Equilibrium and Kinetic Studies of Cu(II), Ni(II) and Cd(II) Adsorption from Aqueous Solution by Chemically Modified Corn Cob

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Adsorption of copper, nickel and cadmium ions from aqueous solution by poly(acrylic acid) and polyacrylamide modified corn cob was investigated. The modified corn cob was characterized by optical microscope, FTIR, CHNO elemental analysis and N2 adsorption-desorption. The effect of parameters on heavy metal adsorption including contact time and concentration were studied. The results showed the maximum adsorption capacities of chemically modified corn cob were 239.55, 156.46 and 361.89 g kg⁻¹ for Cu(II), Ni(II) and Cd(II), respectively. Langmuir isotherm was fitted with the adsorption equilibrium and the pseudo-second order was fitted with the adsorption kinetics for all metal ions. The adsorbents were easily regenerated by 0.1 mol dm⁻³ HCl solution up to four cycles with the removal performance of 59-100%.

Key Words
Corn cob, Heavy Metal, Adsorption

1. Introduction
Nowadays heavy metals are the environmental priority pollutants and becoming one of the most serious environmental problem ⁶. Because of the rapid development of industrial activities, heavy metals wastewaters are discharged into the environment increasingly, especially in developing countries. So these toxic heavy metals should be removed from the wastewater to protect the environment.

Agricultural wastes have been interested in using as the potential adsorbent for heavy metals treatment because of their abundance, economic viability and adsorption capacity ⁷. Corn cob is an inexpensive agriculture residue from the large production crops. It has been reported that approximately 18 kg of corn cob is produced by 100 kg of corn grain ⁸, but most are used as animal feed or burnt without utilization ⁹. Corn cob waste can be used as heavy metal adsorbent in the natural form or modified by some chemical treatment. The metal-binding capacity of natural corncob was low compared with the other traditional adsorbents ¹⁰. The adsorption capacities of native corn cob were in the range of 4-25 g kg⁻¹ for Cd(II), Cu(II) and Zn(II) ⁶, ¹¹, ¹². Adsorption capacity of corn cob can be considerably enhanced by direct chemical modification with phosphoric acid ¹³, citric acid ¹⁴, nitric acid ¹⁵ or treatment by esterification/hydrolysis using methanol/ NaOH ¹⁶, and the reported adsorption capacities were in the range of 21-86 g kg⁻¹. Indirect modification by graft copolymerization is one of the alternative procedures that provided high efficient cellulose-based metal adsorbent ¹⁷. The grafted cellulose with various functionality for heavy metal adsorption have been reported such as acrylic acid ¹⁸, acrylamide ¹⁹, acrylonitrile ²⁰, ²¹ and glycidyl methacrylate ²². Acrylic acid and acrylamide contain carboxyl (-COOH) and amide (-CONH₂) groups. They provide high electron donor characteristic, which is capable of coordinating with metal ions through the carbonyl oxygen atom, oxygen and nitrogen atoms ²³.

This work focuses on the modification of cellulose from corn cob waste with acrylic acid (AA) and acrylamide (AM) using ammonium persulfate (APS) as an initiator and N,N'-methylenebisacrylamide (MBA) as a cross-linker. The chemical composition and properties of the adsorbents were
investigated. The adsorbed amount, kinetics and equilibrium isotherm for Cu(II), Ni(II) and Cd(II) were discussed.

2. Experimental

Corn cob was treated by 7 wt% NaOH with 12 wt% urea aqueous solution to obtain the purified cellulose. 30 g of alkali-treated cellulose (CC) was dispersed in 100 cm$^3$ of monomer aqueous solution (114.2 g dm$^{-3}$ of AA or 90 g dm$^{-3}$ of AM) in a conventional polymerization glass reactor. The solution was purged with nitrogen and heated up to the reaction temperature. Then, the mixture of MBA (0.20 g) and APS (0.25 g) was added under continuous stirring. The reaction temperature was kept constant at 70$^\circ$C. The gross polymer was extracted by distilled water to remove homopolymer (PAA or PAM), neutralized with 2.0 mol dm$^{-3}$ NaOH solution and washed until neutral. The neutralized product was dehydrated with acetone and then dried. The granular product in 18-60 mesh size was obtained by milling machine and sieve. Corn cob cellulose modified with poly(acrylic acid) and polyacrylamide were designated as CPAA and CPAM, respectively.

The products were characterized by optical microscope (OM), universal attenuated total reflection Fourier transform infrared spectroscopy (UATR-FTIR), elemental analyzer (CHNO) and $N_2$ adsorption-desorption instrument.

Kinetic adsorption experiment was performed using 0.05 g of adsorbent in conical tubes containing 25 cm$^3$ of metal solution (Cu(II), Ni(II) and Cd(II)) at concentration of 200 g m$^{-3}$, pH 5.5, 303 K and agitation of 150 rpm for various contact times (0.5-120 min). In the equilibrium isotherm experiment, 0.05 g of adsorbent was charged into 25 cm$^3$ of metal solution at various concentrations (100-1500 g m$^{-3}$), pH 5.5, 303 K and agitated at 150 rpm for 120 min. After adsorption process, the supernatant was collected and analyzed by atomic absorption spectrometry (AAS). The adsorbed amount (q [g kg$^{-1}$]) was calculated using the equation as follows:

$$q = \frac{C_i - C_f}{M} \cdot V$$

where $C_i$ and $C_f$ [g m$^{-3}$] are the initial and final concentrations, $m$ [kg] is adsorbent weight, and $V$ [m$^3$] is the volume of the solution.

The reusability study was carried out using 0.05 g of adsorbent in 200 g m$^{-3}$ metal solution and pH 5.5. After 120 min, the adsorbent was separated from solution by filtration. Desorption was performed by dispersing these spent adsorbent into 25 cm$^3$ of 0.1 mol dm$^{-3}$ HCl solution and agitating at room temperature for 30 min. The recovered adsorbent was neutralized with 0.1 mol dm$^{-3}$ NaOH solution, washed with deionized water until neutral and reused for next adsorption cycle.

3. Results and Discussion

The optical images of unmodified corn cob, CC, CPAA and CPAM before and after Cu(II) adsorption are illustrated in Fig. 1. The particle size of alkaline-treated corn cob (40-100 μm) was smaller than that of the parent corn cob due to the removing of lignin and hemicellulose in alkaline treatment process. The images of CPAA and CPAM showed clear layer of grafted polymer covered cellulose particle. After Cu(II) adsorption, the adsorbent was expanded about 1.5 times and the color was changed to deep blue regarding to the presence of Cu(II).

Fig. 2 presents the FT-IR spectra of CC, CPAA and CPAM. For CC (Fig. 2a), the broad adsorption band at 3000-3600 cm$^{-1}$ was attributed to the stretching vibration of O-H, the band at 2850 cm$^{-1}$ was assigned to C-H stretching, the band at 1140 cm$^{-1}$ was assigned to C-O of primary hydroxyl stretching, and the band at 1020 cm$^{-1}$ was attributed to the C-O-C anti-symmetric bridge stretching. After modification, the new bands of the carboxyl groups stretching (C=O) at 1690 cm$^{-1}$ and 1640 cm$^{-1}$ appeared for both CPAA and CPAM. For CPAM, the bending vibration of amine (N-H) at 1590 cm$^{-1}$ and primary N-H adsorption bands of amide groups (-CONH$_2$) that splits into two bands overlapped with O-H at 3120 cm$^{-1}$ were observed. These results confirmed...
the presence of carboxyl and amide functional groups on the modified corn cob cellulose.

From CHNO analysis, the results showed percentage of the chemical elements in CC (C 43.34%, H 6.42%, N 0.09%, O 50.16%), CPAA (C 44.44%, H 6.10%, N 0.39%, O 49.07%) and CPAM (C 46.23%, H 7.39%, N 13.49%, O 32.89%). The results from experimental were close to the mass elementary composition of CC (C 44.45%, H 6.22%, N 0.00%, O 49.34%), CPAA (C 48.98%, H 5.74%, N 0.32%, O 44.97%) and CPAM (C 49.04%, H 6.84%, N 14.28%, O 29.83%) based on percentage of grafting efficiencies (89.40% for CPAA and 89.98% for CPAM). These results confirmed the existing of the grafted polymer in chemically modified corn cobs which were 0.0111 mol-PAA-g⁻¹-CPAA and 0.0141 mol-PAM-g⁻¹-CPAM, respectively.

Surface area of unmodified corn cob, CPAA and CPAM modified corn cob were calculated from the isotherm data using Brunauer-Emmette-Teller model (BET). The results are shown in Table 1.

The adsorbed amount of Cu(II), Ni(II) and Cd(II) on CPAA and CPAM as a function of contact time are shown in Fig. 3. The adsorbed amount was sharply increased within 30 min and then became equilibrium. The fast adsorption rate in the first stage might relate to the large number of available sites on the adsorbent surface. The larger surface area enhances the rate of adsorption, which corresponded to the results in Table 1. However, after this stage, the slow adsorption process was due to the accumulation of saturated ions on the surface.

Kinetic models were used to examine the rate of the adsorption process and propose potential rate-controlling step. The kinetics of the adsorption of heavy metal ions on the adsorbent surface were determined by two kinetic models as follows:

**Pseudo-first order kinetics:**

\[ \ln (q_e - q_t) = \ln q_e - k_1 t \]  

**Pseudo-second order kinetics:**

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]

where \( q_e \) [g kg⁻¹] is the equilibrium adsorbed amount, \( q_t \) [g kg⁻¹] is the adsorbed amount at various time, \( k_1 \) and \( k_2 \) are rate constant of pseudo-first order kinetics and pseudo-second order kinetics, respectively and \( t \) [min] is contact time.

Table 2 showed the kinetics study results of Cu(II), Ni(II) and Cd(II) adsorption by CPAA and CPAM. The results showed the pseudo-second order kinetics parameters...
gave the theoretical adsorbed amount values ($q_{e,cal}$) that agree well with the experimental values ($q_{e,exp}$), and the linear correlation coefficient ($R^2$) of the pseudo-second order kinetics plots for the adsorption of adsorbents for all metal ions were above 0.99. In addition, this results indicated that the adsorption kinetics of Cu(II), Ni(II) and Cd(II) onto CPAA and CPAM were controlled by chemical process 10) 17). The chemical reaction is involved in a valence forces through sharing or exchanging of lone-pair electrons from the functional groups to the metal ions 18).

The adsorbed amount for CPAA and CPAM as a function of concentration are shown in Fig. 4. The adsorbed amount was increased with an increase in initial concentration. The maximum adsorbed amount for Cu(II), Ni(II) and Cd(II) were achieved at 239.55, 156.46 and 361.89 g kg$^{-1}$ for CPAA, respectively and 148.41, 101.55 and 238.06 g kg$^{-1}$ for CPAM, respectively.

The equilibrium isotherms were used to express the surface property and affinity of an adsorbent for adsorbate. In this study, two typical isotherms were used for fitting the experimental data.

The Langmuir isotherm describes the uptake of heavy metal ions occurring on a homogenous surface by monolayer adsorption, and there is no interaction between the adsorbed ions. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{b q_m} + \frac{C_e}{q_m}$$

(4)

where $C_e$ [g m$^{-3}$] is the equilibrium concentration of metal solution, $q_m$ [g kg$^{-1}$] is the maximum adsorbed amount, and $b$ [m$^3$ g$^{-1}$] is a Langmuir constant that relates to the heat of adsorption. The $q_m$ and $b$ values were calculated from the slopes ($1/q_m$) and intercepts ($1/b$) of linear plots of $C_e/q_e$ versus $C_e$.

The Freundlich isotherm model is the empirical relationship and assumption based on metal ions adsorption on a heterogeneous surface. It has a linear form as follows:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F$$

(5)

where $K_F$ and $n$ are the Freundlich constant and calculated from the slope ($n$) and intercept ($\ln K_F$) of linear
plots of ln qe versus ln Ce.

From Table 3, the adsorption results showed that maximum adsorbed amount from experimental of CPAA was higher than that of CPAM. It is possibly caused by the affinity of carboxylic (-COOH) and amide (-CONH₂) groups, which have different amount for valence electrons, towards heavy metal ions 20) 21). In addition, the equilibrium parameters showed that Cu(II), Ni(II) and Cd(II) adsorption were fitted with Langmuir isotherm. The results showed Langmuir isotherm gave the theoretical adsorbed amount (qm,cal) that agree well with the experimental values (qm, exp), whereas the linear correlation coefficient (R²) for the adsorption of the adsorbents for all metal ions was above 0.98. Furthermore, this indicated that the uptake of heavy metal ions occurring on a homogenous surface by monolayer adsorption, and there is no interaction between the adsorbed ions.

The reusability of adsorbent for various metal ions was observed at metal concentration of 200 g m⁻³, pH 5.5 and 120 min. For first adsorption cycle of CPAA and CPAM, the adsorbed amount of Cu(II), Ni(II), and Cd(II) were closed to 100%. However, only Cd(II) performed high adsorbed amount after reused up to four cycles. For Cu(II) and Ni(II), the adsorbed amount decreased to 78% and 59%, respectively. This can be explained by the binding ability of metal ions to the specific functional groups. The ionic radius of each metal is Cd(II) 0.95 pm, Cu(II) 0.73 pm, and Ni(II) 0.69 pm. The protonation of some active sites after regeneration caused the competitive adsorption of H⁺ and metal ions which led to the difference in heavy metal removal performance. CPAM performed lower adsorbed amount than CPAA which is attributed to the inherent non-ionic characteristic of amide groups of polyacrylamide.

### 4. Conclusion

Alkali-treated corn cob was chemically modified with poly(acrylic acid) and polyacrylamide. The maximum adsorbed amount for Cu(II), Ni(II) and Cd(II) were achieved at 239.55, 156.46 and 361.89 g kg⁻¹ for CPAA and 148.41, 101.55 and 238.06 g kg⁻¹ for CPAM. The reusability of the modified cellulose adsorbents maintained over 59-100% for four adsorption cycles. The different types of modified functionality affected the heavy metal adsorption behavior due to their functional group characteristics. The kinetics result indicated that the adsorption followed pseudo-second order model. The adsorption isotherm was fitted with Langmuir isotherm model. The modified cellulose adsorbents from corn cob could be an alternative for low-cost and efficient adsorbent for removal of hazardous heavy metal from aqueous system.

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