm for several contact hours from 1 to 24h.

Effects of adsorbent dosage and initial solution concentration

To investigate the dependence of metal ion adsorption on sorbent dose equilibrium adsorption capacity, certain dosage ranging from 0.2 to 40 g/L of adsorbent was mixed with initial metal ion concentration of 100 mg/L and agitated for 24 hours. The initial concentration of metal ion solution was varied between 5 and 800 mg/L for batch isotherm studies. The experiments were performed at the predetermined optimum pH-value of 5.0 for copper and mercury and 6 for lead. After each adsorption process was complete, adsorption (%) which is the percentage of metal ion adsorbed on the film related to the quantity present at the beginning of the test was calculated by Equation **1** while the adsorbed-phase concentration (metal ion uptake capacity (Q_e), was calculated by Equation **2** (OECD, 2000).

$$Adsorption\ (\%) = \frac{(C_0 - C_e)}{(C_0)} \times 100 \qquad (\mathbf{1})$$

$$Q_e = \frac{(C_0 - C_e) \cdot V_0}{m_{film}} (mg\ g^{-1}) \qquad (\mathbf{2})$$

where:

C_o (mg/L) represents the initial concentration of metal ion, C_e (mg/L) represents the metal ion concentration after adsorption, $V_0(L)$ is the volume of the solution, and m_{film} is the mass (g) of the adsorbent. Q_e (mg/g) is the adsorption amount of metal per gram of adsorbent.

Analysis

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and UV-Visible spectroscopy techniques were employed to measure the residual metal ion concentration in the solutions. Copper(II) and lead(II) ion concentrations were measured with Spectro ICP-AES Ciros CCD. 380 V. instrument. Mercury(II) ion concentration was measured with UV-Visible spectrophotometry, as described by Snell (1959, p. 39) and later used by others (Vieira & Beppu, 2006). The method involves the formation of a mercury thiocyanate complex $\{Hg(CNS)_4^{2-}\}$ whose electronic absorption band is 297 nm. The complex was formed by adding 5 mL of NH_4SCN solution (5% w/w) in 5 mL of initial solution, followed by dilution to 100 mL before measurement.

Reusability test procedure

The reusability of the Ch-DAC sorbent samples was assessed by repeating the sorption-desorption cycling test five times. Each adsorbate film of 1 g/L dosage was immersed in 100 mL of 100 mg/L metal ion solution and agitated at 150 rpm for 24h. The residual metal concentration was measured as mention before. The adsorbed metal ions were desorbed from the sorbent using 0.5 mol/L HCl (10 mL), and then the amount of metal ions was determined again after each sorption-desorption cycle. To use sorbent in the next cycle, the sorbent was washed several times with DI water and dried at 60 °C for 24 h. The desorption (%) was calculated by using Equation 3.

$$Desorption\ (\%) = \frac{(C_d - C_e)}{(C_0 - C_e)} \times 100 \qquad (\mathbf{3})$$

where C_0 and C_d are the initial concentration (mg/L) and desorption equilibrium concentration (mg/L), respectively.

Results and discussion

Characterization results

The surface conditions of the films under Field Emission - Scanning Electron Microscopy (FE-SEM) before and after adsorption, showed evidence of metal ion adsorption. **Figure** 1 represents the typical FE-SEM micrographs of a Ch-DAC (0.167) film before and after adsorption of Pb(II) ions at pH 2 and 6 respectively. As shown in **Figure** 1(a), the surface is clear, and uniform micropores are observable at 500μm magnification (detailed pore characterization is given in **Table 2**). However, **Figure** 1(b) shows metal ion dense part on the surface of the Ch-DAC (0.167) film after adsorption of lead ions at pH 2; while **Figure** 1(c) is the same film after adsorption of lead ions at pH 6. The micrographs obtained indicate that a significant increase in lead ion adsorption occurred at higher pHs, especially that of pH 6. The micrograph also shows that the surface condition on the Ch-DAC film remained somewhat swollen after the contact with lead ion solution. Similar observations were made with mercury and copper adsorbed films (**Figure 2**).

The EDX analysis was employed to confirm whether the surface of the azacrown ether chitosan films was composed of copper, lead and mercury ions. EDX spectra of neat chitosan film and some metal ion-adsorbed films are presented in **Figure** 3(a – g). As presented in **Figure** 3(a), in the case of neat azacrown ether chitosan films, the characteristic peaks of respective metal ions did not appear. However, peaks for carbon, oxygen and nitrogen all belonging to the sorbent material appeared. In the case of metal ion-adsorbed films (**Figure** 3(b – g)), the peaks for copper, lead and mercury ions were clearly exhibited. Their relative intensities were found to change with respect to varying azacrown ether content and pH of the adsorbate.

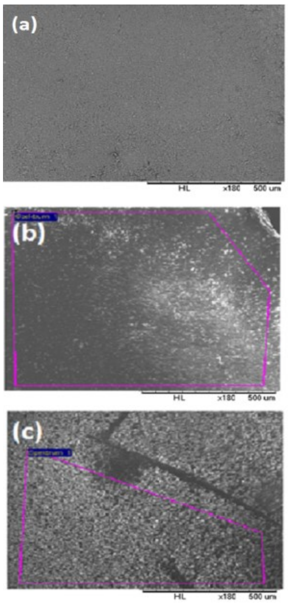


Figure 1. *FE-SEM photograph of Ch-DAC (0.167) azacrown ether-chitosan films: (a) before adsorption of lead ions; (b) after adsorption of lead ions at pH 2; and (c) after adsorption of lead ions at pH 6.*

Mole ratio used	S_{DR} (m^2g^{-1})	V_t (cm^3g^{-1})	V_{micro} (cm^3g^{-1})	pH_{zpc}
1:0	0.7634	0.00051	0.00027	7.64
1:0.125	3.0036	0.00210	0.00110	7.43
1:0.167	4.2325	0.00250	0.00150	7.13
1:0.25	3.8456	0.00260	0.00140	6.00
1:0.50	3.2597	0.00190	0.00120	5.50

Table 1. *Physical characteristics of Ch-DAC films as a function of the DAC content.*

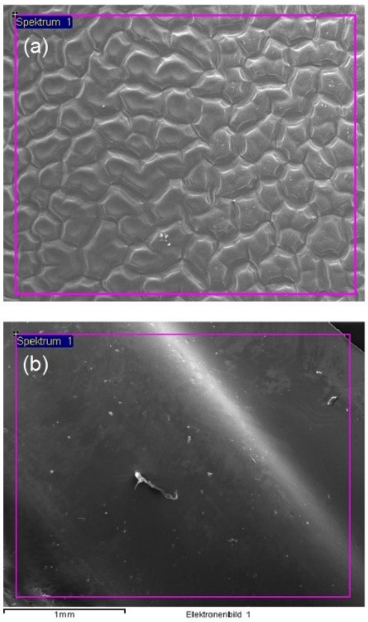
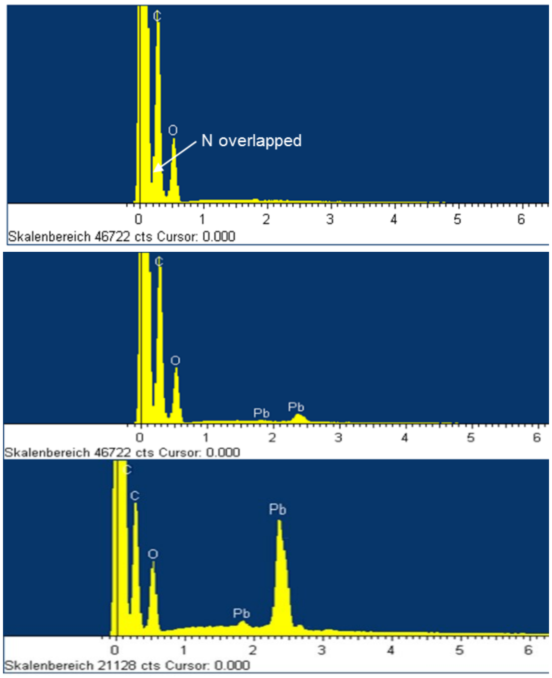


Figure 2: *Examples of metal adsorbed Ch-DAC films (a) copper adsorbed Ch-DAC film (b) mercury adsorbed Ch-DAC film.*



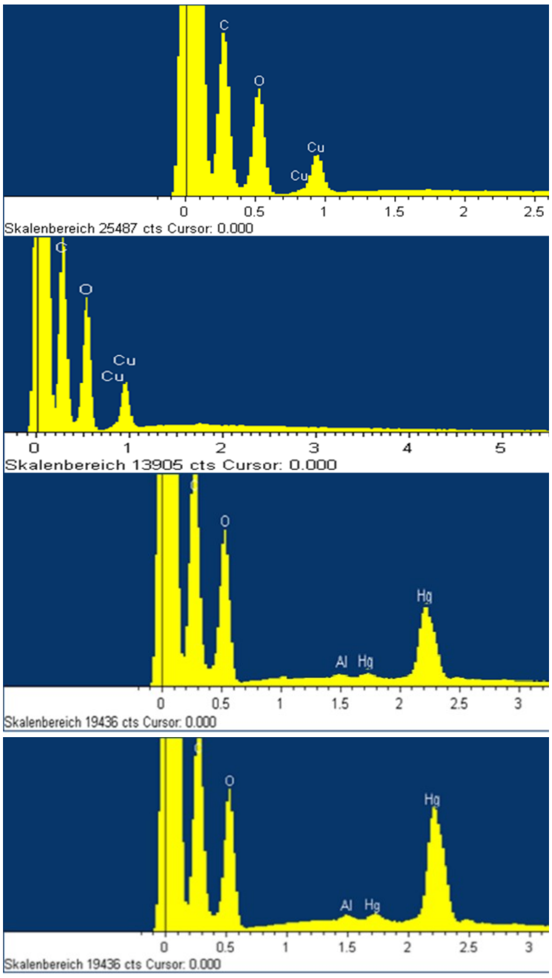


Figure 3: *EDX spectra of (a) neat chitosan film and (b) – (g) some metal ion-adsorbed films.*

Zero-point charge (pH_{zpc}) analysis

Before adsorption of metal ions was carried out, the surface charge of the azacrown ether films was quantified by zero-point charge or isoelectric point (pH_{zpc}) determined by drift method (Noh & Schwarz, 1989). The method can be used to determine the pH at which the adsorbent surface has net electrical neutrality. It also influences the pH at which cations are favorably adsorbed, which is normally higher than the pH_{zpc} (Noh & Schwarz, 1989). **Figure** 4 depicts the pH_{zpc} values obtained. The neat chitosan films exhibited the highest pH_{zpc} value of 7.6 and as the DAC content increased in the Ch-DAC films, pH_{zpc} decreased up to 5.50. The values found ranged from 7.6, 7.4, 7.1, 6.0, 5.5 for Ch-DAC film ratios 1:0, 1:0.125, 1:0.167, 1:0.25 and 1:0.5 respectively. The reducing values of pH_{zpc} of the studied materials puts into evidence that, incorporating azacrown ether into chitosan decreases the pH at which positively charged metal ions are adsorbed. Since, the knowledge of pH_{pzc} allows one to hypothesize on the ionization of functional groups and their interaction with metal species in solution; at solution pHs higher than pH_{pzc}, sorbent surface is negatively charged and could interact with metal positive species while at pHs lower than pH_{pzc}, solid surface is positively charged and could interact with negative species increasing competition for ions.

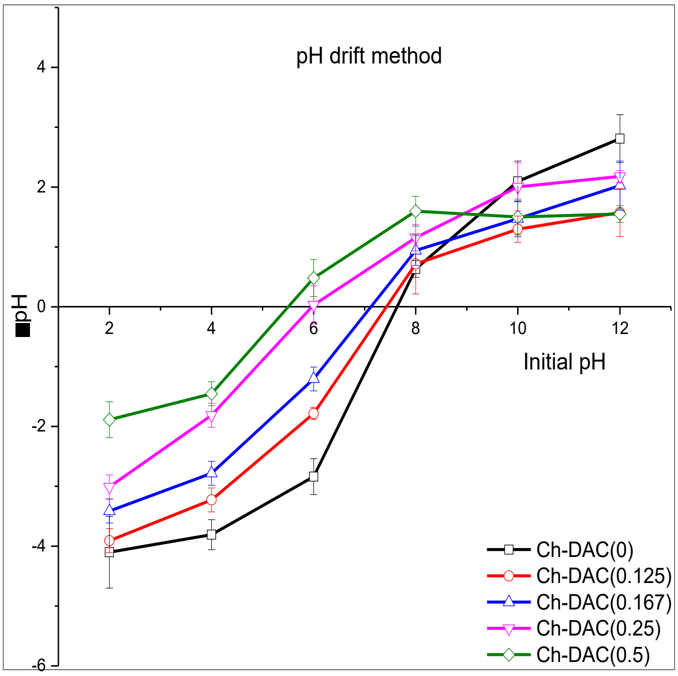


Figure 4. *The change in pH (ΔpH) which results from adding Ch-DAC samples to dilute NaCl solutions of different pH levels is monitored as a function of the initial pH.*

Infrared analysis

The FTIR spectroscopy technique can be used for chemical characterization of the sorbents and to identify probable attractions between the metal ions and functional groups on the sorbent surface. **Figure** 5a & b shows FTIR spectra of free Ch and the Ch-DAC (0.125) and Ch-DAC (0.25) sorbents before and after mercury sorption. The band observed at 3539 cm^{-1} of spectra (iii) and (iv) whose samples contained DAC content of 0.125 and 0.25 mol/mol Ch respectively verifies an interaction between mercury ion and crown ether fragment. In the absence of Hg^{2+}, sample Ch-DAC (0.25) with DAC content of 0.25 did not exhibit this band (spectrum (i)); likewise sample

$Hg^{(2+)}$-Ch-DAC(0) with DAC content of 0 too did not (spectrum (ii). The Ch amine peaks recorded in the range of 1655 – 1642 cm^{-1} (amide I), 1596 – 1590 cm^{-1} (free -NH_2 and 1396 – 1378 cm^{-1} (amide III) become broad and exhibit a shift in the Hg-sorbent complex. This result showed that the amine functional groups of Ch-DAC surface are involved in binding the metal ions. Similarly, spectra for Pb^{2+}-Ch-DAC and Cu^{2+}-Ch-DAC complexes exhibited the same results. They too verify the binding interaction between DAC and the amine groups of Ch with the ions.

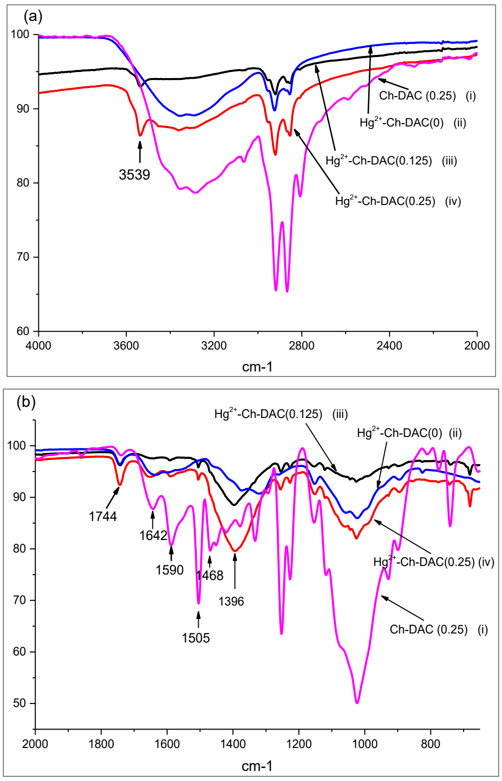


Figure 5. *Representative FTIR spectra of raw Ch and Ch-DAC sorbents before and after sorption of (Hg(II) ions.*

Adsorption

Changes in the initial solution pH during adsorption

The effects of adsorption on the pH changes of metal ion solution contacting the Ch-DAC films was investigated with time by allowing adsorption process to take place at uncontrolled initial pH. The initial pH of the solutions before immersion of films was ~3.4 (Hg^{2+} solution) ~4.98 (Pb^{2+} solution), ~5.6 (Cu^{2+} solution), and ~6.7 (free DI water). As shown in **Figure** 6(a) – (d), pH increases initially and then levels off to an equilibrium. The pH changes for lead (~4.98 – 6.5) and mercury (~3.4 – 5.4) showed a larger pH drift and reached equilibrium within 5 hours, but for copper (~5.6 – 6.4), equilibrium was reached after 10 hours. An increase in pH during adsorption indicates a decrease in cation concentration in the solution due to the uptake by sorbent active sites and may suggest ion-exchange mechanism for adsorption of protons and metal cations. The pH of metal solutions at which the adsorption is conducted is a major parameter controlling metal adsorption processes (He et al., 2010; Tokalıoğlu, Yılmaz, Kartal, Delibaş, & Soykan, 2009). Solution pH, together with the pH_{pzc} of the material determine the level of electrostatic or molecular interaction between the adsorbent and the adsorbate owing to charge distribution on the material. In the previous work, Juang and Shao (Juang & Shao, 2002) also reported a rise in the pH of copper(II) ion solution after metal sorption with glutaraldehyde crosslinked chitosan beads. Jeon and Höll (Jeon & Höll, 2003) also measured a pH increase during Hg(II) adsorption on aminated chitosan beads. When the Ch-DAC films in this work were contacted with distilled water at the initial pH of 6.7 (**Figure** 6(d)), the pH also rose slightly to about 7.2. Thus, this confirmed that adsorption of hydrogen ions from water into the film's active sites is possible. Alternatively, the films might release some negative ions into water causing the rise in pH.

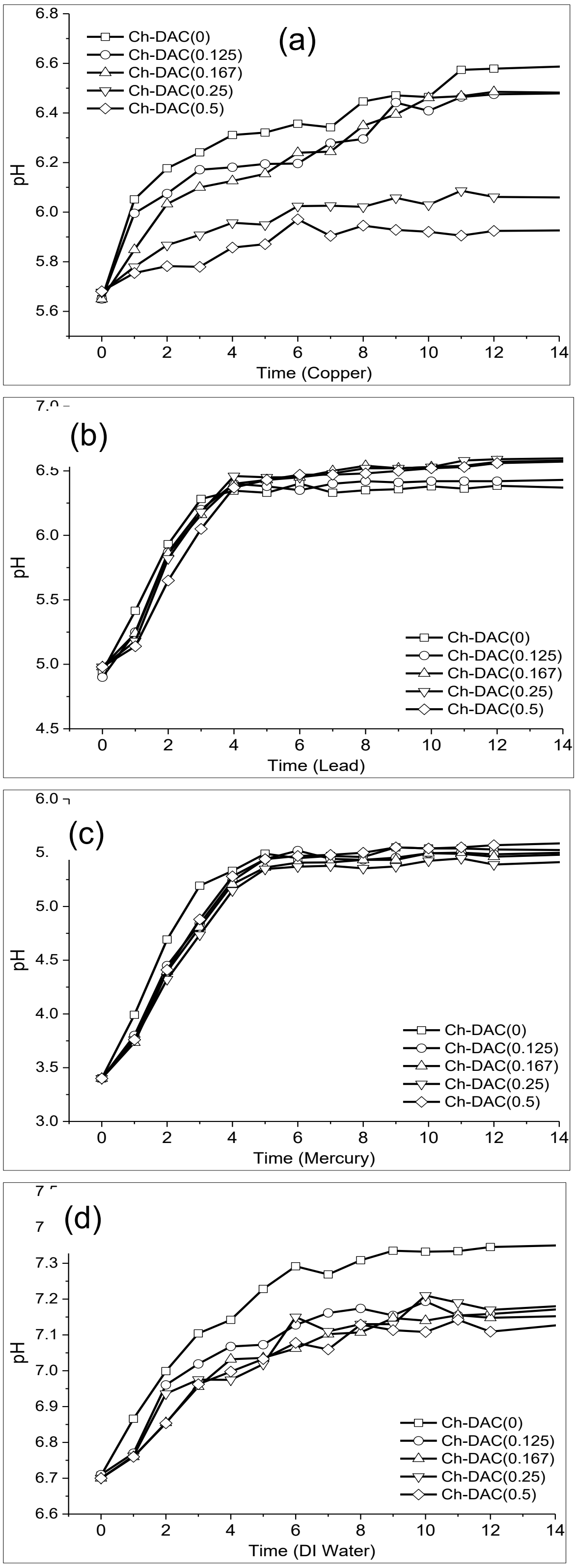


Figure 6(a-d). *pH changes with time for all the Ch-DAC films in 100 mL g⁻¹ metal solutions and in water (adsorbent dose, 1 g/L; shaking speed, 150 rpm; 23 °C).*

Effects of equilibrium pH (pHeq) on adsorption capacity

The effects of equilibrium pH (pH_{eq}) on the amounts of sorption of Pb^{2+}, Hg^{2+}, and Cu^{2+} on Ch-DAC films are shown in **Figure** 7. To measure the influence of the azacrown ether presence in the Ch films on adsorption capacity, the initial pH was left uncontrolled until reaching equilibrium. It is found that the adsorption capacity is significantly improved by the presence of the azacrown ether in the chitosan films compared to neat chitosan films. Under comparable conditions (e.g., molar equivalent DAC content), Ch-DAC (0.5) samples exhibit the highest sorption ability for all metal ions (73% for Mercury, 60% for Lead, and 75% for Copper). In summary, as the DAC content increased, so was the adsorption capacity ranging from 55 – 73% for Mercury, 46 – 60% for Lead, and 62 – 75% for copper. It is also found that as adsorption capacity increased with increasing DAC content, the pH_{eq} also rose for mercury and lead solutions. This is due to competitive sorption of proton and metal ions, which was supported by experiments that the solution pH becomes higher after metal sorption. But it was not the case for copper solutions. As the DAC content increased, pH_{eq} decreased, suggesting that there could be a different adsorption mechanism for copper ions as compared to lead and mercury.

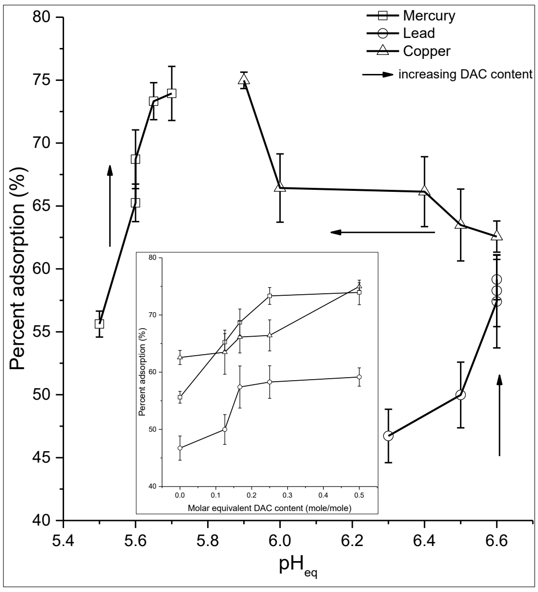


Figure 7. *Effect of equilibrium pH on the adsorption capacities (% removal) of Ch-DAC films for Cu(II), Pb(II) and Hg(II) ions with uncontrolled initial pH solution (100 mL, 200 mg/L, 0.1 g adsorbent dose, 24h contact time).* ***Inset****: equilibrium adsorption capacities of the films as a function of DAC content under the same conditions.*

3.1.1 Effect of solution pH on adsorption capacity

The effects of pH on amounts of sorption of Hg(II), Pb(II), and Cu(II) ions on Ch-DAC films was further investigated by holding the pH constant over several pH values from 2.0 to 7.0 to find the optimum pH for adsorption. As shown in **Figure** 8 (a) – (c), at pH = 2 the adsorbents presented their lowest metal uptake for all formulations (mostly between 40 and 60%), while at pH = 4 the corresponding values improved slightly to about 60 to 70%. Under acidic condition, there is reversal of charge as chitosan (strong base) favors high numbers of hydrogen (H^+) ions thus causing competitive adsorption. It is found that mercury ions (82-89%), lead ions (83-93%) and copper (~95%) were the highest adsorbed species by most of the Ch-DAC film formulations at pH 5-6. Copper adsorption experienced a significant reduction at pH value above 6 (67-81%). At higher pH values, the ions tend to precipitate, especially Cu(II) (pH>6) and Hg(II) (pH >7) thus negatively affecting the sorption process. It is therefore necessary to avoid such pH values near the zone of precipitation where the metal ions turn colloidal e.g. $Hg(OH)_2$ (s). In all pH values studied for pure Ch films, lowest uptake percentage was recorded confirming that the presence of crown ether improved adsorption capacity. As per the above experimental findings, the optimum pHs were therefore estimated to be ~5-6 for mercury, 6 for lead, and 5 for copper.

Previous work indicated that proper pH adjustment leads to an increase in metal sorption capacity in chitosan adsorbents (Fiol & Villaescusa, 2009; Jeon & Höll, 2003; Kyzas & Deliyanni, 2013). The amount of metal adsorbed may decrease with a further increase or decrease in pH from the optimum as shown in **Figure** 8. This is because the uncoordinated groups such -OH on chitosan chains become -O- at high pH, leading to an increase in degree of "solubilization" of metal-sorbent complex (Juang & Shao, 2002). Such behavior is more apparent at lower DAC content because of the larger amount of the uncoordinated -OH groups on the chitosan films.

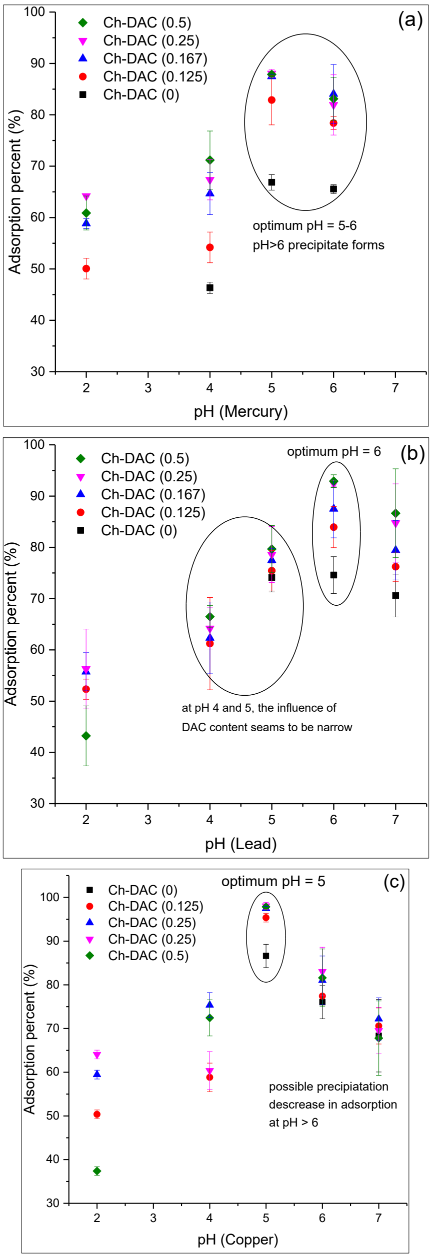


Figure 8. *Effect of pH on the adsorption capacities (% removal) of Ch-DAC films for: (a) Cu(II), (b) Pb(II) and (c) Hg(II) ions (100 mL, 100 mg/L, 0.1 g adsorbent dose, 24h contact time).*

Effect of adsorbent dosage

Once the optimum adsorption pH of the metal ions was established for each film sample, the effect of adsorbent dosage on the adsorption (%) was obtained by changing it from 0.05 to 3 g/L at 22-23 °C, a pH value of 5 with a representative Ch-DAC (0.167) film sample. As observed from **Figure** 9, the increase in the adsorption (%) continued until the maximum adsorption was approached near 2 g/L of sorbent. Above this value, adsorption (%) remains nearly constant. Increasing the sorbent dose caused an increase in the ratio of sorbent weight (solid phase) per solution volume, so the adsorption (%) increased. This translates to removal efficiency of about 88% for lead, 93% for copper and 95% for mercury. However, increasing the sorbent dosage beyond 3 g/L against the original solution concentration of 100 mg/L did not result in a remarkable improvement in metal ion adsorption. This could imply that the adsorption method may not 100% remove all the metal ions from dilute solutions. It can therefore be suggested that there may be room for further method improvements such as incorporating column filtration in addition to stir-tank method in case of very dilute solutions.

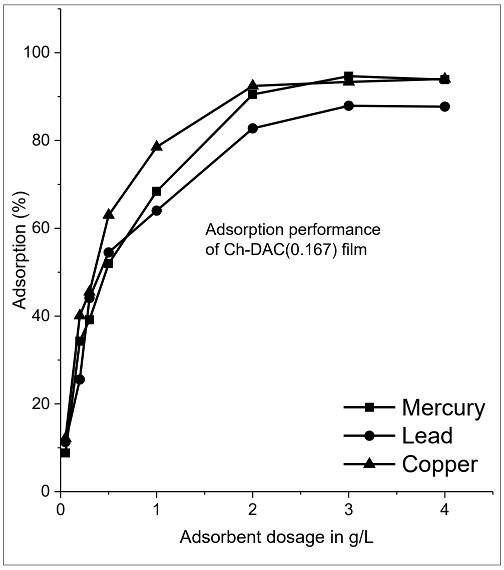


Figure 9. *Effect of sorbent dosage on the sorption of Hg(II), Pb(II) and Cu(II) onto the Ch-DAC (0.167) sorbent film (initial metal ion concentration: 100 mg/L; pH 5*

Sorption isotherm models

Under optimum pH value of 5, further adsorption studies were performed for different metal concentrations to determine the adsorption isotherms for each metal ion. The equilibrium concentrations in the solution were determined and the amount adsorbed was calculated from the depletion of the metal ion in the solution. The Langmuir adsorption isotherm equation which relates the amount of the test substance adsorbed to the concentration of the test substance in solution at equilibrium was used to calculate the content of the metal ion adsorbed on the films after the adsorption test. The work involved altering the initial concentration of the solution in the range of 5 – 800 mg/L under the optimized batch conditions. The adsorbed mass per unit mass of sorbent was plotted as a function of the equilibrium concentration of the metal ion according to the OECD Guidelines for the Testing of Chemicals (OECD, 2000). The adsorption equilibrium data for Cu(II), Pb(II) and Hg(II) ions were analyzed with the linear form of Langmuir adsorption isotherm per **Equation** 4. Linear plots were obtained where values of Q_m and K_L were calculated from the slope and intercept of the Ce/Qe versus Ce plots (**Figure** 10(a) – (c).

It was observed that in all the experiments, DAC grafted films exhibited superior percent removal when compared to neat chitosan adsorbents (**Figure** 10(a-c). The maximum sorption capacities (Q_m) of raw Ch for Hg maximum sorption capacities (Q_m) of raw Ch for Hg(II), Pb(II) and Cu(II) ions were calculated as 100 mg/g, 130 mg/g and 116 mg/g, respectively. **Table 2** also shows the maximum sorption capacities for Ch-DAC sorbents. It is observed that the maximum sorption capacities significantly increased as compared to the raw Ch sorbents. As the DAC content increased so did the sorption capacities (**Figure** 11). The highest sorption capacity was associated with the Ch-DAC (0.5) for both lead (256 mg/g) and copper (143 mg/g) metals while mercury had the highest Q_m (200 mg/g) for Ch-DAC (0.167). The results suggest that incorporation of azacrown ether onto chitosan improved the equilibrium sorption capacity two-fold compared to raw chitosan.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{K_L Q_m} \qquad 4$$

where Q_e (mg/g) and C_e (mg/L) are the equilibrium metal concentrations in the solid and liquid phase, respectively, and Q_m (mg/g), and K_L (L/g) are the Langmuir constants related to the saturation adsorption capacity and binding energy (affinity), respectively.

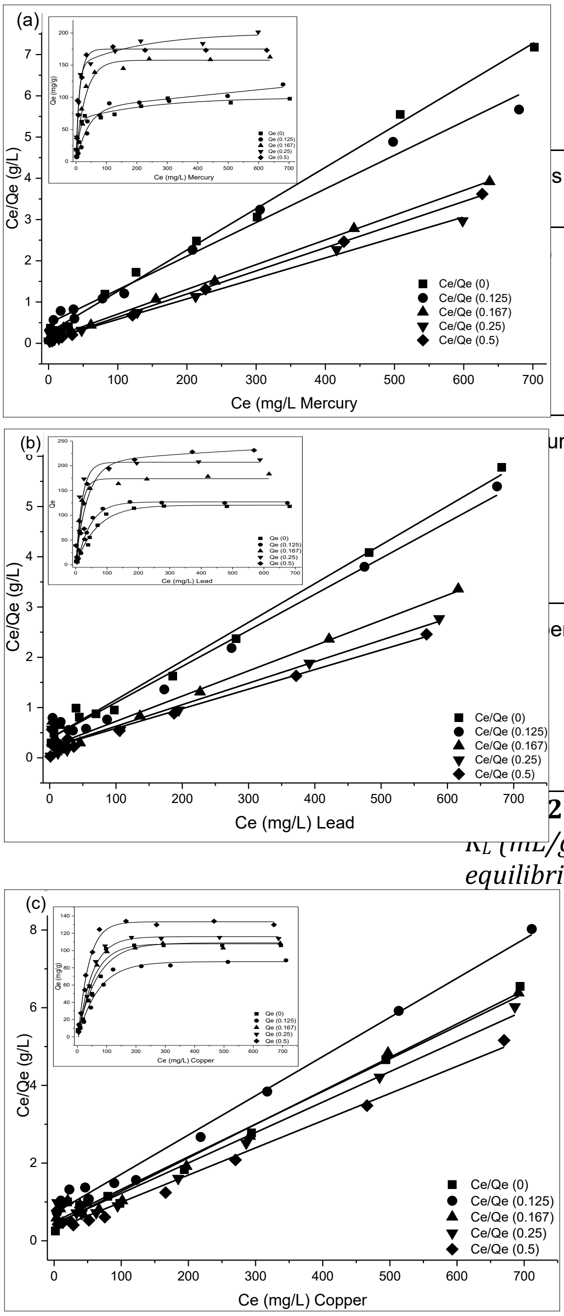


Figure 10. *Nonlinear and Linear Langmuir isotherm plots obtained for the sorption of (a) Hg(II), (b) Pb(II) and (c) Cu(II) onto raw Ch, and Ch-DAC sorbents.*

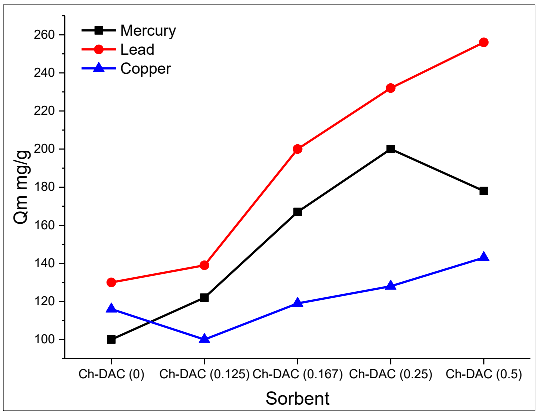


Figure 11. *Langmuir isotherm saturation adsorption capacity for mercury, lead and copper*

s	Films	Langmuir		
		Qm (mg/g)	K_L (mL/g)	R^2
	Ch-DAC (0)	130	0.020	0.99
	Ch-DAC (0.125)	139	0.019	0.98
	Ch-DAC (0.167)	200	0.022	0.98
	Ch-DAC (0.25)	232	0.021	0.94
	Ch-DAC (0.5)	256	0.020	0.96
ury	Ch-DAC (0)	100	0.039	0.99
	Ch-DAC (0.125)	122	0.017	0.98
	Ch-DAC (0.167)	167	0.055	0.99
	Ch-DAC (0.25)	200	0.059	0.99
	Ch-DAC (0.5)	178	0.076	0.99
er	Ch-DAC (0)	116	0.021	0.99
	Ch-DAC (0.125)	100	0.014	0.99
	Ch-DAC (0.167)	119	0.017	0.98
	Ch-DAC (0.25)	128	0.018	0.98
	Ch-DAC (0.5)	143	0.024	0.98

2. *Linear Langmuir isotherm parameters Q_m (mg/g), K_L (mL/g) and correlation coefficient (R^2) for the adsorption equilibrium capacity of raw Ch and Ch-DAC sorbents.*

Reusability performance

High repeated availability is important for an adsorbent to significantly reduce overall adsorption cost. This can be estimated by the extent of the recovery of metal ions adsorbed from wastewaters by means of the sorption-desorption cycling studies. As seen from **Figure** 12, after five cycles, the adsorption (%) decreased from 89 to 62 for mercury, 93 to 54 for lead and 95 to 46 for copper. The efficiency of desorption (%) decreased from 86 to 62 for mercury, 88 to 54 for lead, and 93 to 46 for copper. In general, the data obtained in this study indicate that the Ch-DAC sorbents can be used up to five cycles before their sorption efficiency decreases to about 50%.

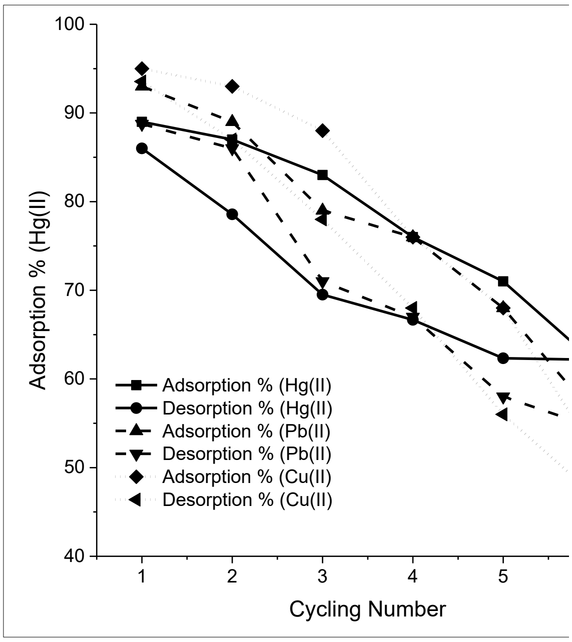


Figure 12. *Plots of adsorption-desorption data for the evaluation of reusability of Ch-DAC sorbents for the sorption of Hg(II), Pb(II) and Cu(II).*

Conclusions

A novel azacrown ether crosslinked chitosan (Ch-DAC) sorbents were prepared and characterized by using EDX, FE-SEM, zero-point charge analysis, and FTIR techniques. The Ch-DAC sorbents were successfully applied as novel biocomposite sorbent for the removal of the Hg(II), Pb(II) and Cu(II) ions from aqueous solution using the batch method. The experimental parameters that influenced the adsorption (%) include azacrown ether content, pH of the metal solution and metal ion concentration. The Langmuir monolayer sorption capacities of the raw chitosan for Hg(II), Pb(II) and Cu(II) was 100 mg/g, 130 mg/g and 116 mg/g respectively. Treatment of Ch with azacrown ether improved the sorption capacities to between 122 – 200 mg/g for Hg(II), 139 – 256 mg/g for Pb(II) and 100 – 143 mg/g for Cu(II) respectively. This meant that the modified sorbents improved the Ch adsorption performance by about two-fold within four to five hours of adsorption. The prepared Ch-DAC sorbents could remain stable in acid pH solutions. They were also able to be recovered successfully by using 0.5 mol/L HCl solution and had good reusability. The Ch-DAC biocomposite materials prepared demonstrate that use of azacrown ether to crosslink Ch is a potential method to improve adsorption of heavy metals from aqueous solutions.

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Declaration

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