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The Application of Carbon-Chitosan Composite Imprinted Cu in the Wastewater Treatment

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Article Info	ABSTRACT
  Corresponding Author: Annisa Fillaeli, Department of Chemistry Universitas Negeri Yogyakarta Email: annisa_fillaeli@uny.ac.id	This research aimed at determining the effect of chitosan in synthesizing imprinted Cu carbon-chitosan composite properties, the effect of imprinting Cu in carbon-chitosan composites to the adsorption efficiency and adsorption capacity of Cu in electroplating waste via batch methods, and the regeneration pattern of the composite. Composites were characterized using FTIR and SEM-EDX. In FTIR spectra, the addition of Cu caused the reduction of -OH and -NH functional groups intensity as the active site of Cu chemical bonding in 3448.72 cm-1. SEM-EDX analysis showed that the carbon-ionic imprinted chitosan composites after desorption contains the element of C = 60.17%, O = 38.8%, Cu = 0.83% and Na = 0.85%. The optimizations of Cu adsorption were studied from the concentration pattern of its variable, measured with Atomic Absorption Spectroscopy (AAS). The results showed that an optimum concentration for adsorption of Cu was 75 mg / L and an optimum contact time for adsorption of Cu was 24 hours with adsorption efficiency of 98.54% and adsorption capacity of 2.62 mg/g respectively. The adsorption yield of electroplating waste showed the adsorption efficiency of 31.62% and adsorption capacity of 367,79 mg/g respectively. Regeneration test was investigated from adsorption-recovery-reactivation (A-Rcov-RAct) steps. This regeneration test was carried out in three cycles. Recovery test was carried out using EDTA 0.05 M and 0.1 M HCl solutions. The efficiency of reactivation was identified from adsorption ability after activated with 0.1 M NaOH from two routes of recoveries. The results showed that recover agents do not influence the adsorption percentage, while to the recovery percentage progress, HCl 0.1M > EDTA 0.05M. All routes of reactivation showed the similar results in average 99% *Keywords: chitosan, activated carbon, imprinted, adsorption efficiency, adsorption capacity, regeneration*

1.   INTRODUCTION

Electroplating waste is potentially harmful to the environment because it contains heavy metals such as Cu, Cr, Cd, Pb, Zn and Ni. The Indonesia Ministry of Population and Environment (1990) included copper in the high toxic waste group along with the elements of Hg, Cd, Pb and Zn. Based on the regulation no.82 of 2001 of Indonesia, the threshold for Cu is < 0.02 mg/L. However, Novita, et al, (2015) found that Cu content from the silver industrial wastewater in Kota Gede Yogyakarta showed the level of 84,9350 mg/L. It potentially stimulates a serious impact.

According to Palar (2004), phytoplankton will die at a Cu concentration of 0.01 mg/L because Cu inhibits enzyme activity in phytoplankton cell division. Additionally, Cu concentrations in the range of 2.5-3.0 mg/L in water bodies will kill fish. Cu (II) ions can accumulate in the brain, skin tissue, liver, pancreas and myocardium. Therefore, it is prominent to propose the strategy of how to reduce Cu in water bodies (Anita, et al, 2017).

Adsorption is the most widely methods due to its safely used, does not have side effects endanger health, does not require complicated and expensive equipment, is easy to work with and the most important things, the adsorbent can be regenerated so it reduces the potential accumulation of waste materials. To implement the effectivity and efficiency of adsorption, batch method is considered easier than the column method. The former is easy to install and only requires smaller amounts of adsorbent compared to the latest.

Subarman, et al, (2013) reported that the batch method is more effective in reducing polluted substances. Another report completed the findings with the used adsorbent which have high capability in batch adsorption process. That is activated carbon (Prabowo, 2009). The activated carbon showed high adsorption capacity with high surface area, even though in some cases it has limited ability in adsorbing metal ions. To overcome this problem, activated carbon is supported by other material such as chitosan which also has good adsorption records. Both carbon and chitosan are mixed to be made composite. This is expected to increase the synergistic effects (Dahlena, et al., 2018) because the carbon itself is capable to adsorb high concentration and then the adsorption is supported by two functional groups of chitosan, namely the amine group and the hydroxyl group, that these polycationic free amine group causes chitosan to be able to bind metal ions (Lasindrang, 2014).

To enhance the capability of gaining more target adsorbate being physically attached to the adsorbent, the selectivity of the adsorbent materials is considered to create. One of the strategies in making adsorbent is molecularly imprinting synthesis technique. The imprinted technique is carried out to form a cavity that is identical to the analyte so that is expected to increase the adsorption of target in the matrix. In this research, the higher Cu adsorption, the better water quality will get. Therefore, this research use the imprinting technique approach to increase the capability of the carbon-chitosan composite in adsorbing Cu from wastewater.

The promising imprinted material in handling wastewater of Cu contamination is predicted will stimulate the common problem of adsorbent-adsorption phenomenon, such as leaving the saturated adsorbent of target adsorbate that cannot be capable to use in the next cycle. If the focus is given to the material strength, the result showed that is still good. In this time, the material just needs the addition treatment like regeneration procedure. Regeneration is the process of renewing the adsorption capacity of an adsorbent by an activator. In the study of heavy metal adsorption, NaOH is one of the good regenerators for the adsorbent regeneration process. NaOH is easy to obtain and has good ability to activate functional groups in the adsorbents (Ayu Herning, et al., 2014).

Research focuses on adsorbents to regenerate through adsorption, recovery, and reactivation steps. The adsorbent, Cu imprinted chitosan-carbon, cross-linked by glutaraldehyde, acetaldehyde or formaldehyde. From the three cross-linkers, it will find the best chemical cross-linker that supports to the strength of the adsorbent. The adsorbent characteristics are tested based on its swelling, functional groups of compounds (FT-IR) and surface image of materials (SEM-EDX). Regeneration is carried out in adsorption, recovery and reactivation steps. The adsorption process is done in several times. After the adsorbent is saturated, it is needed to recover the Cu from the adsorbent by using EDTA and HCl as desorption agents. The last step in regeneration process is carried out by immersing the adsorbent using NaOH as an activator. All the concentration is measured by atomic absorption spectrophotometer (AAS) to monitor the progress.

2.   RESEARCH METHOD
2.1.   Composite synthesis

A 500 ppm $CuCO_3$ solution in the 1% acetic acid was prepared as Cu (II) stock. 0.5 grams of chitosan was dissolved in 20 mL of Cu (II) solution and stirred for 60 minutes at room temperature. The homogeneous gel then forms overnight. The next stage is adding 0.125 grams of activated carbon into the gel of chitosan-Cu mixture. It was stirred for 1 hour and then let stand for 15 minutes. The mixture formed is then dripped using a pipette into 50 mL of NaOH and ethanol provided in the shaker. After 15 minutes the beads are formed, then filtered. Crosslinking reaction was done by soaking beads granules into cross-linking agent: glutaraldehyde, formaldehyde and acetaldehyde for 24 hours of each agent. Cu inside the beads then being released by desorption method using a solution of EDTA 0.05 M and or HCl 0.1 M. After immersing the composite in the desorption agent for 2 hours, the mixture then filtered and the clear solution was analyzed using AAS. The last step of imprinted composite synthesis was soaked the composite using NaOH 0.1 M for 1 hour, filtered, and washed with water and dried to a constant weight.

2.2. Swelling test

Determination of swelling degrees can be done by soaking composites into aquadest for 24 hours and weighed as wet. The degree of swelling is expressed as:

$$\% \text{ degree of swelling} = \frac{wo - wi}{wo} \times 100\%$$

Descriptions: wo=wet weight (g), wi= dry weight (g)

2.3. Composite Characterization

Cross-linked imprinted composite chitosan-carbon are characterized by InfraRed (IR) and SEM-EDX spectrophotometers.

2.4. Determination of optimum contact time

A total of 0.2 grams of imprinted chitosan carbon composites are inserted into a 100 mL bottle containing 10 mL of simulated solution then in the shaker at a variation of contact time of 1; 2; 24; 32 and 48 hours.

2.5. Determination of optimum concentration

Adsorption using ionic imprinted chitosan carbon composites is performed at a concentration variation of 50, 75 and 150 mg/L.

2.6. Determination of adsorption efficiency of Cu

$$\% \text{ Adsorption efficiency} = \frac{Co - Ca}{Co} \times 100\%$$

Information:

Co=sample concentration before adsorption (mg/L)

Ca = sample concentration after adsorption (mg/L)

2.7. Determination of adsorption capacity of Cu

$$Q = \frac{(Ci - Cf) \times V}{W}$$

Information:

Q = the number of ions adsorbed in the adsorption (mg/g)

Ci = sample concentration before adsorption (mg/L)

Cf = sample concentration after adsorption (mg/L)

V = volume of solution

W = mass of adsorbent (gram)

2.8. Regeneration test

The regeneration test was done via 3 steps, which are adsorption-recovery-reactivation. The recovery process was tested by EDTA 0.05 M and HCl 0.1 M. Adsorbent recovery was done twice, 24 hours and 2 hours by soaking. Reactivation adsorbent was done using NaOH solution, carried out along 2 hours by soaking the adsorbent into the agent solution. followed by the process of washing adsorbents using aquadest to neutral pH, then adsorbents are dried using an oven until the adsorbent mass is constant

3. RESULTS AND ANALYSIS

This synthesis produces a black beads shape with a slightly hard texture. Here is a composite image of the carbon chitosan imprinted Cu.

Figure 1. Composite synthesis results

These results were obtained starting by dissolving Cu (II) in acetic acid which was used to dissolve chitosan. According to Sugita, P (2009) chitosan dissolves best in acetic acid. The chitosan solution was then left overnight with the aim that the chitosan and metal solution could react completely. The addition of metal solution into chitosan serves to form complex bonds between metal ions with the active group (NH_2) in chitosan so that it is expected to form a cavity that is specific for Cu. The next step is to add chitosan hydrogel to the activated carbon.

Beads were formed by dripping chitosan-carbon hydrogel into NaOH-Ethanol solution. Chitosan polymerization was stopped when injected into NaOH to form smaller polymer units (Zenobia et al., 2017). The addition of a few drops of ethanol into NaOH serves to make the beads harder. Ionic imprinted beads are then crosslinked. The low chemical stability and mechanical properties of the hydrogel may be soluble in the medium (Abdul-Mohzen, A.M., et al.; 2012). Therefore, the hydrogel needs to be crosslinked to change the structure of the chitosan polymer to be more rigid. It is hoped that the cross-linking process can increase the mechanical and chemical strength of the beads.

The use of glutaraldehyde as a crosslinking agent was chosen because of its low cost and relatively fast preparation. In addition, glutaraldehyde was chosen because research (Siti, 2012) showed that chitosan hydrogel was more crosslinked with glutaraldehyde > acetaldehyde > formaldehyde. Glutaraldehyde produces a tight and rigid structure because glutaraldehyde has two carbonyl functional groups (C=O) which are favored by the amine group in chitosan.

3.1. Swelling test

The swelling test was carried out by immersing the composite in distilled water for 24 hours (Titin, et al, 2013). The comparison of swelling test between chitosan without carbon and chitosan with carbon, respectively, is 120% and 60%. The ability of chitosan to absorb water causes chitosan beads to have a higher degree of swelling (Alauhdin and Widiarti, 2014).

3.2. FTIR Characterization

The FTIR spectrum is shown in Figure 2 below. From the FTIR spectrum of chitosan powder and composite chitosan-carbon, it showed overlapping vibrations of the group -NH and -OH groups found at the absorption of the wave number 3433.29 cm^{-1}. The band at 2877.79 cm^{-1} and 1080 cm^{-1} indicated -CH group and C=O group respectively. The FTIR spectrum of carbon-chitosan composite and carbon-chitosan imprinted Cu showed the same band at 1635.64 cm^{-1} wavenumber. This suggested that the presence of a C=N group described the successful cross-linking process of glutaraldehyde (Akhmad, et al., 2015). In addition, the FTIR results of the imprinted carbon-chitosan composite also showed an uptake at the wave number 3448.72 cm^{-1}. This is due to the presence of metal ions added to the composite which causes the reduced mass of the function groups -OH and -NH as the active sites. The shift in the wavenumber was influenced by the bond formed between the hydroxyl and amine groups and the added ions (Shofiyani, et al., 2015).
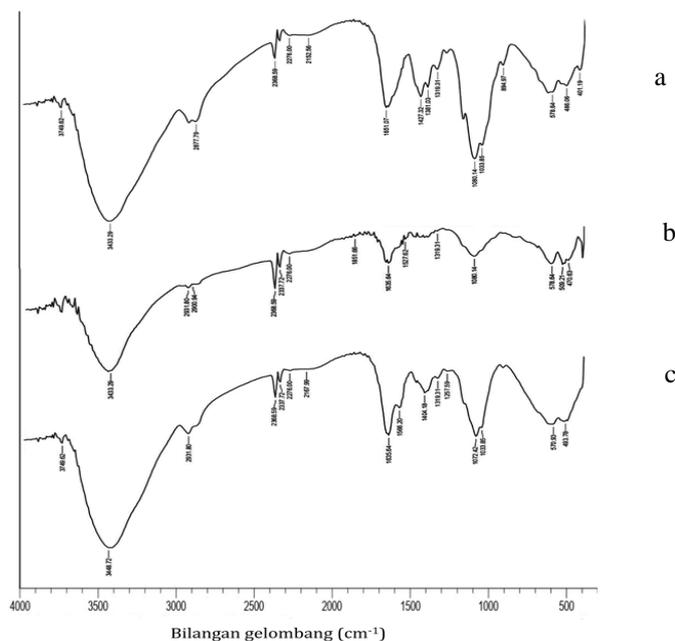
Figure 2. FTIR spectrum; a = chitosan, b = chitosan carbon, c = imprinted carbon-chitosan

3.3.   SEM-EDX characterization

The characterization of the carbon-chitosan composite imprinted Cu with SEM-EDX showed in Figure 4-6 below.
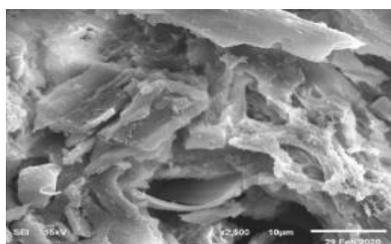

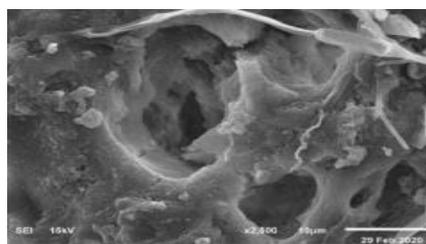**Figure 3.** Composite before desorption (2500 magnification)

Figure 4. Composite Carbon-Chitosan imprinted Cu (2500 magnification)

From the results of SEM characterization, it can be seen that in adsorbents that have been done Cu desorption looks at a larger cavity when compared to the results of SEM before Cu desorption. This indicates that there is an influence in the Cu desorption process to the adsorbent cavity. The next characterization is to use SEM-EDX. The purpose of this characterization is to find out the composition contained in the adsorbent. The results of EDX SEM characterization can be seen in Table 1.

Table 1. SEM-EDX characterization results

Elements	Composites Before Desorption Cu (%)	Composites After Cu Desorption (%)
C	63.99	60.17
O	32.68	38.98
Cu	3.33	0.83
Na	-	0.85

Based on Table 1 it can be seen that the Cu content before desorption > after desorption. Based on the data obtained, Cu was successfully removed from the desorption process which

amounted to 75.08%. The result is different from the results of desorption measurement using SSA which is 97.48%. This is possible because SSA is measured in the form of liquids while SEM EDX is measured in the form of solids. In addition, another possibility is that when measuring using SSA, the measurable substance is only the target metal while when measuring SEM-EDX there are other substances that are measured in the analyte such as the presence of the element Na. The Na element is detected when the SEM-EDX measurement is taken, it is because the Cu desorption process uses Na_2EDTA so that there is potentially a Na element attached to the composite.

3.4.   Adsorption of Carbon-Chitosan Composite Imprinted Cu

Concentration variation is carried out in a simulated solution with a concentration of 5; 75 and 150 mg/L. Data on efficiency and adsorption capacity for concentration optimization can be seen in Table 2.

Table 2. Adsorption efficacy data and adsorption capacity for concentration variation

Concentration variation	Adsorption efficiency	Adsorption capacity
5 mg/L	92.40	0.155
75 mg/L	98.54	2.62
150 mg/L	85.69	4.21

From the data, it was seen that the carbon-chitosan composite imprinted was able to absorb Cu optimally at a concentration of 75 mg / L with an adsorption pH of 5.   Adsorption Cu decreased at a concentration of 150 mg / L which has an adsorption pH of 4.8. That's because in the acidic pH there was protonation of the amine group ($-NH_2$) in the chitosan to $-NH_3^+$ which reduced the number of active sites on the adsorbent surface to adsorption Cu. H^+ ions in solution can compete with metal ions for active sites so as to degrade suspended ions (Ikhsan, et al., 2017). In addition, Cu adsorption also decreased in the concentration of 5 mg / L which has an adsorption pH of 5.6. That was because at pH 5.6 Cu(II) begins to form deposits of $Cu(OH)_2$ while at pH 7.1 Cu settles perfectly (Shevla, 1990)

3.5.   Adsorption Carbon-Chitosan Composites Imprinted Cu in the Contact Time optimization

The variation in contact time is done at 1 ;2; 24 ; 32 and 48 hours. Adsorption efficiency and capacity data can be seen in Table 3. Optimum contact time was generated within 24 hours with adsorption efficiency of 98.54%. These results are influenced by the cross-linking process using glutaraldehyde. In previous studies, the cross-link reaction of a hydrogel will produce a denser and tighter structure so that its mechanical properties will be better because the structure is not easily fragile (Rohindra, et al., 2004). The cross-link reaction of the carbon-chitosan imprinted Cu using glutaraldehyde lasts for 24 hours. The longer the reaction time of the cross-link bond, the higher the cross-link formed between the amine group in the chitosan and the carbonyl group in the cross-linker agent. However, with the tightness of the structure can reduce the efficiency of adsorption because the target ion will be more difficult to get into the adsorption, so it takes time for the adsorbate to be optimal in the adsorption process (Abdel-Mohzen, A.M, et al., 2011).

Table 3. Adsorption Efficacy Data and Adsorption Capacity for Contact Time Variations

Contact time (hours)	Adsorption efficiency	Adsorption capacity
1	22.87	0.60745
2	27.95	0.7425
24	98.54	2.61728
32	97.62	2.5929
48	96.44	2.56145

3.6. Regeneration

This process was done via adsorption-recovery-reactivation steps in 3 cycles. The adsorbent used was the one which reached optimal concentration and contact time along Cu adsorption process. The different route was in the recovery mode. The recovery routes were using EDTA 0.05 M (A) and HCl 0.1 M (B) respectively. The results of adsorption efficiency data and adsorption capacity in those two routes can be seen in Table 4 and 5. After that, the reactivation using NaOH 0.1M was done.

Table 4. Adsorption efficiency and adsorption capacity I, II, III via A route

Adsorption	Concentration (mg/mL)		Adsorption efficiency (%)	Adsorption capacity (mg/g)
	Initial	End		
I	67.904	1.932	97.15 %	3.298
II	67.904	0.521	99.23 %	3.370
III	67.904	0.367	99.46 %	3.377

Table 5. Adsorption efficiency and adsorption capacity I, II, III via B route

Adsorption	Concentration (mg/mL)		Adsorption Efficiency (%)	Adsorption Capacity (mg/g)
	Initial	End		
I	67.904	0.321	99.53 %	3.380
II	67.904	0.251	99.63 %	3.382
III	67.904	0.174	99.74 %	3.386

Based on the results there was an increase in adsorption efficiency from adsorption I to adsorption III but the decrease is not too significant. All the routes provided the significant value of reduction, which notably reached more than 95% that indicated the adsorbent was still good to further use. However, if it concerned to the number of adsorption efficiency percentage, HCl 0.1M showed better trend compared to EDTA 0.05M (Syauqiah et al., 2016). In A route, EDTA acts as ligands and Cu plays as the central atom. EDTA is a good type of ligand for binding to certain types of metals. EDTA has electron donor atoms namely O in the -OH and N groups forming a stable complex. In the process of recover Cu using HCl solution, HCl only acts as a solvent for Cu. HCl cannot bind and form complex compounds with Cu like EDTA does. Cu has a higher (more positive) drop potential than hydrogen, so there will only be a process of ion exchange between hydrogen and Cu atoms. In this case, the percentage of reaching higher efficiency of HCl due to the higher dissolved of Cu, indicated that HCl is recommended solvent for Cu systems. On the other hand, Cu recovery rate that exceeds 100% is due to the amount of Cu which was left along the imprinting process.

The recovery process was done in two consecutive steps, stirring along 24 hours continued with 2 hours the same treatment. The purpose of the second stirring was to make sure that Cu retained in the adsorbent was properly permanent. Reactivation aimed to restore the function of the active site of the chitosan so that adsorbents can bind the target molecule back and rearrange the groups that have been used in the adsorption process (Aulia et al., 2017). The results of reactivation efficiency in adsorbents via A and B routes showed effective results, due to NaOH's role as regenerant that was able to reactivate sites on adsorbent surfaces well so that adsorption capacity on adsorbents increased. A good recovery rate in the previous process also plays an important role in improving regeneration efficiency.

3.7. Adsorption of Carbon-Chitosan Composite Imprinted Cu in Electroplating Waste

The electroplating waste from silver industrial waste Kotagede Yogyakarta has high acidity as received. The pH was 0.3. The adsorption efficiency of electroplating waste was 31.617% with an adsorption capacity of 367.79 mg / g. This was because the acidity of electroplating waste influenced

the role of Cu in the aqueous media. Normally, Cu dissolves in water media with a pH of ≤ 5 while at pH 6 < pH >7 is only a small part (Roy, et al., 2006). And so, this condition made Cu tends to be available in acidic water than in the more basis like the composite. In addition, chitosan has easily soluble in acids so an aqueous media with a pH of 0.3 will damage the formation of polymer because chitosan as the part of composite is significantly soluble. The competition of H+ and Cu ions to bind to the active group of chitosan becomes greater if it is in an acidic condition due to the greater number of H+ ions.

4. CONCLUSION

The results of FTIR carbon-composite imprinted Cu showed a shift in absorption at the wavenumber of 3448.72 cm^{-1} due to the addition of Cu to the composite while the SEM image showed a greater cavity after the Cu desorption process. The EDX provided information that the imprinted composite contained elements C = 60.17%, O = 38.98 %, Cu = 0.83 % and Na = 0.85 %. The optimum concentration in adsorption of chitosan-carbon composite imprinted Cu was 75 mg/L with the 24-hours optimal contact time, with adsorption efficiency of 98.54% each and adsorption capacity of 2.61728 mg/g respectively. Applied the imprinted composite to the industrial electroplating wastewater yielded the efficient adsorption of 31.617% and an adsorption capacity of 367.79 mg/g.

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