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Research paper

Competitive Adsorption of Cu2+, Pb2+ and Ni2+ on Thiourea Modified Spent Grated Coconut (Cocos Nucifera)

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Abstract

The behavior of thiourea spent grated Cocos nucifera (TSGC) as an adsorbent for simultaneous removal of Cu2+, Pb2+ and Ni2+ ions from aqueous solutions in ternary system was investigated. TSGC was characterized by using a CHNOS analyser, a Fourier transform infrared (FTIR) spectrometer and a scanning electron microscope coupled with energy dispersive spectrometer (SEM-EDS). Complexation was one of the main mechanisms involved as indicated by the FTIR spectra. The pseudo-second-order and Langmuir isotherm models best fit to the adsorption experimental data. The maximum adsorption capacities (mmol.g-1) of heavy metal ions by TSGC were in the order of Cu2+ (1.38) > Pb2+ (0.32) > Ni2+ (0.24). Overall, TSGC showed a higher selectivity for the Cu2+ ion.

Keywords: *adsorption; Cocosnucifera; selectivity; hard-soft acid base; electronegativity; ionic radii*

1. Introduction

The rapid growth of human population has triggered the increased demand for different types of goods and services to fulfil humans' needs, which resulted in the continuous growth of industries such as electrical, electronics, mining, metallurgical, automotive, energy, chemical, cosmetic, petrochemicals and others. These industries are known to consume a large amount of heavy metals and responsible for the release of heavy metal ions into water bodies. Among the common divalent heavy metal ions that can be found in industrial wastewaters include Pb2+, Cu2+, Cd2+, Zn2+, Co2+, and Ni2+ which could contribute to adverse effect to human and environment if their tolerance levels are exceeded [1]. Due to the potential health hazards, different treatment methods have been introduced to remove these heavy metal ions from aqueous solutions, which include precipitation, membrane filtration, reverse osmosis, coagulation, flocculation, and adsorption. Adsorption can be considered as a cheap and an effective technique to recover low concentrations of heavy metal ions and numerous adsorbent materials have been tested which include zeolite, activated carbons, nanomaterials, and lignocellulosic wastes. Agriculture sectors are responsible for the huge production of solid wastes and quite often, the wastes are reused as a fertilizer or being burned off causing serious air pollution. Converting lignocellulosic wastes into many value-added products would help reduce solid waste problems and ensures a more sustainable practice in agriculture sectors. Spent grated coconut (SGC) is known to contain fibre, protein, pectin, carbohydrates, fat, cellulose, hemicellulose, and lignin [2]. Previously, SGC has been applied as an adsorbent for recovering Ni2+ and methylene blue in a single adsorbate solution [3,4]. However, polluted water often contains different types of metal ions. The performance of an adsorbent can be affected and complicated interaction between metal ions and adsorbent can happen when different types of metal ions are present simultaneously in a solution. To the best of our knowledge, there has been no work reported on the use of SGC for simultaneous recovery of heavy metal ions from a ternary system. Therefore, this work explained the adsorption behaviour of thiourea treated SGC towards Pb2+, Cu2+ and Ni2+ with an emphasis on the concept of hard soft acid base (HSAB), electronegativity and ionic radii.

2. Result and Discussion

2.1 Characterization of TSGC

Fig. 1 shows the FTIR spectra of HSGC and TSGC (before and after heavy metal ions adsorption). In HSGC, the broad and strong peak at 3362 cm-1 corresponds to both stretching vibration of amine (-NH2) and hydroxyl (-OH) groups [5]. The peaks correspond to the C-H groups were evident at 2921 and 2852 cm-1. The intense peak observed at 1744 cm-1 was attributed to the stretching of C=O groups due to presence of carboxylic acid. The intense peaks observed at 1061, 1030, and 1010.19 cm-1 were assigned to the stretching of C-O, which overlap with C-N groups. The FTIR spectrum of TSGC shows some shift in the wavenumbers or reduction and increment of the intensity of the peaks after thiourea treatment. There were more peaks observed at 3368, 3268, and 3162 cm-1 which correspond to the presence of more –NH2 groups. The thiourea process had successfully introduced more amino groups on the surface of TSGC, hence, an increment in the intensity of the peak was observed at 1606 cm-1. The presence of C=S group was confirmed by the peaks in the range of 700 to 110 cm-1. The involvement of the amino (-NH2) groups in forming complexes with heavy metal ions could be confirmed by the low intensity of the peak at 1636 cm-1. The -OH and -COO- groups also could be involved in the binding of metal ions as the peak intensities in the range of 3000 to 3600 cm-1 and at 1745 cm-1 were reduced after heavy metal ions adsorption. The shift in the wavenumber from 1080 to 1060 cm-1 and disappearance of the peak at 728 cm-1 would suggest the binding of heavy metal ions with sulphur groups. Based on the FTIR spectra, the main functional groups that took part in the adsorption of heavy metal ions include –OH, -NH2, -COO-, C-O-C, and C=S groups and the mechanisms involved could be chemisorption, ionic, and electrostatic interaction.

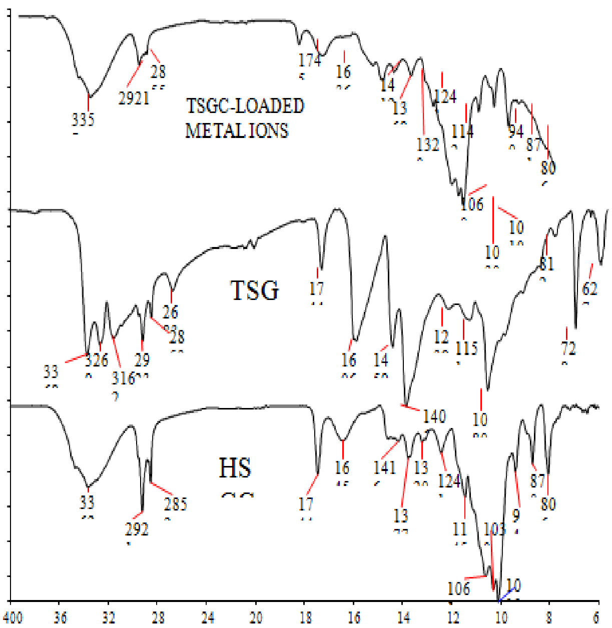

Fig.1: FTIR spectra of HSGC and TSGC (before and after heavy metal ions adsorption)

A further confirmation of heavy metal ions adsorption on TSGC was obtained from the SEM image and EDX spectrum as shown in Fig. 2. The SEM image shows rough and uneven surface, which could favour the adsorption of heavy metal ions. All the three heavy metal ions were confirmed being adsorbed on TSGC as presented by the EDX spectrum.

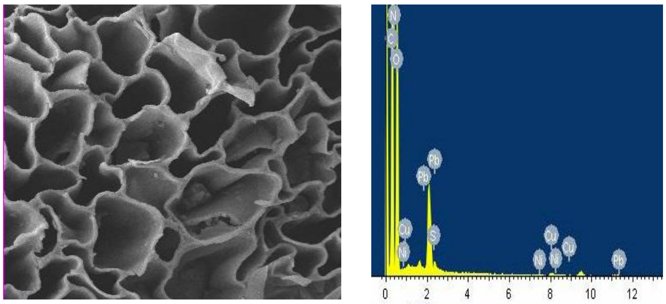

Fig.2: SEM image (at 1000x magnification) and EDX spectrum of TSGC after heavy metal ions adsorption

Table 1 shows the percentage of N and S in TSGC had increased after being treated with thiourea. The presence of lone pair of electrons in N, S and O could act as the adsorption sites for the heavy metal ions. According to the hard-soft acid base (HSAB) theory, N, S, and O atoms were classified as intermediate, soft, and hard base, respectively [6].

Table 1: Ultimate analysis of HSGC and TSGC

Element	HSGC	TSGC
C	44.07	32.28
H	5.27	4.45
N	2.20	15.15
S	0.19	12.73
O^a	48.27	35.39

^{a} *by difference*

2.2 Adsorption Kinetics

Fig. 3 shows the adsorption kinetics of Pb2+, Cu2+, and Ni2+ ions in a ternary system at equimolar initial concentration of 0.1 mmol/L.

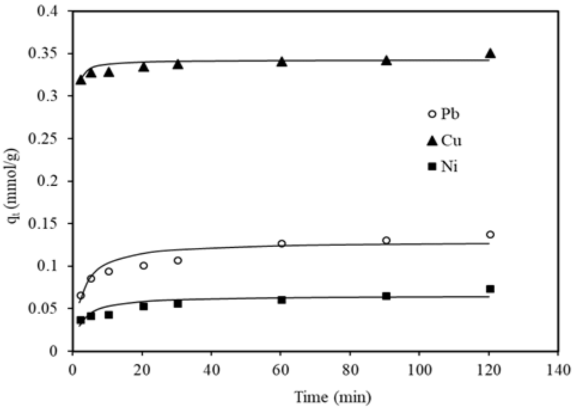

Fig.3: Adsorption kinetics of Pb2+, Cu2+ and Ni2+.

The plots revealed that the amount of heavy metal ions adsorbed increased as the contact time was increased with Cu^{2+} recorded the highest amount of adsorption. The required time to reach equilibrium was 20, 60 and 30 min for Cu^{2+}, Pb^{2+}, and Ni^{2+}, respectively. The data were further analysed using the non-linear form of pseudo-first-order [7] and pseudo-second-order [8] models given by equations 1 and 2, respectively.

$$q_t = q_e(1-e^{k_1 t}) \tag{1}$$

$$q_t = q_e^2 k_2 t/(1+k_2 q_e t) \tag{2}$$

where q_t, k_1 and k_2 represent the amount of metal ions adsorbed ($mmol.g^{-1}$) at time t (min), the pseudo-first-order constant (min^{-1}) and pseudo-second-order rate constant ($g.mmol^{-1}.min^{-1}$), respectively. The R^2 and χ^2 values are summarized in Table 2. The $q_{e,cal}$ values (at equilibrium) obtained from the pseudo-second-order equation were in agreement with the experimental values ($q_{e,exp}$). The χ^2 values recorded by the pseudo-second-order were much lower than the pseudo-first-order. Therefore, adsorption of heavy metal ions fitted well to the pseudo-second-order model. In addition to the highest amount of adsorption as shown in Fig. 3, Cu^{2+} also had the highest rate of adsorption compared to Pb^{2+} and Ni^{2+} as indicated by the k_2 values. Thus, TSGC surface had a greater affinity for Cu^{2+}.

Table 2: The pseudo-first-order and pseudo-second-order kinetics parameters calculated for Cu2+, Pb2+, and Ni2+ adsorption on TSGC

Heavy metals	qe, exp	Pseudo-first-order				Pseudo-second-order			
		qe, cal	k1	R2	χ2	qe, cal	k2	R2	χ2
Pb2+	0.132	0.120	0.293	0.628	0.016	0.129	3.060	0.796	5x10-3
Cu2+	0.344	0.339	1.461	0.421	0.001	0.342	18.75	0.554	1x10-4
Ni2+	0.066	0.061	0.301	0.462	0.013	0.066	6.218	0.583	4x10-3

2.3 Adsorption Isotherm

Adsorption isotherm was performed at the equilibrium time and it could reveal information on the behavior of interaction between the adsorbates (heavy metal ions) and TSGC surface. The adsorption isotherm plots for all heavy metal ions are presented in Fig. 4.

The maximum adsorption capacities for Cu2+, Pb2+ and Ni2+ were 1.38, 0.32 and 0.24 mmol/g, respectively. Cu2+ showed the C1-type isotherm, also called constant isotherm partition [9], in which the availability of adsorption sites remained constant at all Cu2+ concentrations. This isotherm type also suggested the higher affinity of Cu2+ for the adsorption sites than the solvent. Pb2+ and Ni2+ on the other hand, had maxima (sub-group of mx), followed by a fall in slope after the maxima. This phenomenon is associated to a greater solute-solute attraction than solute-adsorbent attraction when the solute concentration is increased. The isotherm results indicated that most adsorption sites available in TSGC had a higher affinity for Cu2+ than Pb2+ and Ni2+. The adsorptive behaviour of TSGC can be explained based on the concept of hard-soft acid base (HSAB), electronegativity and ionic radii of the heavy metal ions. $C^{u2+,}$ Pb^2+ and Ni2+ are classified as intermediate acids [10]. According to the HSAB theory, a ‘soft acid’ would prefer to bind to a ‘soft base’ while ‘intermediate acid’ binds to ‘intermediate base’ and a ‘hard acid” would bind strongly to a ‘hard base’. Among these three metal ions, Pb2+ is considered as the softest acid while Ni2+ is considered as the hardest acid. Therefore, Pb2+ would form complexes with the S atoms (soft-base) in C=S groups, whereas Ni2+ tends to form complexes with the O atoms (hard-base) in -OH and -C-O-C- groups. The -COO- group on the other hand was able to bind the metal ions via ionic attraction. The N atoms in -NH2 groups, having an intermediary base character would form more stable complexes with Cu2+. Regarding the electronegativity, Cu2+ has the highest electronegativity value (1.372), followed by Ni2+ (1.367) and Pb2+ (1.225) [11]. Cu2+ would experience a greater force of attraction to the adsorption sites compared with Ni2+ and Pb2+. Hence, Cu2+ would be preferably adsorbed. Besides having the highest electronegativity value and intermediary acid property, Cu2+ has a smaller radius than Pb2+ (0.72 Å for Cu2+ versus 1.32 Å for Pb2+, which means Cu2+ is 83% smaller than Pb2+). This suggested that Cu2+ experienced less steric hindrance and has a higher accessibility to the adsorption sites than Pb2+. Due to its large ionic size, Pb2+ would be much difficult to coordinate to S atoms. Despite of the smallest ionic radius, Ni2+ recorded the lowest adsorption capacity, demonstrating a very low affinity of TSGC for a hard acid.

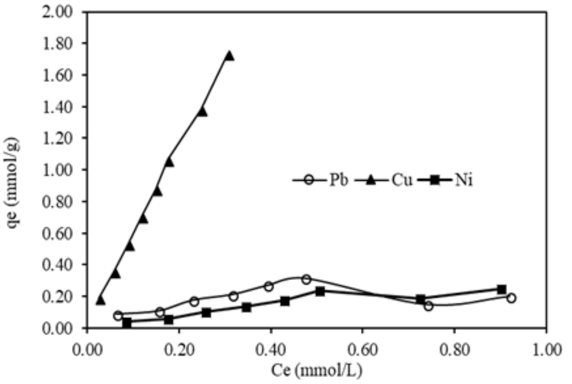

Fig.4: Isotherm plots of Pb2+, Cu2+ and Ni2+ on TSGC

3. Experimental

3.1 Chemicals and Material

All heavy metals were of analytical grade and were purchased from Merck, Germany. The stock solutions (1 mmol/L) of Pb2+ and Ni2+ were prepared by dissolving a known amount of Pb(NO3)2 and Ni(NO3)2.6H2O in 1 L deionised water (DW). Cu2+ stock solution was prepared from the 1000 mg/L Cu2+ standard solution. Appropriate dilution of the stock solutions with DW was carried out to obtain the desired concentration of each heavy metal ion to be used later in the adsorption experiments. The spent grated coconut (SGC) was obtained from a local market in Jengka, Malaysia. The sample was washed several times using DW to remove dust and insoluble impurities before drying in an oven at 378 K for 24 h. For defatting process, the sample was soaked in hexane for 16 h under continuous stirring before drying in an oven at 343 K for 3 h. The hexane washed SGC (hereafter called HSGC) was stored in a container for further chemical treatment.

3.2 Preparation of Thiolated Spent Grated Coconut

The thiourea treated SGC process was performed according to the method reported by Wang et al. [12] with modification. A weight of 16.1 g of HSGC and 15.2 g of ammonium thiocyanate (NH4SCN) was mixed in a 250-mL round bottom flask containing 150 mL of ethanol. The mixture was refluxed at 353 K for 6 h under continuous stirring. The hot mixture was cooled to room temperature and the solid product in the form of powder was filtered, then washed several times with ethanol. The powder was dried in an oven at 323 K overnight and stored in an airtight plastic for further use. The thiourea treated spent grated coconut was designated TSGC.

3.3 Characterization of TSGC

The presence of functional groups in HSGC and TSGC (before and after heavy metal ions adsorption) was confirmed by using a Fourier transform infrared (FTIR) spectrometer (PerkinElmer, Spectrum RXI, USA). The scanning electron microscope (SEM, JEOL JSM-7900F, USA) coupled with energy dispersive X-ray (EDX) spectrometer was used to analyse the surface morphology and to detect the presence of heavy metal ions on TSGC surface. The ultimate analysis of TSGC was determined by using a CHNOS analyser (Elementar, vario MICRO cube, Germany).

3.4 Batch Adsorption Experiments

Adsorption kinetics were performed at 0.20 mmol/L of equal molar concentration of each heavy metal ion. A weight of 0.02 g TSGC was added to the ternary metal solution in 100 mL Erlenmeyer flasks, stirred at 360 rpm and at room temperature (298 K). The pH of solution was fixed at 4 and the contact time was varied over time periods of 2, 5, 10, 20, 30, 60, 90 and 120 min. The equilibrium isotherm was carried out at six different concentrations (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 mmol/L) of equal molar concentration of each heavy metal ion. A weight of 0.02 g TSGC was added into each solution while the pH of solution was fixed at 4. The temperature was maintained at 298 K and all solutions were stirred at 360 rpm for 2 h. After adsorption, the mixture was filtered, and the filtrate was analysed for heavy metal concentration by using an inductively coupled plasma-optical emission spectrophotometer (ICP-OES, Agilent, model 5110, USA). All experiments were performed in duplicates and the results are presented as the average. The amount of each heavy metal ion adsorbed (q) was calculated using equation 3.

$$q = (C_o - C_t).V / m \quad (3)$$

where C^o and C^t are the initial and final metal ion concentration (mmol/L) at time t (min), respectively; m is the weight of TSGC (g) and *V* is the volume (mL). The trial-and-error nonlinear methods were performed by using the Solver add-in (Microsoft Excel) to calculate the parameters of adsorption kinetics and adsorption isotherm models. For determining the best fit model, the chi-squared and coefficient of determination formulas were used, given by equations (4) and (5), respectively:

$$X^2 = \Sigma \frac{(q_{e,\exp} - q_{e,cal})^2}{q_{e,cal}} \quad (4)$$

$$R^2 = 1 - \frac{\Sigma(q_{e,\exp} - q_{e,cal})^2}{\Sigma(q_{e,\exp} - q_{e,mean})^2}$$

$$= \frac{\Sigma(q_{e,cal} - q_{e,mean})^2}{\Sigma(q_{e,cal} - q_{e,mean})^2 + \Sigma(q_{e,cal} - q_{e,\exp})^2} \quad (5)$$

where $q_{e,exp}$ and $q_{e,cal}$ are the amount of metal ions adsorbed ($mg.g^{-1}$) at equilibrium determined from equation 3 and the model after using the Solver add-in, respectively; and $q_{e,mean}$ ($mg.g^{-1}$) is the mean of $q_{e,exp}$ values.

4. Conclusion

Adsorption of Cu^{2+}, Pb^{2+}, and Ni^{2+} on TSGC surface was confirmed from the FTIR and EDX spectra. The rate of adsorption was much faster for Cu^{2+} and adsorption obeyed the pseudo-second-order kinetic model. TSGC was found to have a higher selectivity for Cu^{2+} in the ternary adsorption system. The higher amount of Cu^{2+} adsorbed compared with Pb^{2+} and Ni^{2+} suggested that nitrogen (an intermediate base) was the dominant atom involved in the formation of complexes. The soft and hard base atoms represented by S and O atoms, respectively had a little effect on the uptake of Pb^{2+} and Ni^{2+}. In conclusion, the HSAB concept, electronegativity and ionic radii of metal ions played crucial roles in explaining the simultaneous adsorption behaviour of Cu^{2+}, Pb^{2+}, and Ni^{2+} on TSGC.

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