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Synthesis of CMC Pectin Hydrogel (1:2) Using the Freeze-Thaw Method and its Benefit as an Adsorbent

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ABSTRACT

Research has been conducted on the manufacture of hydrogels from CMC and Pectin (1:2), which can be applied as an adsorbent. The Citarum River is included in the category of the most polluted river in the world, because it contains chemicals that can reduce water quality. One of the pollutants is the Cu^{2+} metal, precisely at the entrance point of the Citarum river which exceeds the threshold. Cu^{2+} metal is not biodegradable and can accumulate in the human body, which causes severe health problems. Metal Cu^{2+} can cause toxic effects on fish body tissues that can induce the production of Reactive Oxygen Species (ROS). CMC and pectin are organic materials that are used as hydrogels to absorb Cu^{2+} metal. Hydrogel CMC/Pectin is analyzed using FTIR by having groups O-H, C=O, C-H, OH bending, COOH stretching vibration and C-O-C. The result from BET is that the hydrogel has a surface area of 3.706 m^2/g and is classified as a type 1 isotherm graph, and has small pores. The optimum condition of the adsorption process occurs at a concentration of 260 ppm, using the Langmuir isotherm model and has an adsorption capacity of 19.76 mg/g with an absorption efficiency of 68.60%.).

Keyword: *Adsorption, CMC, Cu Metals, Hydrogel, Pectin*

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INTRODUCTION

Water pollution is of the serious global problem caused by increasing industrialization and urbanization (Darban, Shahabuddin, Gaur, Ahmad, & Sridewi, 2022). According to World Bank environmental and natural resource processing data, Citarum river is ranked first as the most polluted river in the world (A. Prayoga, Umam, & Miharja, 2022). The heavy metals Cd, Cr, Cu, Hg, Ni, Pb and Zn are harmful pollutants contained in citarum river (Febrita & Roosmini, 2022). Among these metals, Cu metal contains metals that exceed the minimum limit that has been set, especially at the entrance of the Citarum river, which is 40,34 mg/kg (G. Prayoga, Utomo, & Effendi, 2022). The heavy metal come from petroleum refining, metal plating, mining, battery manufacturing and paint making activities (Ariffin et al., 2017; Darban et al., 2022).

Heavy metals are pollutants that are very difficult to remove naturally from the environment, are not biodegradable, and are toxic if their concentrations exceed the permissible limits in the ecosystem (Darban et al., 2022). Some health problems caused by the heavy metal Cu include insomnia, heart problems, hyperactivity, arthritis, insomnia, nausea/vomiting and schizophrenia (Ariffin et al., 2017). In addition, Cu metal is also detrimental to aquatic living things such as fish, because even at low concentrations, it can cause toxic effects on fish body tissues that can induce the production of Reactive Oxygen Species (ROS) that cause oxidative stress responses in fish (Garai, Banerjee, Mondal, Mahavidyalaya, & Arambagh, 2021). Some methods that can reduce heavy metals in wastewater are membrane filtration, coagulation, ion exchange, adsorption, electrochemical treatment technologies and so on (Türkmen, Bakhshpour, Akgönüllü, Aşır, & Denizli, 2022). The most widely used method for reduce heavy metals is adsorption.

Adsorption is a process that is considered one of the most efficient, inexpensive, environmentally friendly and easy to operate methods to reduce heavy metals from contaminated water (Darban et al., 2022; Türkmen et al., 2022). The use of rice husk biochar, beet sugar pulp, TiO_2, activated carbon, clay, CMC and LMP pectin (Low Methoxyl Pectin) are often used in the adsorption process in powder form (Baiya, Nannuan, Tassanapukdee, Chailapakul, & Songsrirote, 2019; Darban et al., 2022; Putri Rahayu, Wulan Harisma, Syamsuddin, & Mulyati, 2021). However, this adsorbent material has weaknesses, namely high production costs if applied on a large scale and it is difficult to separate from water after the decontamination process. Another usable alternative that can be used is hydrogel (Weerasundara, Gabriele, Figoli, Ok, & Bundschuh, 2021). Hydrogel is an economical material that can be applied as an adsorbent that has the potential to absorb contaminants in water such as Cu metal because it has high porosity, good mechanical properties and easy handling.(Darban et al., 2022).

Hydrogels are synthesized using natural sources include polyvinyl alcohol (PVA), alginate, chitosan, carboxyl methyl cellulose CMC, pectin, hyaluronic acid (HA), polyethylene glycol (PEG) and many other ingredients (Darban et al., 2022; Seida & Tokuyama, 2022). The method of making hydrogel is chemically using cross-lingking and physically freeze-thawing. Previous research on the process of forming hydrogels from PVA and CMC raw materials using freeze-thaw techniques can improve properties that do not affect biocompatibility, biodegradability, and nontoxicity of polymer gels (Zainal et al., 2021). CMC and pectin can act as adsorbents to absorb and stabilize metal ions, by hydroxyl and carboxyl groups on structure and biodegradability (Martínez-Sabando, Coin, Melillo, Goyanes, & Cerveny, 2023; Sayed, Hany, Abdel-Raouf, & Mahmoud, 2022; Wang & Wang, 2016; Zhao & Li, 2021). The combination of CMC and pectin has been performed as a membrane layer (Elma et al., 2023). This research focuses on making hydrogels from CMC and pectin raw materials at a ratio of 1:2 using the freeze-thaw method with a fixed pH of 5.

METHODS

Materials

The tools used in this study were a freezer box, beaker glass, oven, hydrogel mold, pH meter, spatula and digital scale. While the materials used are CMC, pectin, aquadest, and $CuCl_2$ metal.

Preparation of adsorbents and adsorbates

CMC and Pectin used as adsorbent were obtained from a Chemical and Pharmaceutical Store in Yogyakarta. Each of the next ingredients is dissolved in 10 w/v% and then mixed in a 1:2 ratio. Then, the solution is put into an ice cube mold with a cube size of 1.5 cm x 1.5 cm and put in a freezer box at a temperature of -20 ^{o}C for 6 hours (Wang & Wang, 2016). After that, the sample is removed from the freezer box to undergo the thawing process for 1 hour a temperature of 30 ^{o}C. The Freeze-Thaw process lasts 5 cycles. The sample that has undergone the next freeze-thaw process is in the oven for 40 min with a temperature of 100 ^{o}C, which aims to remove excess water content in CMC/pectin hydrogel. Against CMC, pectin and hydrogel adsorbent CMC/pectin spectroscopy analysis of fourier transform infrared (FTIR) was carried out to observe the chemical function group and Brunauer Emmet Teller (BET) to observe the surface area of the CMC/Pectin hydrogel. The Cu metal solution is dissolved from the $CuCl_2$ solution, which is then varied in concentration.

Adsorption Experiment

In determining the optimum conditions for the adsorption of Cu metal ions by the CMC/pectin hydrogel, batch experiments are conducted. The determined optimum conditions are in the form of adsorbate concentration and contact time. The batch adsorption process is performed in a sample box. Hydrogel and Cu metal solution are placed input into the sample box during the set time. Hydrogel extraction uses mini tweezers to separate CMC/Pectin hydrogel from the Cu metal solution. The concentration of the Cu metal solution. The concentration of the Cu metal solution after undergoing the adsorption process is then determined by AAS (Atomic Absorption Spectrophotometer analysis), in order to observe the remaining Cu metal content contained in the solution. The percentage of allowance efficiency and adsorption capacity of Cu metal are calculated by equations (1) and (2):

$$\%E = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

$$q_e = \frac{C_0 - C_e}{w} \times V \quad (2)$$

Where E is the elimination efficiency; C_0 is the initial concentration of the solution (mg/L); Ce indicates the final concentration of the solution (mg/L); qe is the adsorption capacity (mg/g); V is the volume of the solution (L) and w is the weight of the adsorbent (g).

Determination of the isotherm adsorption equation

The experimental data used are data on the variation of adsorbate concentration that will be tested on the equation of the Langmuir and Freundlich isotherm. The Langmuir isotherm use the assumption that the maximum adsorption capacity occurs due to the presence of a monolayer of adsorbate layers on the adsorbent surface. This indicates that the adsorbed molecule is flat on the surface, the adsorption energy is constant and does not depend on the nature of the surface, occurs without interaction between adsorbate molecules and is irreversible. The bonds formed are usually chemical bonds that can be covalent or ionic between bonds between adsorbate molecules and adsorbents (Treybal, 1980). The langmuir isothermic equation can be seen in equation (3):

$$\frac{1}{q_e} = \frac{1}{ab}\frac{1}{C_e} + \frac{1}{b} \quad (3)$$

Where: qe is the amount of adsorbate absorbed by each adsorbent mass at equilibrium (mg/g); a is the Langmuir equilibrium constant, (L/mg), KL; b is the maximum absorption capacity on the surface of the solid (mg/g), qm Ce = Concentration at equilibrium (mg/L).

The Freundlich isotherm assumes that adsorption occurs on heterogeneous adsorbent surfaces and that each molecule has a different adsorption potential. The bonding that occurs only physically takes place due to the presence of Van Der Waals force or a relatively weak attraction between the adsorbate and the adsorbent surface (Sawyer, McCarty, & Parkin, 1994). Freundlich's adsorption isothermic equation is written on the basis of equation (4):

$$log q_e = log K_f + \frac{1}{n} log C_e \quad (4)$$

Where: qe is the amount of adsorbate absorbed by each adsorbent mass at equilibrium (mg/g); Kf is the equilibrium constant of Freundlich(mg/L); 1/n is the intensity of adsorption; Ce is the concentration at equilibrium (mg/L).

RESULTS AND DISCUSSION

Hydrogel

Hydrogels that have been made from CMC and pectin (1:2) are textured like yupi candy which can be seen in figure 1. After an experiment, that the hydrogel applied to the $CuCl_2$ solution must be fresh, because if the hydrogel applied is not fresh, the way the adsorbent works as a binder for Cu metal ions is weakened. Therefore, the percentage of absorption of Cu metal ions is very small. In addition, the hydrogel that has been made does not last long, only lasts up to 3 hours.

Figure 1. Fresh hydrogel

Chemical functional group analysis

The results of the FTIR spectrum in figure 2 show that CMC and pectin are classified as complex carbohydrates characterized by the presence of Hydroxyl groups seen at 3256,02 and 3325.55 cm^{-1}, while the hydroxyl groups in hydrogels (1:2) are at a peak of 3268,79. The absorption area of 1734.87 cm^{-1} which shows the presence of a C=O carbonyl group is a characteristic of CMC. In addition, the C=O carbonyl group in pectin and hydrogel is 1734,93 and 1735,13 cm^{-1}. With the characteristic under the C=O carbonyl group which is 1586, 1590 and 1589 cm^{-1} there is a C=O Stretch vibration carboxylic group (COOH). 1014,40 – 1246,44 cm^{-1} is a C-O-C group (ether) (Elma et al., 2023).

In figure 2 in the CMC and hydrogel lines, it is found that the C-O-C group with a peak of 1020,28 cm^{-1} and 1013.19 cm^{-1}, while in pectin, the ether group is at the wavelength of 1012.53-1233.37 cm^{-1}. Wavelengths 1322,28, 1322,56, 1322,93 cm^{-1} is the peak of the -OH bending Vibration group bond. It can be concluded that the

CMC/Pectin hydrogel has an O-H hydroxyl group and COOH carboxyl as a Cu^{2+} metal binder so that it can be applied as an adsorbent. The bond that occurs between CMC/pectin is physically bonded because there is no new CMC and Pectin hydrogel group due to the interaction of the two components

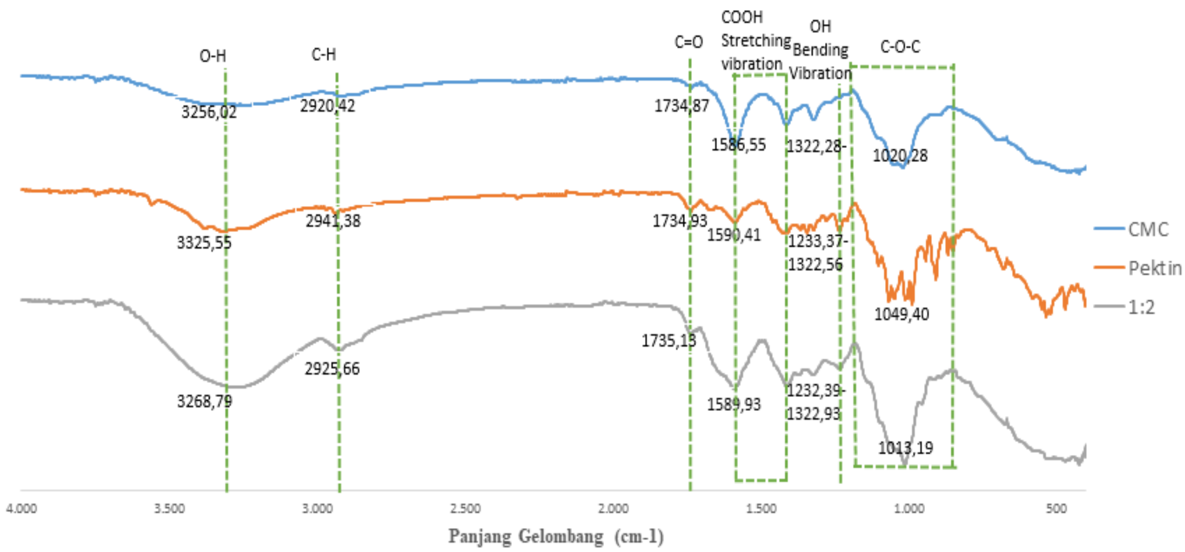

Figure 2. Chemical functional group test results

Surface area characterization

The results of the test showed that the surface area of the hydrogel was 3.706 m²/g. In addition, from the results of BET, you can find out the type of isothermic graph and pore class by analyzing figure 3.

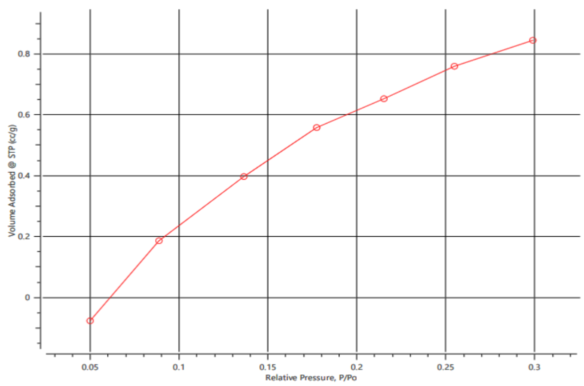

Figure 3. Isoterm BET graph

Brunaeur classified the IUPAC book isothermic adsorption into five types of curves and in figure 3 shows that the curve belongs to type 1 isothermic graphs. This type is called the Langmuir isotherm, which describes single-layer (monolayer) adsorption. The number of adsorbate molecules approaches the limiting price when P/P0 approaches one. This type is usually obtained from small porous adsorbents.

Determination of optimum concentration

The optimum concentration can be determined using adsorbate concentration variations, namely 223 ppm, 260, 298 ppm and 372 ppm, using the contact time of 60 min. The condition of other parameters is fixed, namely Cu solution with pH 5 as much as 10 ml and adsorbent weight 0.0905 grams. Figure 4 shows the experimental results and the highest allowance efficiency is obtained at a concentration variation of 260 ppm which is 68.60% which is the optimum concentration with an optimum adsorption capacity of 19.7 mg/g.

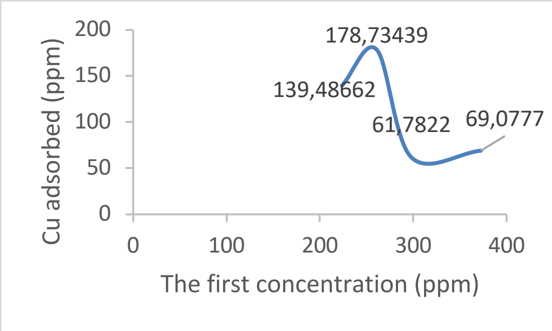

Figure 4. Optimization graph of the effect of concentration on the adsorption process

Determination of isotherm adsorpsi equation

Table 1 shows the results of Langmuir and Freundlich isotherms for the adsorption of Cu metals in hydrogels taken from concentration variation data in optimization experiments. According to table 2 that the value of R^2 for the Langmuir isotherm is 0.9459 and for the Freundlich isotherm is 0.9134. The value of R^2, which is close to 1 can mean that there is a greater influence and stronger relationship between variables. Base on the comparison of the two equations, it is found that the experimental data is more in accordance with the langmuir isothermic equation.

The Langmuir isothermic adsorption model assumes that the entire active side of the adsorption has the same affinity, and the adsorption process on one active side is independent of the other active side and is constant. The value of the KL parameter (Langmuir Constant) is an isothermal type marker, if the value of KL = 0 then the adsorption process is irreversible. Preferred adsorption process (favorable) if the test result shows a value of 0 < KL< 1. The linear isothermal adsorption process is indicated by the value of KL=1, while if the value of KL>1 the adsorption process that occurs is an unfavorable phenomenon. The KL value in this study from the Langmuir isothermic equation is 0.5, which shows that the adsorption process is preferred (favorable). Then, the adsorbent used is the appropriate adsorbent for the type of adsorbate (Singh, 2016). Therefore, the CMC/Pectin hydrogel adsorbent is suitable for use in the absorption of Cu metal.

The adsorption adopted in this experiment shows the Langmuir isotherm, which means that the adsorption takes place chemically or by monolayer chemisorption. Monolayer adsorption occurs due to chemical bonds that are usually specific, so that the adsorbent is able to bind the adsorbate with the chemical bond between the Cu metal and its hydrogel surface. The type is in accordance with what is analyzed in BET, namely the isotherm chart type one (langmuir).

Table 1. Isothermic graph comparison results

Isoterm	Equation	R^2	Kf	Kl
Langmuir	y = -9.6322x+0.1744	0.9459	-	0.018
Freundlich	y =-0.7288x+2.6339	0.9134	36.32	-

Cu metal adsorption using Hydrogel CMC/Pectin has an adsorption capacity that is not much different from CMC/PVA hydrogel, but smaller than biochar which has an adsorption capacity of 60.48 mg/g. CMC/Pectin hydrogel adsorbent has a drawback where the applied hydrogel must be fresh in order to absorb Cu metal and only last up to 3 hours. If applied to the Cu solution for more than 3 hours, the hydrogel will experience mechanical damage such as being easily torn when lifted so that the separation process needs to use filter paper.

Interaction between the adsorbent and adsorbate

The interaction that occurs between the adsorbent and the Cu solution is a coordination interaction known as chelation interaction, which is the formation of a covalent bond in which one atom shares both electrons. Cations (Cu metal) bind to the carboxyl and hydroxyl groups because they contain free electron pairs, so that the adsorption process of Cu metal occurs on the hydrogel surface (Danikas, Vardakis, Sarathi, & Morsalin, 2021). FTIR analysis that has been carried out on the hydrogel shows that the hydroxyl and carboxyl functional groups can act as coordination sites for Cu metal adsorption (Rodrigues, Carlos, Medina, & Fajardo, 2019)

CONCLUSION

Hydrogel CMC/Pectin (1:2) can be applied to the Cu metal adsorption process because it has a carboxyl and hydroxyl group as a binder for Cu metal ions by having a surfce area of 3.706 m^2/g. The optimum condition of the adsorption process is obtained at an adsorbate concentration of 260 ppm with allowance efficiency and adsorption capacity of 68.60% and 19.76 mg/g. The adsorption isothermic equation that corresponds to the experimental data is the Langmuir isotherm with a KL value of 0.018 L/g. Langmuir's isotherm shows that the adsorption of Cu metal ions occurs in one layer and adsorption occurs chemically.

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