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Removal of Cu (II) and Cd (II) Ions from Environmental Water Samples by Using Cellulose Acetate Membrane

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Abstract

Cellulose Acetate Membrane (CAM) which has been prepared by using a casting technique was utilized as an adsorbent for heavy metal ions adsorption. The CAM was characterized by Field Emission Scanning Electron Microscopy (FESEM), BET surface area (BET) and Fourier Transform Infrared Analysis (FTIR). The adsorption of Cu (II) and Cd (II) ions on CAM were investigated. The influences of several variables such as pH, adsorbance dosage, initial metal concentration, kinetic parameter, desorption and reusability on the adsorption capacity of the CAM was investigated in a batch adsorption mode. The adsorption capacity increased with the increasing of initial concentration of Cu (II) and Cd (II) solutions and followed the Freundlich model and pseudo second order kinetic mechanism. Desorption of metal ions was accomplished with 1 M Sulphuric acid and Hydrochloric acid solution for Cu (II) and Cd (II) ions. The adsorption capacity did not change significantly in reusability study when three adsorption experimental cycles were conducted. In conclusion, CAM is possible to be used as an alternative adsorbent for the removal of heavy metal ions from environmental water samples.

Keywords: Heavy metal ions; Cellulose acetate; Membrane; Adsorption studies

Introduction

Heavy metals like copper ion and cadmium ion are among the most toxic types of water pollutants and these metals are risky to the surroundings and human health when they are emitted tremendously to the environment [1]. Pollution from heavy metals is one of the main sources of contamination in environment [2]. One of the environmental pollution was water pollution caused by untreated released of effluent by industries like mining operations, paper industries, fertilizer industries, batteries, pesticides galvanizing plants and thermoplastics [3]. Due to these reasons the removal of heavy metal ions in environmental water samples is one of the best significant areas of the analytical chemistry [4]. Thus, treatment of environmental water samples containing heavy metals has become essential in order to increase the quality of water.

Many treatment processes that have been used to remove heavy metal ions from environmental water samples include ion exchange, membrane filtration, chemical precipitation, adsorption and reverse osmosis [5]. Adsorption is preferred as an economic and effective method for heavy metal ions removal since most of these methods are suffer from high cost. Adsorption is used for water purification in many industries due to its availability of different adsorbents, applicability on large scale, easily handling, high efficiency and possible low cost.

Activated carbon is commonly used in adsorption. Many low-cost adsorbents have been used to remove heavy metal ions as to avoid the high cost of activated carbon such as rice husk ash [3], wood sawdust modified sugarcane bagasse [6], waste biomass, chitosan [7] and cellulose acetate membrane [8]. CAM is one of the good sorbent since it is low cost and renewable. Moreover CAM has comparatively high modulus, tensile strength and adequate flexural and is a micro dispersion sorbent which enhance the capability to adsorb the heavy metal [8] as CAM is grafted with functional groups such as $-OCOCH_3$ and –OH groups, so that CAM can bond with heavy metal ions through surface complexation mechanisms [9]. The aim of the study was to explore the possible use of the CAM for the removal of Cu (II) and Cd (II) ions from environmental water samples. Batch experiments were conducted to examine the Cu (II) and Cd (II) ions adsorption efficiencies for CAM and further investigate the effects of various parameters such as pH, adsorbance dosage, initial metal concentration, kinetic parameter, desorption, accuracy and precision and reusability on the adsorption of ions onto the adsorbent. The obtained results showed that the CAM could be used as an alternative adsorbent for the removal of Cu (II) and Cd (II) ions from environmental water samples.

Materials and Methods

Materials

Cellulose acetate which in the form of white powders was purchased from Sigma-Aldrich (Pty.) N,N-dimethylformamide (DMF), acetone and methanol were all analytical grade supplied by R&M chemicals and were used as received. Copper and Cadmium standard solution were analytical grade from Merck and were used to prepare the heavy metal ion solutions for adsorption experiments. All the metal ion

solutions and standards were prepared using distilled water. The pH value of the solution was adjusted with 0.1 M H_2SO_4 or NaOH solutions prior to mixing with the adsorbent.

Preparation of Cellulose Acetate Membrane (CAM)

CAM was prepared by mixing 1 g of cellulose acetate (CA) with 15 ml of a mixture of acetone and dimethyl formamide (DMF) with 2:1 ratio. Then, 2 ml of the mixture were casting on a glass plate forming a membrane. The membrane was left to evaporate and dry at room temperature for 30 minutes. The resulting membrane was peeled using distilled water. After the process, the membrane was ready to use and stored in a dry place.

Characterization of Cellulose Acetate Membrane (CAM)

The morphology of the CAM was observed by using a Perkin Elmer FTIR spectrometer, Spectrum 100. Pressure was applied to a solid sample on the universal diamond top-plate, Attenuated Total Reflectance (ATR) to produce spectra. CAM was snapped in a liquid nitrogen environment to produce enlarged images and also obtain surface morphology of the adsorbent using FEI NOVA NANOSEM 230. The samples were coated with gold or gold palladium on the surface with an extremely thin layer (1.5-3.0 nm). The electrical voltage was controlled below 10 kV to prevent possible collapse of the samples. The specific surface area of the CAM was measured at liquid nitrogen temperature using a nitrogen adsorption desorption instrument (BELSorp Mini II).

Adsorption studies

Batch adsorption experiments were carried out to determine the adsorption capacity of CAM towards Cu (II) and Cd (II) ions adsorption. A fixed size (4 cm^2) of CAM which weighed (0.012 g) was utilized in order to calculate the adsorption constant using different isotherms. Adsorption measurements were carried out at room temperature. 35 ml of 5 ppm Cu (II) and Cd (II) ions solutions were used. The membrane (0.012 g) was added to vial that contained 5 ppm of Cu (II) ion in 35 ml solution and was stirred for 15 minutes. The initial and final concentrations of the solutions measured were determined by FAAS at the maximum adsorption wavelength and the adsorption capacities of the adsorbent were calculated [1]. After equilibrium was attained, the adsorption and metal uptake capacity for each sample was calculated by using the equation below:

$$q_e=(C_o-C_e)/M \times V \quad [1]$$

The percentage of removal of heavy metal ion from the solutions was calculated by the following equation.

$$\% \text{ Removal}=(C_o-C_e)/C_o \times 100 \quad [2]$$

Where q_e is the amount of metal ion adsorbed at equilibrium (mg g^{-1}), V is the volume of the heavy metal solution (L) and M is the mass of adsorbent (g). C_o (mg L^{-1}) is the initial metal ion concentration and C_e (mg L^{-1}) is the final metal ion concentration in the solution.

The similar procedures were repeated by using 5 ppm of Cd (II) ion sample solution.

Desorption, accuracy and precision and reusability study

0.035 g (9 cm^2) and 0.012 g (4 cm^2) of CAM were added into 35 ml solutions of Cu (II) and Cd (II) ions (with an initial concentration of 5 ppm and a solution pH value of 8 for Cu (II) ion and 10 for Cd (II) ion). After the adsorption process, membrane was removed from the solutions and the membrane was added into 35 ml of desorption solvent. Three different desorption solvent used were 1 M Hydrochloric acid, Nitric acid and Sulphuric acid. After the sonication process for 10 minutes, then the membrane was removed from the solutions and the final concentration of metal ion solutions were determined by using FAAS. The percentage of desorption was calculated based on the following equation [10]:

Desorption (%)=(Amount of heavy metal ions desorbed to the desorption medium (mg/g))/(Amount of heavy metal ions adsorbed on the adsorbent (mg/g)) [3]

The collected adsorbent from the solution was dried for reuse. The adsorption experiments were conducted for three times using the same adsorbent to indicate the reusability of the adsorbent while for the accuracy and precision, different adsorbent was used and the adsorption experiments were also conducted for three times.

Real water samples study

For this study, environmental water samples such as lake water, river water and seawater as well as mineral water were used. The optimum conditions adapted from all parameters were applied in order to determine the adsorption capacity (mg/g) of the adsorbent towards Cu (II) ion and Cd (II) ion.

Results and Discussion

Characterization

FTIR characterization CA and CAM: The surface structures of functional groups in the cellulose acetate composite can strongly influenced the metal sorption capacity [11]. FTIR spectra of CA and CAM are shown in Figure 1. Figure 1 shows three important ester bands of CA at 1729 cm^{-1} (C=O ester), 1371 cm^{-1} (C–H bond in –O(C=O) –CH3 group), and 1226 cm^{-1} (–CO– stretching of acetyl group). The broad and strong peak at 3442 cm^{-1} represents the –OH peak intensity of CA.

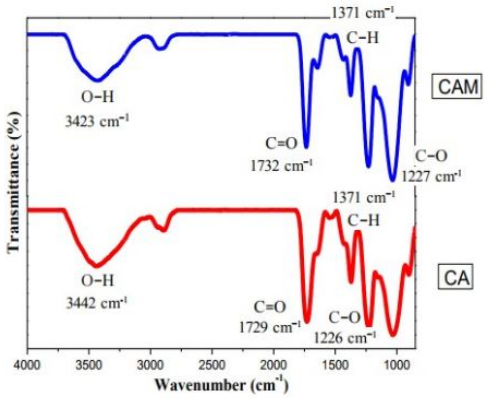

Figure 1: The FTIR spectrum of CA and CAM.

For CAM, the spectrum pattern was similar with CA because CAM originated from the same raw material. The broad band of hydrogen

bonding of –OH groups is detected at 3423 cm^{-1} with a little shift in peak. The CAM also exhibit a little shift in peak of C=O compared to that of CA spectra at 1732 cm^{-1} due to vibrational modes of C=O after casting. In addition, the C–H and –CO– stretching bands are at 1371 cm^{-1} and 1227 cm^{-1} respectively. This is consistent with the result reported by previous study [11].

FESEM images for CA and CAM: The FESEM was used to study the morphologies of the prepared CA and CAM. As shown in Figure 2 (a and b), it can be concluded that after the form changes by CA (from powder to CAM), the diameter are still the same (500 nm) with slight differences in term of the visibility of voids and roughness. The homogeneous structure of CAM indicates that CAM is a favourable candidate for acting as matrix support and more favourable towards the adsorption of analyte.

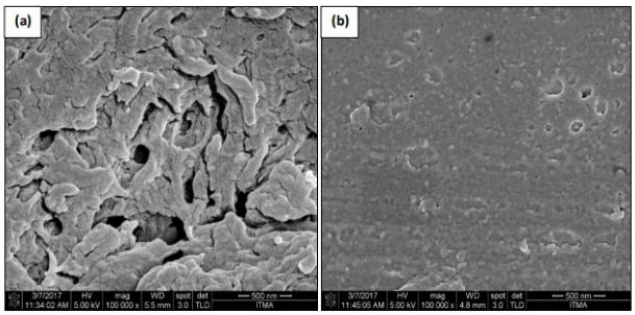

Figure 2: The FESEM of a) CA and b) CAM.

BET surface area of CAM: In the BET analysis, the shape of adsorption isotherm provides qualitative information on the adsorption process and the extent of the specific surface area available to the adsorbate. For a specific type of isotherm, the adsorbent is supposed to possess certain porosity. Therefore, the specific surface area of CAM is 6.37 m^2/g.

Metal adsorption of Cu (II) ion and Cd (II) ion by CAM

pH study: The pH of aqueous solution is an important parameter in the adsorption of metal ions from aqueous solution onto the adsorbent. Figure 3 illustrated that pH obviously influenced the adsorption capacity of the Cu (II) and Cd (II) ions in the solution by the tested adsorbent. The increase in sorption is attributed to the increase in the negative sorption sites available to bind with the Cu (II) and Cd (II) ions. The maximum adsorption capacity of Cu (II) and Cd (II) ions were about 14.22 mg/g at pH 8 and 11.20 mg/g at pH 10 respectively. The free Cu (II) and Cd (II) ions were mainly involved in the adsorption process when the pH was lower than 8 for Cu (II) and 10 for Cd (II) ions. For acidic pH, the concentration of H^+ ions at the surface of the adsorbents is increase thus increase the competition of Cu (II) and Cd (II) ions with H+ ions to bind with the hydroxyl group on the surface of the adsorbents [12]. When the pH greater than 8 and 10, Cu (II) and Cd (II) ions were started to precipitate as $Cu(OH)_2$ and $Cd(OH)_2$. Therefore, the opportunity of Cu (II) and Cd (II) ions to bind to the surface of the adsorbent is lessen. Increases in metals adsorption with increased pH can be explained on the basis of the decrease in positive surface charge and by decrease in competition between proton and metal cations for same functional groups. Formation of soluble hydroxy complexes will decrease the adsorption at higher pH [1]. Thus, pH of 8 and 10 for Cu (II) and Cd (II) ions were applied throughout the study.

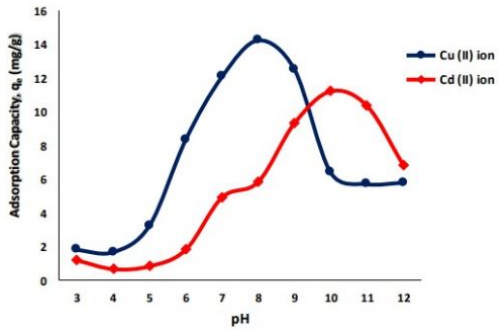

Figure 3: pH study on the uptake of Cu (II) and Cd (II) ions using CAM (adsorbent dosage=0.012 g, t=15 minutes, concentration of Cu (II) and Cd (II) ions=5 ppm).

Adsorbent dosage study: The Figure 4 shows the effect of adsorbent dosage on the adsorption of Cu (II) and Cd (II) ions. The percentage of removal increase as adsorbent doses increases up to 0.035 g and 0.012 g for Cu (II) and Cd (II) ions respectively. This may occur due to the fact that the greater surface area and greater availability of exchangeable sites for the ions provided by the higher dose of adsorbents in the solution [1,12] but beyond the stated masses the change in the Cu (II) and Cd (II) ions removal are decreases. The maximum percentage of removal of Cu (II) and Cd (II) ions were 79.89% and 76.62% at the dosage of 0.035 g for Cu (II) ion and 0.012 g for Cd (II) ion.

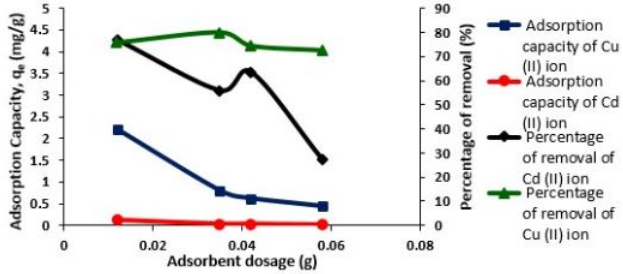

Figure 4: Adsorbent dosage and percentage of removal study on the uptake of Cu (II) and Cd (II) ions using CAM (t=15 minutes, pH=8 for Cu (II) ion and 10 for Cd (II) ion, concentration of Cu (II) and Cd (II) ions=5 ppm).

These results also suggest that after a certain dose of adsorbent, the equilibrium conditions reached. Therefore, the amount of free ions in the solution and the amount of ions bound to the adsorbent remain constant even with further addition of the dose of adsorbent

Isotherm study: The adsorption capacity of Cu (II) and Cd (II) ions are plotted against the initial concentration as shown in Figure 5. From Figure 5, the adsorption capacity of the adsorbent for both Cu (II) and Cd (II) ions increases as the concentration of heavy metals increases. The sorption data obtained for various metal ion concentrations were

analyzed using isotherm models given by Langmuir isotherm and Freundlich isotherm. The Langmuir model is expressed as follows:

$$C_e/q_e=1/(K_L\ q_m)+ C_e/q_m \quad [4]$$

Where q_e (mg/g) is the equilibrium metal ion concentration on the adsorbent, C_e (mg/L) is the equilibrium metal ion concentration in solution, q_m (mg/g) is the monolayer capacity of the adsorbent and K_L (L/mg) is the Langmuir adsorption constant. The Freundlich model is expressed as follows:

$$\ln q_e=\ln K_F+\ln C_e \quad [5]$$

Where q_e (mg/g) is the equilibrium metal ion concentration on the adsorbent, and C_e (mg/L) is the equilibrium metal ion concentration in solution. K_F (L/mg) and n are the Freundlich constants that can be related to the adsorption capacity and the adsorption intensity, respectively.

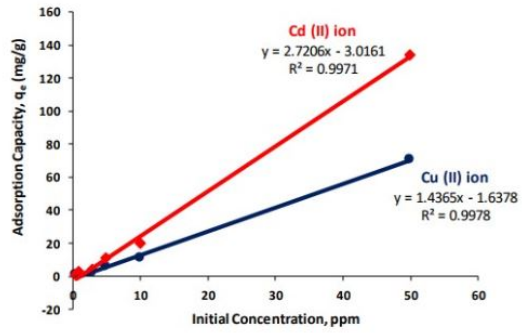

Figure 5: Isotherm study on the uptake of Cu (II) and Cd (II) ions using CAM (adsorbent dosage=0.035 g for Cu (II) ion and 0.012 g for Cd (II) ion, t=15 minutes, pH=8 for Cu (II) ion and 10 for Cd (II) ion).

The Langmuir and Freundlich adsorption isotherms towards Cu (II) and Cd (II) ions from aqueous solution using CAM is presented in Figures 6 and 7 respectively. By comparing the correlation coefficients (R^2) or the value of the regression (R^2) of the plot, it was observed that Freundlich isotherm gives a good model for the adsorption system. The Langmuir and Freundlich constant values are summarized in the Table 1.

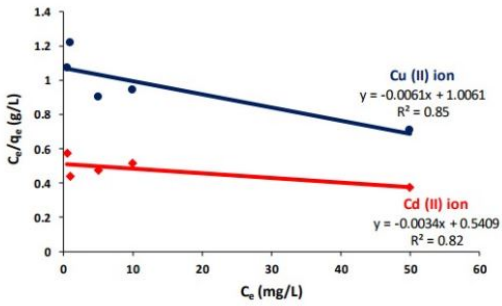

Figure 6: Langmuir isotherm for the sorption of Cu (II) and Cd (II) ions using CAM (adsorbent dosage=0.035 g for Cu (II) ion and 0.012 g for Cd (II) ion, t=15 minutes, pH=8 for Cu (II) ion and 10 for Cd (II) ion).

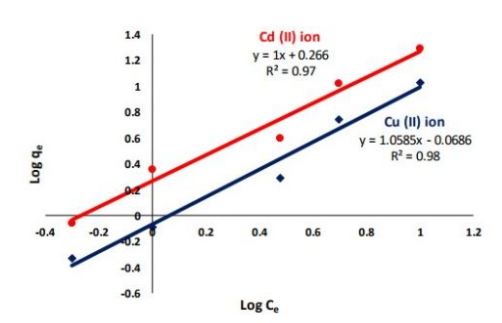

Figure 7: Freundlich isotherm for the sorption of Cu (II) and Cd (II) ions using CAM (adsorbent dosage=0.035 g for Cu (II) ion and 0.012 g for Cd (II) ion, t=15 minutes, pH=8 for Cu (II) ion and 10 for Cd (II) ion).

		Langmuir Isotherm			Freundlich Isotherm		
Adsorbent		**Maximum adsorption capacity, qm (mg/g)**	**Langmuir constant, K_L (L/mg)**	**Correlation coefficient, R^2**	**Freundlich constant, K_F (mg/g)**	**Freundlich constant, n**	**Correlation coefficient, R^2**
CAM	Cu (II) ion	-163.93	-0.0061	0.85	0.93	1.06	0.98
	Cd (II) ion	-294.12	-0.0063	0.82	1.3	1	0.97

Table 1: Langmuir and Freundlich parameters for adsorption of Cu (II) and Cd (II) ions onto CAM.

Freundlich isotherm described adsorbate adsorbent systems in which the extent of adsorbate coverage is considered to be a multilayer process in which the amount of adsorbed solute per unit mass of adsorbent increases gradually [13] and also provides the information about heterogeneity of adsorption sites. It assumes neither limited levels of adsorption nor homogenous site energies. The ability of a particle to bind is independent of whether nearby sites are occupied. Each adsorbate molecule occupies only one site and remained at the site until it is desorbed. The larger value of n may indicate a stronger interaction between the adsorbate and the adsorbent because n value related to adsorption intensity at a particular temperature. Linear adsorption leads to identical adsorption energies for all sites. That is

why this isotherm provides excellently fitting data of highly heterogeneous adsorbent systems.

Kinetic study: The adsorption capacity of Cu (II) and Cd (II) ions on CAM as a function of various contact time (5-30 minutes) using 5 ppm initial concentration is shown in Figure 8. As can be seen, the adsorption process of Cu (II) and Cd (II) ions on CAM occurred rapidly within the first 5 minutes, which were probably due to the abundant availability of active sites on the adsorbent and also due to the rapid attachment to the adsorbent surface [14]. This is due to the fact that, initially all sorbent sites are vacant. After that period, the increase of adsorption is very low due to the decrease of vacant active site on the adsorbent surface [15]. The system reached equilibrium after about 20 minutes. The adsorption kinetic data was analyzed using the pseudo-first-order equation and pseudo-second-order equation which are expressed as follows:

$$\ln (q_e - q_t) = \ln q_e - K_1 t \quad [6]$$

$$t/q_t = t/q_e + 1/K_2 q_e^2 \quad [7]$$

Where K_1 (min^{-1}) and K_2 (g/mg/min) are the equilibrium rate constants of pseudo-first-order and pseudo-second-order equation, respectively.

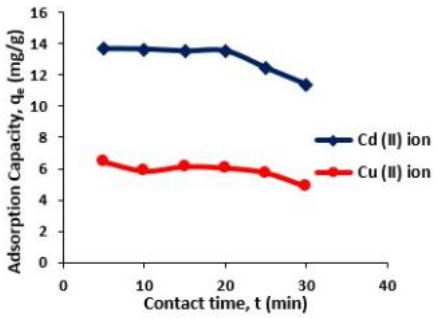

Figure 8: Kinetic study for the sorption of Cu (II) and Cd (II) ions using CAM (adsorbent dosage=0.035 g for Cu (II) ion and 0.012 g for Cd (II) ion, t=5-30 minutes, pH=8 for Cu (II) ion and 10 for Cd (II) ion).

The fitting plots are shown in Figures 9 and 10. The kinetic parameters acquired from fitting results are summarized in Table 2. According to the correlation coefficients, the pseudo-second-order equation is the better model to describe the adsorption processes. The overall rate of the Cu (II) and Cd (II) ions sorption process appear to be controlled by chemical processes involving valency forces through sharing or exchange of electrons between sorbents and sorbates [16]. From these figures (Figures 9 and 10), it can be concluded that in the first phase (Figure 9), Cu (II) and Cd (II) ions are quickly adsorbed on the external sites of the adsorbent material, which dominates the initial kinetics of sorption [16] which gave the non-linear and <0.6000 R^2. In the second phase (Figure 10), Cu (II) and Cd (II) ions slowly diffuse in the pores of the material and are adsorbed onto the internal sites [17].

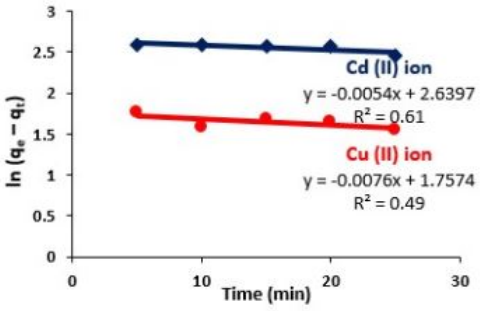

Figure 9: Pseudo-first order kinetic for the sorption of Cu (II) and Cd (II) ions using CAM (adsorbent dosage=0.035 g for Cu (II) ion and 0.012 g for Cd (II) ion, t=5-30 minutes, pH=8 for Cu (II) ion and 10 for Cd (II) ion).

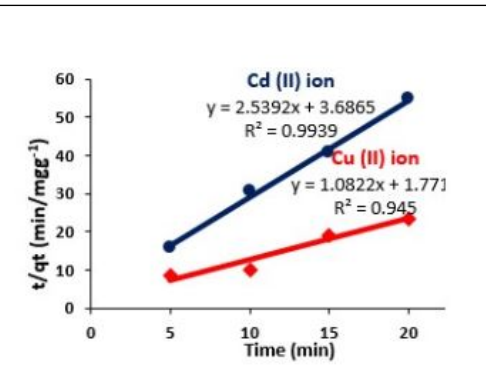

Figure 10: Pseudo-second order kinetic for the sorption of Cu (II) and Cd (II) ions using CAM (adsorbent dosage=0.035 g for Cu (II) ion and 0.012 g for Cd (II) ion, t=5-30 minutes, pH=8 for Cu (II) ion and 10 for Cd (II) ion).

			Pseudo-first order			Pseudo-second order		
Adsorbent		**Amount of adsorption, q_e experiment (mg/g)**	**Rate constant, K_1 (min)**	**Amount of adsorption, q_e calculated (mg/g)**	**Correlation coefficient, R^2**	**Rate constant, K_2 (g/mgmin)**	**Amount of adsorption, q_e calculated (mg/g)**	**Correlation coefficient, R^2**
CAM	Cu (II) ion	5.85	131.58	5.8	0.49	0.66	0.92	0.95
	Cd (II) ion	10.77	185.19	14.01	0.61	1.75	0.39	0.99

Table 2: Pseudo-first order and pseudo-second order parameters for the adsorption of Cu (II) and Cd (II) ions onto CAM.

Desorption study: Desorption study was performed to evaluate the regeneration ability of prepared adsorbent in order to find a suitable desorbing agent. In this study, different desorbing agents were used (Hydrochloric, Nitric and Sulphuric acid). The desorption efficiencies of various desorption agents are shown in Table 3. From Table 3, Cu (II) and Cd (II) ions has higher desorption efficiencies with 1 M Sulphuric acid and Hydrochloric acid since 1 M Sulphuric acid and Hydrochloric acid has proven to be the best desorbing agent for Cu (II) and Cd (II) ions respectively. This may be attributed to the ion exchange interaction of Cu (II) and Cd (II) ions by H^+ ion. Complete desorption was not possible because of the complexation and electrostatic reactions occurred between the metal ions and the sorbent [12].

Types of acid		Percentage of desorption, (%) 1 M
Hydrochloric Acid, HCl	Cu (II) ion	29.42
Sulphuric Acid, H_2SO_4		32.06
Nitric Acid, HNO_3		13.58
Hydrochloric Acid, HCl	Cd (II) ion	44.21
Sulphuric Acid, H_2SO_4		20.34
Nitric Acid, HNO_3		21.07

Table 3: Desorption parameters for regeneration of CAM.

Reusability study: The adsorption properties of the recovered CAM are shown in Figure 11. As shown, the adsorption capacity for Cu (II) and Cd (II) ions is slowly decreasing with reusing cycles, which may be attributed to the loss of some number of adsorption active sites during each of the desorption process. From this, it can be explained that this membrane can only be used in single removal procedure in order to avoid any carry over effect.

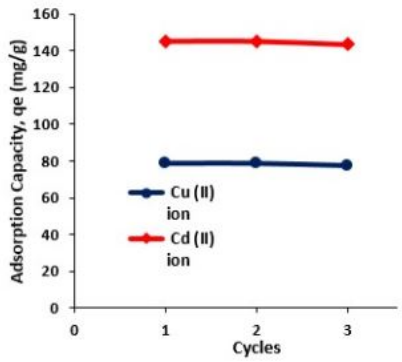

Figure 11: Reusability for the sorption of Cu (II) and Cd (II) ions using CAM (adsorbent dosage=0.035 g for Cu (II) ion and 0.012 g for Cd (II) ion, t=5 minutes, pH=8 for Cu (II) ion and 10 for Cd (II) ion).

Accuracy and precision study: The determination of accuracy and precision were carried out with three replicate measurements of Cu (II) and Cd (II) ions solutions. Repetition measurements are important to give closeness value of these 3 measured values and the true value of the quantity being measured. These indicated that this method can be accepted as these values give good precision and accuracy for the adsorption of Cu (II) and Cd (II) ions. Table 4 shows the value of accuracy and precision from calculated RSD and relative recovery from the results obtained. The value of accuracy and precision are calculated from relative recovery (RR) and relative standard deviation (RSD) shown below:

$$RR=(S/\bar{x}) \times 100\%$$

$$RSD=(\bar{x}/q_e \text{ from calibration}) \times 100\% \text{ [8]}$$

	Accuracy and Precision (RR % ± RSD %)		
Adsorbent		**5 ppm**	**50 ppm**
CAM	Cu (II) ion	88.35 ± 21.33	85.88 ± 0.24
	Cd (II) ion	78.01 ± 5.29	86.55 ± 0.23

Table 4: The value of accuracy and precision of CAM.

Real water sample study: The applicability of CAM for the removal of Cu (II) and Cd (II) ions was tested by using real environmental water samples from sea, lake and river water as well as mineral water. CAM was added to the water samples without any pretreatment. Table 5 shows the concentration of water samples before and after removal while Tables 6, 7 and 8 shows the effectiveness of Cu (II) and Cd (II) ions removal by CAM. The value of all adsorption capacities for the removal of Cu (II) and Cd (II) ions from the environmental water samples are less than 1 ppm, indicating that the concentration of heavy metal ions in the water samples are very low and within the allowance limit reported by WHO [18].

		Concentration before removal (ppm)		Concentration after removal (ppm)	
		Cu (II) ion	Cd (II) ion	Cu (II) ion	Cd (II) ion
Lake Water	Bahau	0.19	0.01	0.05	0.006
	Shah Alam	0.06	0.11	0.04	0.02
	Cheras	0.1	0.11	0.09	0.02
River Water	Pahang	0.03	0.03	0.01	0.004
Seawater	Melaka	0.13	0.03	0.1	0.023
Mineral Water	DESA	0.08	0.02	0.05	0.017
	Summer	0.08	0.025	0.08	0.015

Table 5: Concentration of environmental water samples before and after removal.

		River Water		Sea Water	
		Pahang		Melaka	
Adsorbent		Adsorption capacity, q_e (mg/g)	Percentage of removal, (%)	Adsorption capacity, q_e (mg/g)	Percentage of removal, (%)
CAM	Cu (II) ion	0.03	68.77	0.04	21.9
	Cd (II) ion	0.08	86.58	0.02	19.51

Table 6: Percentage removal of Cu (II) and Cd (II) ions from environmental water samples (river water and sea water).

		Lake Water					
		Shah Alam		Bahau		Cheras	
Adsorbent		Adsorption capacity, q_e (mg/g)	Percentage of removal, (%)	Adsorption capacity, q_e (mg/g)	Percentage of removal, (%)	Adsorption capacity, q_e (mg/g)	Percentage of removal, (%)
CAM	Cu (II) ion	0.03	27.1	0.22	71.87	0.01	6.09
	Cd (II) ion	0.27	82.32	0.01	39.05	0.26	82.64

Table 7: Percentage removal of Cu (II) and Cd (II) ions from environmental water samples (lake water).

		Mineral Water			
		DESA		Summer	
Adsorbent		Adsorption capacity, q_e (mg/g)	Percentage of removal, (%)	Adsorption capacity, q_e (mg/g)	Percentage of removal, (%)
CAM	Cu (II) ion	0.05	36.11	0.12	48.26
	Cd (II) ion	0.01	9.9	0.03	36.03

Table 8: Percentage removal of Cu (II) and Cd (II) ions from environmental water samples (mineral water).

Conclusion

Cellulose Acetate Membrane (CAM) was successfully prepared by casting technique and was utilized for the adsorption towards heavy metal ions in environmental water samples. The membrane was characterized by Field Emission Scanning Electron Microscopy (FESEM), BET surface area (BET) and Fourier Transform Infrared Analysis (FTIR) while the qualitative and quantitative determination of heavy metal ions were analysed by Flame Atomic Adsorption Spectrometry (FAAS). The active sites of adsorbent consist of $-OCOCH_3$ and –OH groups where Cu (II) and Cd (II) ions interact. The ability of adsorption of Cu (II) and Cd (II) ions by using CAM was investigated and the parameters used were pH, adsorbant dosage, initial concentration, kinetic parameter, desorption, accuracy and precision and reusability. The adsorbent was tested for removal of Cu (II) and Cd (II) ions from environmental water samples obtained from river, sea, lake and drinking water.

The formation of CAM was confirmed by FTIR analysis at peaks of the broad band of hydrogen bonding of –OH groups detected at 3423 cm^{-1}. The CAM also exhibit a peak of C=O at 1732 cm^{-1} due to vibrational modes of C=O after casting and the C–H and –CO– stretching bands detected at 1371 cm^{-1} and 1227 cm^{-1} respectively. Adsorption experimental results indicate that higher initial pH value corresponds to higher adsorption capacity. The optimum adsorption condition of CAM towards Cu (II) and Cd (II) ions was at pH 8 and pH 10 with adsorption capacity of 14.22 mg/g and 11.20 mg/g respectively. Moreover, 0.035 g and 0.012 g of adsorbent was optimum for Cu (II) and Cd (II) ions adsorption as corresponding to the maximum adsorption efficiencies with percentage of removal about 79.89% and 76.62% respectively.

The maximum sorption capacities as calculated from Freundlich isotherm for Cu (II) and Cd (II) ions were 0.93 and 1.30 mg/g respectively. The sorption of Cu (II) and Cd (II) ions by CAM based on kinetic study showed a pseudo-second order kinetic model and the rate constant K2 was 0.66 and 1.75 g/mg min. In desorption study, the highest percentage of desorption of Cu (II) and Cd (II) ions towards CAM was accomplished by 1 M Sulphuric acid and Hydrochloric acid solution with 32.06% and 44.21%. The adsorption capacity did not change significantly in reusability study when three adsorption experimental cycles were conducted. In conclusion, CAM was found to be effective for the removal of Cu (II) and Cd (II) ions in real environmental water samples obtained from river, sea, lake and drinking water.

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