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Reuse of Newspaper As An Adsorbent For Cu (II) Removal By Citric Acid Modification

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Abstract. High Consumption of paper, bring the impact of the waste paper itself. And the utilization of the paper is limited to recycled products and crafts, whereas paper such as newspaper still contains cellulose that can be potential to be used as a heavy metal adsorbent. In this study, newspaper was dissolved in sodium bicarbonate to reduce various impurities and then was reacted with citric acid (CA). The modified adsorbent was characterized by FTIR and was tested for adsorb Cu(II) in artificial solution. After adsorption process, the solution was filtered and analysed using Atomic Absorption Spectrophotometer (AAS). The adsorption experimental data was fitted to Langmuir, Freundlich, Tempkin, and Dubinin-Radushkevich for equilibrium model and was fitted to pseudo first order reaction and pseudo second order reaction for kinetic studies. The result showed that CA-modification newspaper able to remove heavy metals Cu(II) in solution.

1 Introduction

The growth of pulp and paper industry is still increasing. Over 400 million metric ton paper and cardboard are produced worldwide every year and consumtion of paper reached 400% in the last 40 years [1]. From newspaper to paper wrap, paper is still everywhere and mostly ends up in landfills so it will produce accumulated paper waste.

Meanwhile, the utilization of the paper is limited to recycled products and crafts, whereas paper such as newspaper still contains cellulose that can be used as a heavy metal adsorbent. Exposure to heavy metals can cause cancer in humans. For example Copper (Cu), if humans consumed continuously will cause irritation, itching, skin diseases, cancer, liver, kidneys and lungs [2].

Activated carbon as adsorbent has been widely used. However, activated carbon is an expensive material and activated carbon is widely used for adsorption of organic components instead of heavy metals [3].

Old newspapers is one source of cellulose and has the potential to be used as a heavy metal adsorbent. As research conducted by Chakravarty et al [4] used the newspaper that has been modified as adsorbent, capable of reducing the metal content of Zn 9.20 mg / g with initial concentration of Zinc 10.31 mg / lt. Then Chakravarty et al [2] conducted a study with an adsorbent newspaper to absorb Cu (II), obtained a maximum loading capacity of 30 mg / g with initial concentration of Cu (II) 20 mg / l. Dehghani et al [5] using old newspapers that have been modified to absorb chromium of 59.88 mg / g (64%) with a dose of adsorbent 3 g / l and a contact time of 60 minutes. Marshall [6] enhanced the adsorption capacity of soybean hulls for copper uptake by employing base treatment before modification with citric acid (CA). Pitsari et. al [7] showed that Citric Acid- modified newspaper pulp is an effective adsorbent for the removal of Pb^{2+} from wastewater. Lignocellulosic materials exhibit high metal removal ability that is attributed to the sorption properties of cellulose and its affinity towards metal ions. Metals interact with the negatively charged functional groups of cellulose such as carbonyls, carboxyl groups, hydroxyls, phenolics and sulfonic acids [7]. Therefore newspaper needs to be modified. One of treatment for modified is by using citric acid to form esterification [3].

2 Materials and Methods

This research was conducted in two stage: the first was preparation adsorbent from old newspapers. Newspaper was reduced in size, then was dissolved in a solution of 10% of sodium bicarbonate. Then the adsorbent filtered and washed with distilled water until pH 6.5-7. Then it was dried in the oven. After that, it was reacted with 0.5 M citric acid for 90 minutes then filtered and washed with 200 ml of distilled water. The adsorbent was dried in the oven until the weight is constant. The adsorbent was characterized by Fourier

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Transform InfraRed (FTIR) .The second stage, the parameters were tested initial concentration of Cu(II), adsorbent doses, and contacted time.

After the adsorption process was complete, the solution was filtered. Both initial and final concentration of $CuSO_4$. 5 H_2O was analyzed using atomic absorption spectrophotometer.

Percent of Cu (II) removal and adsorption capacity, was calculated using the following equation:

$$\% \text{ removal} = \frac{C_i - C_e}{C_i} \text{ x } 100 \qquad [1]$$

Adsorption capacity:

$$q_e = \frac{C_i - C_e}{m} \, x \, V \qquad [2]$$

Information :
Ci: initial concentration of Cu(II) (mg / l)
Ce: the final concentration of Cu(II) (mg / l)
qe: Cu (II) which adsorbed by the adsorbent (mg / g)
V: total volume of solution (liters)
m: dose of adsorbent (g)

Isotherm adsorption Model

Adsorption Model approach which used in this study was the Langmuir, Freundlich, Tempkin, and Dubinin-Radushkevich adsorption. The Langmuir equation model in the form of concentration as follows:

$$q = \frac{QbC}{1 + bC} \text{..}(3)$$

Where q is the adsorbate adsorbed mass per unit mass of adsorbent (mg / g), Q is an adsorption capacity (mg / g), C is the concentration of adsorbate in solution and b is the equilibrium constant. The model of the Langmuir adsorption can be expressed in linear form:

$$\frac{C}{q} = \frac{1}{Qb} + \frac{C}{Q} \qquad (4)$$

Where Q and B are constants, and obtained from plotting a graph C / q vs. C. This equation is a straight line with a slope and intercept Q and Q, b.
The well-known Freundlich equation can be written as

$$\text{Log qe} = \log K_f + \frac{1}{n} \text{ Log Ce} \qquad (5)$$

where *n* and *k* are the Freundlich constant.

The Temkin isotherm has a convenient linear form, which is expressed by the following equation:

$$qe = B \ln A_T + B \ln Ce \qquad (6)$$
$$B = RT/b \qquad (7)$$

where, A_T is Temkin isotherm equilibrium binding constant corresponding to the maximum binding energy (L/g), B is constantly related to the heat of sorption (J/mol), R is the universal gas constant (8.314 J/mol/K), T is absolute temperature at 298 K°, b is Temkin isotherm constant,which indicates the adsorption potential of the adsorbent. Both A_T and B can be determined from a plot qe vs. ln Ce.

Dubinin–Radushkevich (D–R) isotherm :

$$\ln qe = \ln Q_m - k_d\varepsilon^2 \qquad (8)$$

where ε (Polyani potential) is [*RT* ln(1 + 1/*C*e)], *Q*m the theoretical saturation capacity(mg g−1), *k*d a constant related to adsorption energy (mol^2 KJ^{-2}), *R* is the gas constant (kJ mol^{-1} K^{-1}) and *T* is the temperature (K). The slope of the plot ln *q*e versus ε^2 gives the K_d and Q_m values

Adsorption kinetics

The linear form of Lagergren's pseudo-first-order model is generally expressed as follows:

$$\text{Log } (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (9)$$

q_t is the amount of Cu (II) adsorbed at time t (min), k_1 is the pseudo first-order rate constant for the kinetic model (1/min).

Ho and McKay in Deghani et.al [5] described pseudo-second-order model as the kinetic process of the adsorption. The equations can be rearranged to obtain linearized as follows :

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (10)$$

where, k_2 is the rate constant of pseudo-second-order kinetics (g/mg·min).

3 Result and Discussion

3.1 Characterization of adsorbent

The surface functional groups were analysed by Fourier transform infrared spectroscopy (FTIR) in the Treated Newspaper (TN) as describe at Figure 1.

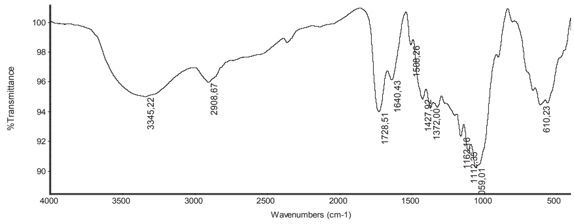

Fig. 1. FTIR spectra of citric-acid modification Newspaper

The FTIR spectra of CA- modified newspaper was in the region 4000- 500 cm^{-1} , showing characteristic cellulose peaks in the range of 1000- 1200 cm^{-1}. The band near 1000- 1100 cm^{-1} corresponds to C- O- C groups from β- (1- 4)- glycosidic bonds in Cellulose. The peaks at 1372 cm^{-1} are assigned to O- H bending and CH_2- wagging vibrations. The band near 3500 cm^{-1} is assigned to hydroxyl vibrations. The wave numbers at 2908 cm^{-1} are characteristic of alkaline groups and the band near 1640 cm^{-1} correspond to bending vibrations of fibres due to the absorbed water. The introduction of additional carboxyl groups to newspaper pulp using CA was further confirmed by characteristic vibration at 1728 cm^{-1} originating from the C=O stretch of ester carbonyl group and carboxylate ions which was the result of CA esterification [7].

3.2 Effect of adsorbent dose

Fig. 2 shows the adsorption of Cu(II) with varying weight of the adsorbent. It indicates that the uptake of Cu(II) increases as the adsorbent dose increases from 0.05, 0.1, 0,25, 0,5 to 1 g which entered into a 50 ml $CuSO_4 . 5H_2O$ with a concentration was 100 mg / l for 60 minutes therefore Cu (II) in solution was decreased.

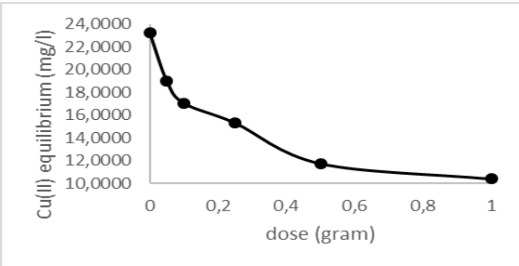

Fig.2. Effect of adsorbent dose

The adsorbent dose of 1 g was able to adsorb 55,30% Cu(II) from 50mL of 23, 27 mgL^{-1} Cu(II) in solution. This increase of Cu(II) removal may be attributed to the active site of the adsorbent surface (Fig.3).

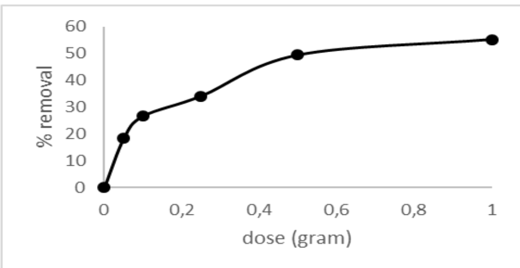

Fig. 3. Removal of Cu(II) as an effect of adsorbent dose

3.3 Effect of initial concentration

The experiments were done with variable initial copper concentration (4.2, 23.27, 35.40, and 42.42 mg/L), with adsorbent dose (1 g/50 mL), contact time (1 h) at room temperature. The percentage of Cu (II) ion uptake on the adsorbent is presented in Fig.4. Fig. 4 shows that by increasing initial Cu (II) concentration, copper removal efficiency is decreased but increased in adsorption capacity (Fig. 5). Thus, results suggest that adsorption capacity and removal efficiency of adsorbent is dependent on the initial concentration of copper [5].

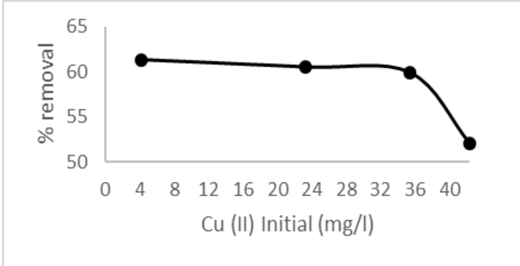

Fig. 4. Removal of Cu(II) as an effect of Cu (II) initial

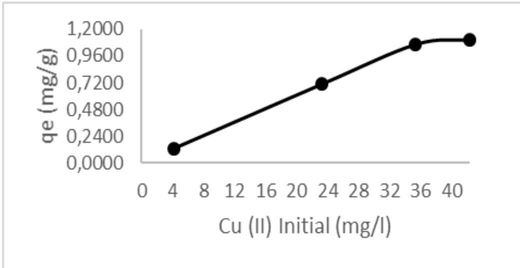

Fig. 5. Adsorption capacity of Cu(II) as an effect of Cu (II) initial

3.4 Effect of contact time

The effect of contact time (15, 30, 60, 90, and 120 minutes) was studied for an initial Cu (II) concentration of 23, 27 mg/L; Adsorbent dose of 1 g/50 mL at room temperature. Fig. 6 shows that Cu (II) in solution was decreased with contact time. The maximum efficiency for removal Cu(II) adsorption was 66,78% at 120 min (Fig. 7).

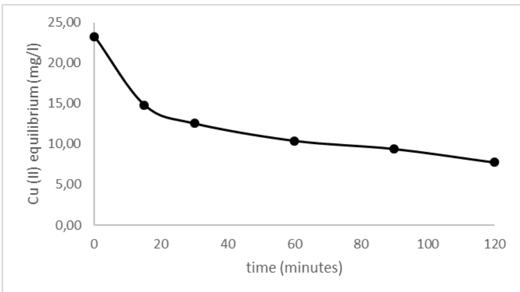

Fig. 6. Effect of contact time

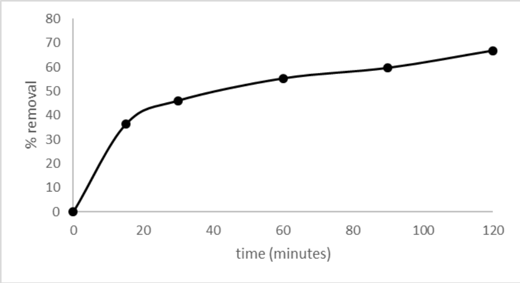

Fig. 7. Removal of Cu(II) as an effect of contact time

3.5 Adsorption Isotherms

The equilibrium adsorption of Cu (II) on the CA-modified newspaper was fitted using adsorption isotherms as discussed before. Fig. 8-11 shows Langmuir, Freundlich, Tempkin, and Dubinin-Radushkevich adsorption.

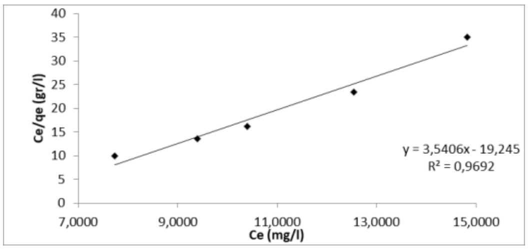

Fig. 8. Langmuir isotherm

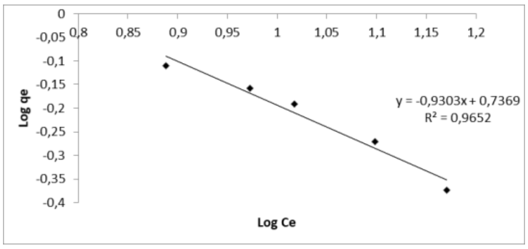

Fig. 9. Freundlich isotherm

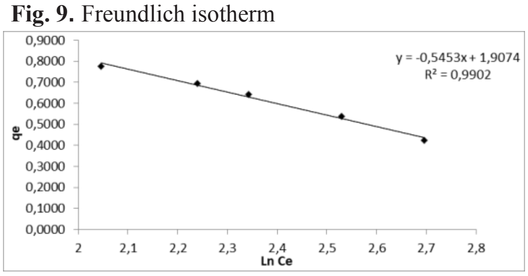

Fig. 10. Tempkin isotherm

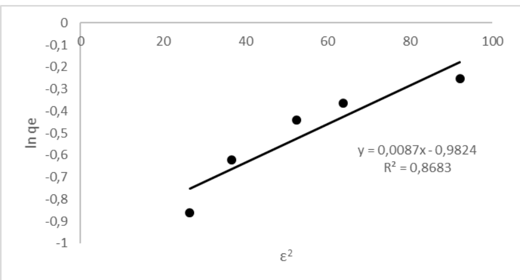

Fig. 11. Dubinin–Radushkevich (D–R) isotherm

Constants values of all four isotherms are presented in Table 1.

Table 1. Isotherm parameters and R^2 values for adsorption of Cu(II) onto CA- modified newspaper

Isotherm	Constants	Value
Langmuir	b (L mg^{-1})	0.1840
	Q_m (mg g^{-1})	0.2824
	R^2	0.9692
Freundlich	n	-1.075
	k_f	5.4563
	R^2	0.9652
Tempkin	A_T (L g^{-1})	0.0298
	B (J mol^{-1})	-0.5453
	R^2	0.9902
Dubinin–Radushkevich	K_d (mol^2/KJ^2)	-0.0087
	Q_m (mg g^{-1})	0.3744
	R^2	0.8683

The results showed that Tempkin gave the best fit for the Cu(II) adsorption by CA-modified newspaper with R^2 = 0.99.

3.5 Adsorption Kinetics

The linear form of Lagergren's pseudo-first-order model shows in Fig.12. and Pseudo- second order shows in Fig.13. at adsorbent dose 1 gram in 50 ml of 23,27 mg/l Cu (II) solution.

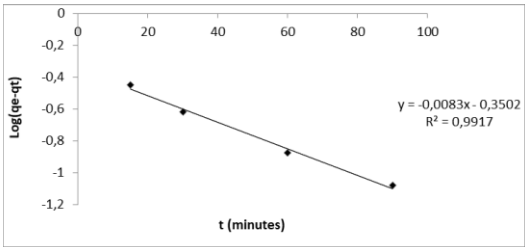

Fig. 12. Pseudo-first-order kinetics plots for adsorption of Cu (II) onto CA-modified newspaper

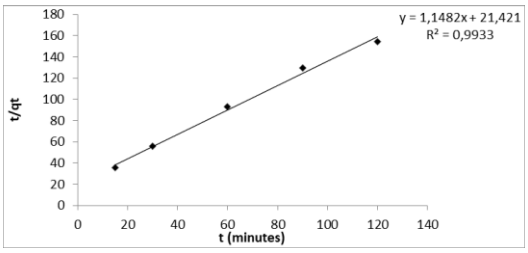

Fig. 13. Pseudo-second-order kinetics plots for adsorption of Cu (II) onto CA-modified newspaper

Kinetic parameters for the removal of Cu (II) by CA-modified newspaper are shows in Table 2.

Table 2. Kinetic parameter for the removal of Cu (II) by CA-modified newspaper

Pseudo 1st order model	k_1	q_e ($mg\ g^{-1}$)	R^2
	0.8065	0.4465	0.9917
Pseudo 2nd order model	k_2	q_e ($mg\ g^{-1}$)	R^2
	0.0354	11.482	0.9933

A comparison of Figs. 12 and 13 showed that pseudo-second-order was the best model for the Copper (II) removal onto CA-modified newspaper with a higher correlation coefficient (R^2 = 0.9933) than for pseudo-first-order (R^2 = 0.9917).

4 Conclussion

The initial concentration of the solution, adsorbent dose and contacted time has been tested in this study. Adsorbent from newspapers which modified citric acid can be used to reduce the levels of Cu (II) in the solution.

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References

1. Pratima Bajpai, *Pulp and Paper Industry*, Elsevier (2015)
2. S.Chakravarty , S. Pimple, Hema T. Chaturvedi, S. Singh, K.K. Gupta. Journal of Hazardous Materials, **159**, 396–403 (2008)
3. David William O'Connell, Colin Birkinshaw , O'Dwyer Thomas Francis. Bioresource Technology,**99**, 6709–6724, (2008)
4. S.Chakravarty, S. Bhattacharjee, K.K. Gupta,M. Singh, H.T. Chaturvedi, S. Maity. Bioresour. Technol,**98** , 3136–3141, (2007)
5. Mohammad Hadi Dehghani , Daryoush Sanaei , Imran Ali , Amit Bhatnagar. Journal of Molecular Liquids, **215**, 671–679, (2016)
6. W.E. Marshall, L.H.Wartelle, D.E. Boler, C.A. Toles. Environ. Technol, **21,** 601–607,(2000)
7. S. Pitsari, E. Tsoufakis, M. Loizidou. Chemical Engineering Journal, **223,** 18-30, 2013.