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Synthesis and Characterization Composite Cellulose-TiO_2 From Sawdust and Its Application as Adsorbent of Cd(II) in Aqueous Solution

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Abstract. Extraction of cellulose from wood sawdust using methanol and hydrochloric acid within the various concentration of 1%, 3%, 7%, and 11% (v/v) for 3 hours has been done. The cellulose has characterized by FTIR spectrophotometer and shows that the best concentration for that process was 7% of HCl. The Cellulose than composited with TiO_2 and used as adsorbent of Cd(II) metal ion in aqueous solution. The adsorption of Cd(II) metal ion at various concentration gave the value of adsorption rate of Cd(II) metal ion in cellulose was 2.10^{-6} with an adsorption energy of 22.3 kJ/mol, meanwhile in cellulose-TiO_2 composite was 3.10^{-7} with an adsorption energy of 20.7 kJ/mol. The sequential desorption of Cd(II) metal ion using H_2O, HCl, and EDTA solutions were applied to know the adsorption mechanism. The result of desorption showed 22.6% of Cd(II) was desorption by HCl and EDTA reagents indicate that chemical interaction has occurred for cellulose adsorbent while for cellulose-TiO_2 composite gave 71.2% desorption by H_2O indicate the physic interaction.

INTRODUCTION

Heavy metals are a type of pollutant found in many industrial wastewaters. The presence of heavy metals is very dangerous for the lives of humans and other living things because the toxicity aspect and nondegradable [1]. Cadmium is one of a heavy metal that is very dangerous substance and can accumulate into the environment, especially settling in the bottom of the water forming complex compounds with organic and inorganic materials. Cadmium naturally is component found in the earth's layers and can enter waters through a series of geochemical processes and human activities [2].

Nowdays to overcome pollution caused by industry are by reducing pollutant concentrations meet to the lowest concentration in the environmental quality threshold before being discharged. One of the commonly used methods is adsorption. The adsorption method is an alternative method that is very suitable with the conditions of developing countries because it is cheaper and practical, especially by using *low cost adsorbents* such as clay material, agricultural waste, rice husk, peat, and *sea food* processing waste [3,4]. The adsorption method is generally based on the interaction of metal ions with functional groups that exist on the surface of the adsorbent through the chemical interaction and usually occurs on the surface of solids that are containing the functional groups such as –OH, -NH, -SH and -COOH [5].

Sawdust is one of biowaste residue from the sawmill process and is categorized as a by-product, measuring about 0.25 mm - 2.00 mm, very light weight in dry conditions. Utilization of wood sawdust as an absorbent material is one of the cheap technologies because the raw material is easily obtained in Sumatera Selatan, Indonesia [6,7]. The wood sawdust contains chemical compounds such as cellulose, hemicellulose, and lignin [8]. The presence of cellulose and hemicellulose makes wood sawdust potential to be used as adsorbent of metal ions in the environment because of the presence of the -OH functional group on cellulose.

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Meanwile research on the adsorption of metal ions Cd (II) has been carried out, such as the research utilizing thiol-silica hybrids from ash rice husk to adsorb metal ions Cd (II) [9]. The utilize humic acid to adsorb metal ions Cd (II) in water medium [10]. For the use of cellulose from wood sawdust as a heavy metal adsorbent has been carried out. Many studies have been carried out on TiO_2 utilization, the chitosan-TiO_2 nanocomposite as photodegradation of methylene blue [11], while impregnation of activated carbon-TiO2 composite and its application in photodegradation of procion red [12]. In this research TiO_2 was added to the cellulose adsorbent to form a composite cellulose-TiO_2 which then be used as an adsorbent for Cd (II) metal ions, This study examined the ability of cellulose-TiO_2 composites to adsorb Cd(II) metal ions. The addition of TiO_2 to cellulose is expected to increase the absorption of Cd(II) metal ions because the active groups of cellulose are more open so that it is easier to interact with metal ions.

EXPERIMENTAL DETAILS

The materials were used in this study wood sawdust containing cellulose and its derivatives in the form of fibers derived from industrial biowaste of *Medium Density Fiberboard* (MDF). The chemicals such as methanol, hydrochloric acid, nitric acid, titanium dioxide, silver nitrate, cadmium chloride monohydrate, and EDTA were directly used after purchase from Merck without prior purification. The solution was prepared by deionized purity water. The Atomic Absorption Spectrophotometer AA-700, FT-IR Spectrophotometer Shimadzu Prestige-21, and JEOL JSM 6510-LA SEM-EDS were used for instrumental measurements.

Cellulose Separation from Wood Sawdust with Maceration Method [7]

The wood sawdust was dried and sifted in size of 80 mesh. Amount of 80 g of wood sawdust were put into 1 L methanol in macerated bottle until is submerged. The maceration process was carried out until the solution is no longer coloured by replacing methanol every 24 h, then filtered to obtain the filtrate and residue. The residue then dried and soaked with HCl for 3 h. The HCl used varies with concentrations of 1%, 3%, 7%, and 11% (v/v). The residue was separated, and then dried to obtained cellulose which was characterized using FT-IR spectroscopy.

Synthesis of Cellulose -TiO_2 Composite from Wood Sawdust

Amount of 7 g of cellulose obtained from the isolation process were dissolved into 100 mL 0.1 M hydrochloric acid, stirred gently until homogeneous. Then the 7 g of TiO_2 was added into the solution and continuously stirred until its evenly mixed, then let it stand overnight to form deposits. The precipitate is then separated from the solution by filtration and then washed with distilled water. The washing process is stopped when no more white solution is formed when the residue is dripped with $AgNO_3$ solution. The precipitate obtained was dried at 80ºC until weighed constant. The obtained cellulose-TiO_2 was characterized using an FTIR spectrophotometer and SEM-EDX analysis.

Effect of Interaction Time

Amount of 0.1 g of cellulose and cellulose-TiO_2 adsorbents were interacted with 10 mL of 25 mg/L Cd(II) metal ion in series of shaking time 10, 20, 30, 60, 120, 135, and 165 minutes. The mixture is filtered and the filtrate is taken to measure the Cd(II) metal ion concentration in the solution by Atomic Absorption Spectrophotometer.

Effect of Initial Metal Ion Concentration

Amount of 0.1 g of cellulose and cellulose-TiO_2 adsorbents was interacted with 10 mL Cd(II) metal ions at various of concentrations of 2,10, 25, 50, and 100 mg/L and its shaken at room temperature with the equilibrium time from the interaction time. The mixture was filtered, then the filtrate was measured for the remaining Cd(II) metal ion in the solution by the Atomic Absorption Spectrophotometer.

Study of Types of Adsorption of Cd(II) Metal Ion Through Sequential Desorption

Amount of 0.5 g of cellulose-TiO_2 adsorbent that was interacted with 50 mL of Cd(II) metal ion at the maximum concentration as a result of the determination of the effect of concentration, then shaking during the maximum time the result of the influence of interaction time. The mixture was filtered to obtain the filtrate and residue, the filtrate was then measured for the levels of Cd(II) metal ion remaining in the solution by Atomic Absorption Spectrophotometer. The residue is dried at a temperature of 80 °C, then desorption separately using 0.1 g of residue with 25 mL of H_2O, 0.1 M HCl, and EDTA 0.1 M solutions. The interaction time is the maximum time the result of the influence of the interaction time at room temperature. After the interaction process, each solution was filtered and the filtrate were analysed for Cd(II) metal ion concentration using Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Cellulose Separation from Wood Sawdust by Maceration Method

Wood sawdust is soaked using methanol repeatedly by replacing methanol solution every 24h until the solution in the bath is no longer coloured. The use of methanol in the process of separating cellulose from wood sawdust because methanol is polar solvent and can dissolve compounds such as fat, carbohydrates, proteins and unwanted secondary metabolites. The resulting residues are cellulose and hemicellulose [13].

Separation of cellulose from hemicellulose was carried out by immersing the residue using hydrochloric acid for 3 h at various variations of HCl concentrations of 1%, 3%, 7%, and 11% (v/v). Cellulose separation results were characterized using FT-IR spectrophotometer. The wavenumbers and the cellulose FTIR spectra from various concentrations of HCl 1%, 3%, 7%, and 11% are show in Figure 1.

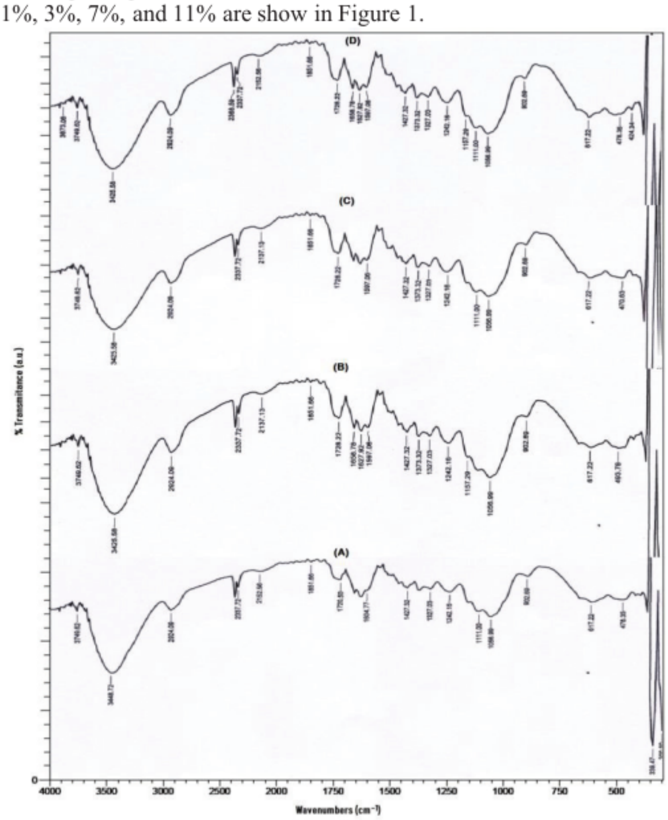

FIGURE 1. The cellulose FTIR spectra maceration at various concentrations of HCl 1% (a), 3% (b), 7%(c), and 11% (d)

The FTIR spectral number in Table 1 shows all wavenumbers that show the functional groups of cellulose appear in all FTIR spectra of cellulose e.g. 3448.5 cm^{-1} -3425.5 cm^{-1} which shows the vibration of the hydroxyl group (-OH), wavenumber 2924.1 cm^{-1} which shows the vibration of the alkyl group (-CH), wavenumber 1427.3 cm^{-1} which shows the vibration of the aryl group (CC), and wavenumbers 1242.2 cm^{-1} - 1056.9 cm^{-1} which shows the vibration of the ether group (CO). When viewed from the groups that appear in the FTIR spectrum, the concentration of HCl was not gave significant effect for the quality of the cellulose produced. The difference is that in figures A, B, and D the absorbance for lignocellulose appears at wave numbers 1658 and 1627 cm^{-1} while in figure C the absorption is absent. It can be concluded the cellulose product from maceration with HCl concentration of 7% then was used as an adsorbent in this study.

Synthesis of Cellulose-TiO_2 Composite from Wood Sawdust

Cellulose with 7% HCl concentration was composited with TiO_2 by a weight ratio of 1:1. The yield of the cellulose-TiO_2 composite was obtained as amount of 11.43 g with rendement percentage about 81.63% (b/b). The composite was characterized by an FT-IR spectrophotometer to identify the functional groups. The FT-IR spectrum for cellulose-TiO_2 composite can be seen in Figure 2.

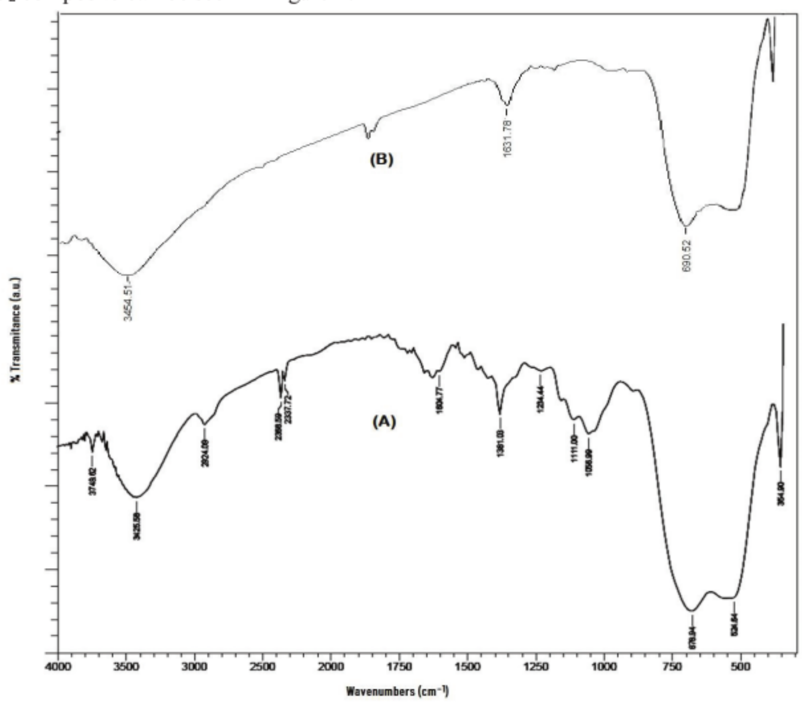

FIGURE 2. The FTIR spectra of cellulose-TiO_2 (a) and TiO_2 standard (b)

The FTIR spectrum image cellulose-TiO_2 hydroxyl (-OH) group appears at wavenumber 3425.6 cm^{-1}, alkyl group (-CH) at wavenumber 2924.1 cm^{-1} , aryl group (C-C) at wave number 1604.8 cm -1 and ether group (C-O) at wave number 1234.4 cm^{-1} -1056.9 cm^{-1}. The Ti-O uptake will appear at wave numbers 500-600 cm^{-1} [14]. In this study cellulose-TiO_2 composite spectrum, the Ti-O appears at wavenumbers 524.6 cm^{-1} and 678.9 cm^{-1}. The cellulose-TiO_2 composite adsorbent was characterized also by SEM-EDS to see the surface morphology and elementals composition of the composite. The composite analysis of cellulose-TiO_2 using SEM with a magnification of 10000 times was shown in Figure 3.

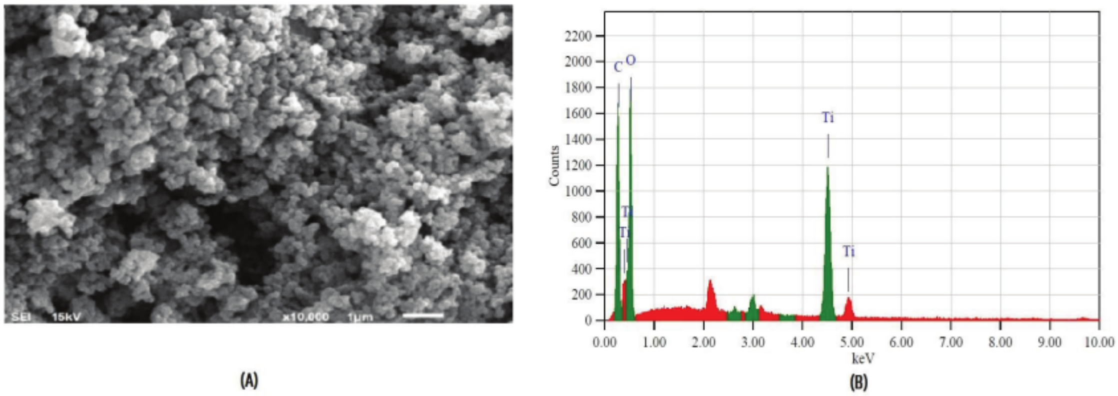

FIGURE 3. SEM image and EDX spectra of cellulose-TiO_2

The composite formation process is expected to enter into *cross linked* TiO_2 possessed by cellulose. Figure 3 shows that the composite surface of cellulose-TiO_2 is porous and it evenly distributed on the cellulose surface.

The EDS results in figure 3(b) show Ti content in cellulose-TiO_2 composites of 17.30%, this proves that TiO_2 is composite with cellulose. The content of C 35.86% and O 46.85% showed that the composite contained cellulose, because C and O were the constituent elements of cellulose.

The Effect of Interaction Time of Cd(II) Metal Ion with Cellulose-TiO_2 Composite

The effect of the adsorption time on the adsorption of Cd(II) metal ion was carried out by interacting 0.1 g of the adsorbent with 10 mL of 25 mg/L Cd (II) metal ion solution in various contact time of 10 to 165 minutes. The equilibrium time of interaction needs to be determined to know the optimum interaction of Cd(II) metal ion on cellulose-TiO_2 and cellulose as a control. The optimum time obtained can be seen in the Figure 4. The relationship between the amount of Cd(II) adsorbed (mg/g) by the adsorbent on each time were presented in Figure 4.

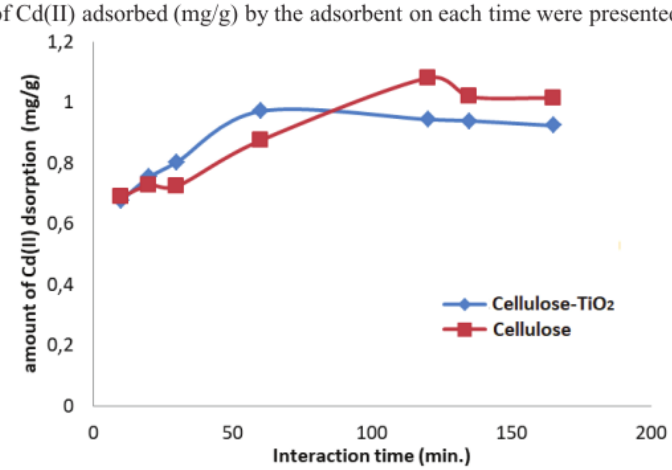

FIGURE 4. The effect of contact time of Cd(II) metal ion onto cellulose and cellulose-TiO_2 composite

Figure 4 shows the optimum time for the interaction of Cd(II) metal ions with cellulose adsorbent and cellulose-TiO_2 occur in the 120th minute and 60th minute, respectively. This is the optimal interaction between the adsorbent and adsorbate, where all active sites of adsorbent has bind to Cd(II) metal ion. The equilibrium points do not persist and tend to slightly decreases, this shows that the adsorbent has in a saturation point and interactions between molecular adsorbents and adsorbate to be rearrangement.

Based on data on the interaction time of adsorbents with Cd(II) metal ion can be calculated the rate constant of adsorption. The rate constant adsorption of Cd(II) metal ion on cellulose and cellulose-TiO_2 composite are presented in Table 1.

TABLE 1. The rate constant adsorption of Cd(II) metal ion on cellulose and cellulose-TiO_2

Adsorbents	**Rate constants**
Cellulose	2.10^{-6}
Cellulose-TiO_2	3.10^{-7}

The rate constant for cellulose adsorbent toward Cd(II) metal ion is of 2.10^{-6} its greater compared to the adsorbent cellulose-TiO_2 of 3.10^{-7}. This shows the ability of cellulose adsorbent interactions with Cd(II) metal ion is faster compared to cellulose-TiO_2.

Metal Ion Concentration

The adsorption capacity of adsorption of Cd(II) metal ion on cellulose and cellulose-TiO_2 were carried out by interact of adsorbent and Cd(II) metal ion in various initial concentrations at the optimum time that was obtained in kinetical treatment. The results of the interaction between the adsorbent and the Cd(II) metal ion in various initial concentrations can be seen in Figure 5. The adsorpton capacity was increase by increasing the initial metal ion concentration that may cause by charge interaction beetwen adsorben and adsorbat.

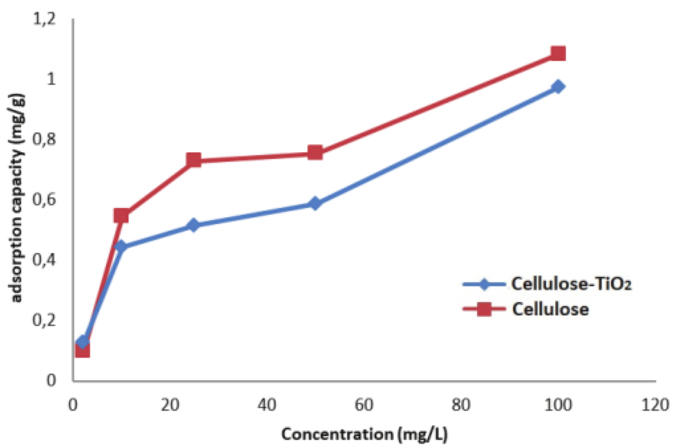

FIGURE 5. The adsorption capacity of cellulose and cellulose-TiO_2 composite to adsorp Cd(II) metal ion.

Determination of the Langmuir and Freundlich isotherm models was carried out using the linear regression method. In Table 2 the Langmuir Isotherm shows the R^2 value are higher at 0.956 compared to 0.9303 for the Freundlich Isotherm for cellulose. The cellulose-TiO_2 adsorbent have the value of R^2 for the Freundlich Isotherm it was slightly greater than the Langmuir Isotherm namely 0.9323 and 0.927, respectively.

TABLE 2. The equilibrium constant and adsorption energy of Langmuir isotherm and the Freundlich isotherm models for cellulose and cellulose-TiO_2 composite to adsorp Cd(II) metal ion.

Adsorbent	**K**		**R^2**		**Adsorption Energy (kJ/mol)**	
Cellulose	751.1	0.0143	0.956	0.9303	22.3	10.6
Cellulose-TiO_2	4051.9	0.0197	0.927	0.9323	20.7	9.8

Based on the energy obtained in the Langmuir Isotherm for cellulose adsorbent which is equal to 22.3 kJ/mol whereas for the for cellulose-TiO_2 adsorbent the energy produced is 20,7 kJ/mol. The interactions that occur are chemical interactions since interaction is specific and involves forces much stronger than physical adsorption. That usually no more than 4.2 kJ/mol and since the forces involved are week [15].

Determine of Adsorption Mechanisms of Cd(II) Metal Ion Onto cellulose and cellulose-TiO_2 composite Through Sequential Desorption

The desorption process where carried out sequentially using desorption reagent namely H_2O, HCl, and EDTA. Water was used as solvent to release metal ions that trapped in adsorbent which involves physics bonds, so the mechanism that occurs is the entrapment mechanism, and HCl reagent will prove the occurrence of an acid-base reaction while EDTA reagent was used as strong ligand that shows complexes mechanism beetwen adsorbent and the metal ion.

Sequential desorption of metal ions Cd(II) on cellulose presented in Figure 6. The HCl desorption reagent produced a greater percentage of Cd(II) metal ions than the H_2O and EDTA of 22.6%. This shows that the adsorption mechanism on Cd(II) metal ions in cellulose is dominated by an acid-base reaction mechanism which means that there is an electronic interaction accompanied by charge formation on metal ions. This shows that the interaction that occurs in Cd(II) metal ion with cellulose is a chemical interaction by the energy.

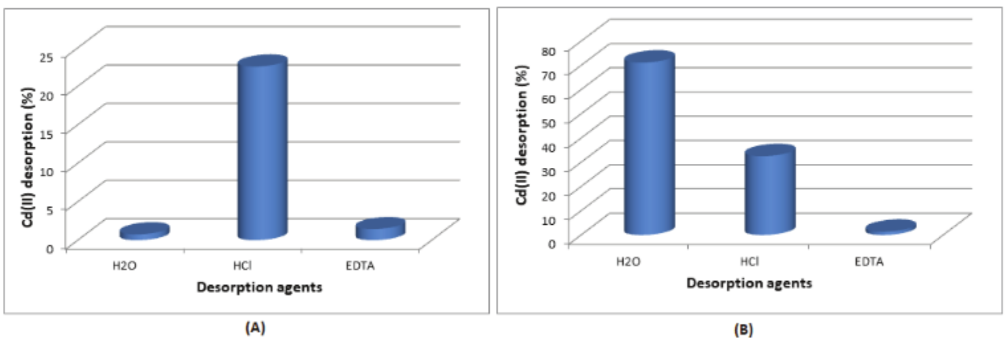

FIGURE 6. The desorption of Cd(II) metal ion by H_2O, HCl, and EDTA agents from (a) cellulose, and (b) cellulose-TiO_2 composite.

Sequential desorption of Cd(II) metal ion on cellulose-TiO_2 presented in Figure 6 shows the desorption occurred for H_2O agent about 65.2% which indicates the presence of ion trapping metal Cd(II) on cellulose-TiO_2 is the highest percentage, following by the HCl agent about 26.3%, and lest amount of Cd(II) able to desorp by the EDTA agent.

CONCLUSIONS

The cellulose was obtain from wood shawdust by maseration process using methanol and HCl in various concentration of HCl 1%, 3%, 7%, and 11%. The cellulose was characterized using FTIR, from the FTIR data the best concentration of HCl was 7%. Cellulose and cellulose-TiO_2 composite where analysed by FTIR and SEM-EDS spectrophotometers. The adsorption of Cd(II) onto cellulose and cellulose-TiO_2 composite have rate constants are 2.10^{-6} and 3.10^{-7} (min^{-1}), respectively. The adsorption energy where 22.3 kJ/mol and 20.7 kJ/mol, respectively. The desorption of Cd(II) metal ions from cellulose adsorbents dominantly by chemical interactions mechanism while at cellulose-TiO_2 composite the interaction dominanlty by physical interaction.

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