



Synthesis and Characterization Materials Modern (CMC-Fe₃O₄-Chitosan-TiO₂) As Portable Adsorbent Toxic Metal (Hg) and Dye Substance (Rh B)

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Abstract. The synthesis of the portable adsorbent material CMC-Fe₃O₄-Chitosan-TiO₂ begins by inserting the CMC-Chitosan mixture into the leaching solution. Next, concentrated NaOH and 3% CaCl₂ were added, then decanted and dried at room temperature. After that, the composite was coated with TiO₂ and then dried in an oven at a temperature below 100 °C. The success of the synthesis was indicated by the presence of specific absorption in FT-IR. 3429 cm⁻¹ hydroxyl group, 2926 cm⁻¹ for the CH/CH₃ group, 1631 cm⁻¹ for the carbonyl group (C=O), 1642 cm⁻¹ which is the CH/CH₃ group, as well as (Fe – O) and (Ti – O) at 400-600 cm⁻¹. In addition, the different surface morphology of the material formed from its basic components is based on SEM characterization sails. Adsorption test results for Hg (II) metal ions were 53% while dyes were 38% with a time of 40 minutes. This research is good for handling watermaster

Keywords: Adsorbent, CMC, Fe₃O₄, Chitosan, TiO₂

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1. Introduction

The environment is currently the object of much research because the environment is a combination of physical conditions which include the state of natural resources such as land, water, solar energy, minerals, as well as flora and fauna that grow on land and in the ocean. Nowadays, environmental issues are garnering increasing attention because they serve as the source of life for humans, animals, plants, and other organisms, all of which mutually influence each other. These issues may manifest as water, soil, and air pollution, thereby affecting the health and safety of living beings. Pollution from toxic substances such as dyes and heavy metal ions can disrupt ecosystems and pose significant risks to human health and the environment [1,2]. Dyes are widely used in the textile industry and constitute one of its main raw materials. It is known that more than 42,000 tons/year of synthetic dyes will be imported between 2017 and 2022 [3]. Approximately 10-15% of used dyes cannot be reused and must be disposed of [4]. Dyes contained in textile industrial waste can pose health hazards, such as skin and eye irritation leading to cancer, and can also cause mutagenesis [5].

In addition to dye pollution, heavy metal contamination is also found in industrial waste [6], such as

arsenic (As), mercury (Hg), lead (Pb), zinc (Zn), and others [7]. The Presence of heavy metals greatly influences soil fertility levels [8]. World Health Organization (WHO) states that mercury has high toxicity and can cause human disorders such as muscle weakness, nerve damage, skin irritation, and vision impairment. Mercury is contaminated in the form of waste discharge that can accumulate in water bodies. More than 90% of the mercury found in surface water comes from atmospheric mercury pollution [9]. Such pollution will have a significant impact on the environment, particularly water pollution. This necessitates various research endeavors for waste management, including biological treatment, coagulation or flocculation, decolorization, detoxification, chemical oxidation, membrane filtration, ion exchange, photocatalysis, and adsorption. Among these methods, adsorption is commonly used due to its simplicity, high efficiency, and the abundance of materials such as activated carbon, clay, biomass, polymers, zeolites, and nanomaterials. One abundant raw material is polymer.

Polymers are interesting materials to study, including natural, synthetic, or modified polymers. One polymer that can be developed is Carboxymethyl Cellulose (CMC), which is a type of cellulose ether polymer [10]. CMC is an anionic molecular compound obtained from the reaction of natural cellulose with caustic alkali and acetic acid. CMC possesses environmentally friendly properties, affordability, good solubility in water, biocompatibility, and biodegradability. CMC can be modified by adding magnetite material during composite formation. Magnetite material can be in the form of Fe_3O_4 easily obtained from iron sand. Fe_3O_4 , also known as black iron oxide, magnetic iron ore, lodestone, ferrous ferrite, or hercules stone, exhibits the strongest magnetism among transition metal oxides [11]. For photodegradation purposes. Various studies on CMC for example, CMC nanoadsorbent is able to adsorb Zn, Fe, Mn and Pb metals above 80%, [12] CMC hydrogel more than 70% on metals ion Cu(II) and Zn(II) [13], membranes chitosan modified with CMC for metal ion Cr(III) reached a capacity of 230.12 mg/g [14], CMC-chitosan based on polyelectrolyte complex was able to adsorb methylene blue dye with a capacity of 165.35 mg/g [15], 97.4% used CMC-chitosan complex for methylene blue [16]. CMC is modified with semiconductor materials. One semiconductor material that can be used is Titanium dioxide (TiO_2) due to its high activity, chemical stability, and non-toxicity [17]. In this research, CMC is composited with chitosan and Fe_3O_4 and coated with TiO_2 . The combination of CMC-Chitosan is expected to enhance adsorption capacity and mechanical strength. Meanwhile, CMC- Fe_3O_4 -Chitosan is expected to provide increased adsorption with a more specific surface. The presence of Fe_3O_4 will facilitate the separation of the composite from the solution through an external magnetic field, while TiO_2 can accelerate the removal of dyes through photocatalysis using UV light, thus creating a portable sorbent material suitable for wastewater.

2. Methods

2.1. Tools and Materials

The tools used in this research were glassware, heating equipment and supporting equipment. Apart from that, instruments such as pH meters, UV-Vis spectrophotometers, Atomic Absorption Spectrophotometry (AAS), Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FT-IR) are also used. The materials used in this research are mineral sand, HCl 37%, iron powder, NaOH, Titanium tetra isopropoxide (TTIP), CaCl_2 , CMC Powder, Chitosan Powder, CH_3OOH , technical ethanol, Rhodamine B pro analysis, 1000 ppm Hg standard solution and distilled water.

2.2. Magnetic separation and leaching process

Separation of iron sand is carried out using a magnet to separate magnetic and non-magnetic minerals, then the iron sand is soaked in technical ethanol for 12 hours and then dried. The leaching process is carried out by heating 200 mL of 20% HCl to a temperature of 100°C. The solution was heated for 30 minutes using a modified hot plate. The leaching process was then continued by adding 2.5 g of iron sand into the solution, after 30 minutes 0.7 g of iron powder was added as a reducing agent and then the mixture continued to be heated for five and a half hours. After the leaching process is complete, the solution is filtered using filter paper.

2.3. Synthesis of KMS-Fe₃O₄-Chitosan-TiO₂

The process begins by adding 30 mL of the leaching solution (FeCl₃) into a beaker, then adding 20 mL of distilled water. Next, make a solution of 2.5% CMC and 0.5% Chitosan (w/v) then mix. (CMC variations mass will be made 0.5; 1.0; 1.5; 2.0 and 2.5% w/v). Next, CMC-Chitosan is added slowly to the leaching solution, thus forming granules. The mixture was kept for 24 hours at room temperature, then 2.3 grams of dissolved NaOH was added. Then washed with distilled water until the pH was neutral, then 20 mL of 3% CaCl₂ was added. Next, magnetic decantation was carried out and dried at 60 °C for 6 hours. Coating CMC-Fe₃O₄-Chitosan with TiO₂ using the dip-coating method. CMC-Fe₃O₄-Chitosan was dipped into 20 mL of TiO₂ solution for 30 minutes and the results were separated through decantation with the help of a magnet and then dried for 12 hours at a temperature of 50 °C. CMC-Fe₃O₄-Chitosan-TiO₂ were characterized using FT-IR and SEM. FTIR is used for every chemical compound, allowing identification of materials with high precision, can also verify the purity of materials and detect contamination or impurities. Meanwhile, SEM is for viewing high resolution which allows detailed observation of the microstructure of materials that cannot be seen with an optical microscope and can observe materials at nanometer size. The selection of concentrations and conditions is based on previous literature.

2.4. Adsorption Test

To see the performance of the portable adsorbent against mercury metal ions (Hg), 100 mL of Hg(II) metal ion solution with a concentration of 40 mg/L was put into a container containing 0.5 grams of adsorbent (2% CMC) and then stirred. Contact time was varied respectively 10, 20, 30, 40, 50 and 60 minutes. The filtrate was separated by filtering and then analyzed by SSA to determine the concentration of Hg(II) metal ions that were not adsorbed. This was done repeatedly with variations in mass (1 gram, 1.5 grams, 2 grams and 2.5 grams).

To see the performance of the portable adsorbent against dye (Rh B), 100 mL of rhodamine B solution with a concentration of 4 mg.L⁻¹ in with 0.2 gram (0.5% CMC) adsorbent at varying contact times of 10, 20, 30, 40, 50 and 60 minutes, then filtered. Next, it was analyzed using a UV-Vis spectrophotometer to determine the remaining concentration of rhodamine B. Repeatedly with variations (1% CMC, 1.5% CMC, 2% CMC and 2.5% CMC).

3. Results and Discussion

3.1. Synthesis results of portable sorbent material (CMC-Fe₃O₄-Chitosan/TiO₂)

Combining more than one polymer is often referred to as a composite. Composites are synthesized using a series of methods based on certain properties and characteristics of each material. Basically, the combination of materials from several materials will have new properties and certain advantages, resulting in new materials that can provide benefits for life. [18] CMC and chitosan have been widely applied, so they continue to be developed for more efficient use by combining magnetic materials (Fe₃O₄) so that it can be portable inside, a new composite is formed from CMC-Magnetite-Chitosan [19].

The mixture between CMC and Chitosan will look like a gel. CMC which is dissolved in water with the help of heating to accelerate solubility is determined by the mass of CMC used, while chitosan is dissolved with acetic acid (CH₃COOH) with optimum conditions (0.5% w/v). CMC and Chitosan can interact with each other with the functional groups they contain. CMC has a hydroxyl group which acts as a negative charge (–O[–]) and Chitosan which has an amine group which can act as a positive charge (–NH₃⁺). Figure 1 Shows interaction of CMC with Chitosan [20]

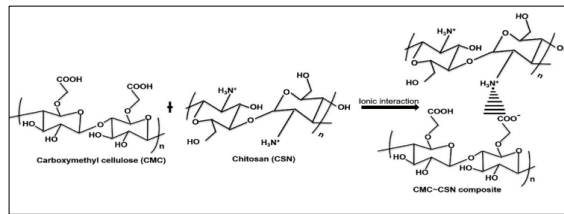


Figure 1. CMC-Chitosan Composite

Magnetite (Fe_3O_4) is formed by immersing the composite in the leaching solution. The composite, which is in the form of clear granules, will turn yellow after being soaked for 6 to 12 hours. This is due to the composite binding Fe^{2+} or Fe^{3+} ions in the solution [21]. Aggregation occurs through electrostatic interactions between anionic CMC and cationic materials. Multivalent metal ions, such as Fe^{2+} or Fe^{3+} can also contribute to the aggregates. For example, incubation of a CMC solution after addition of Fe^{2+} or Fe^{3+} , followed by pH elevation of the solution, results in the formation of a magnetite CMC microcontroller. Composite interactions with Fe^{2+} or Fe^{3+} ions can occur between CMC and $\text{Fe}^{3+}/\text{Fe}^{2+}$ or between $\text{Fe}^{3+}/\text{Fe}^{2+}$ chitosan [22]. In CMC this occurs through cross-linking between the carboxylate group ($-\text{COO}^-$) and the Fe^{3+} ion [23]. Fe^{2+} is trapped in the CMC polymer [24], while chitosan and Fe metal form a complex. The composite that has bound Fe ions is then added with NaOH.

After adding NaOH, washing with distilled water until the pH is neutral so as not to hinder the process of adding CaCl_2 . The function of the CaCl_2 solution is as a cross-linking agent. When mixed with biopolymers such as CMC which have carboxyl groups in the polymer chain, the composite system can be cross-linked. The cross-linking process can occur with ions with two or three valences, for example Ca^{2+} and Al^{3+} [25], due to the chelation process of the carboxyl group, then the granules are filtered and washed with distilled water until the Cl^- ions in details is missing. The Cl^- ion free granules were heated at 60°C for 8 hours. The addition of TiO_2 aims to improve the performance of Rh B dye in the adsorption or degradation process through photodegradation, known as photocatalysis [26]. Figure 2 sorbent material characteristics CMC-Chitosan- Fe_3O_4 - TiO_2 (a). This research (b). Another research [20]

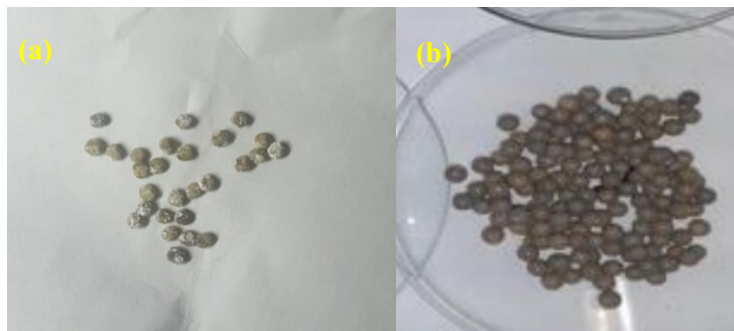


Figure 2. (a). This research (b). Another research

3.2. Characterization FTIR

Table 1. Result Characterization of FTIR

Wave Number (cm^{-1})	Reference	Wave Number (cm^{-1})			Vibration Type
		Another research	CMC	Chitosan	
600	[27]	885	596	596	Fe-O/Ti-O
1060	[27]	1050	1050	1050	C-O
1157		-	-	-	C-N
1462	[27]	1480	1420	1300	CH_2
1631	[27]	1638	1640	1640	C=O
2926	[27]	2980	2980	2980	CH_3
3429	[27]	3413	3474	3423	O-H / N-H

The absorption materials portable of the CMC-Fe₃O₄-chitosan at wave number 3474 cm⁻¹ is the vibration of the hydroxyl group, while at wave number 2980 cm⁻¹ it is C-H resistance in the CH₃ group. The C=O vibration seen at wave numbers 1640 cm⁻¹ and 1420 cm⁻¹ is the C-H vibration in the CH₂ group and C-O vibrations at a wave number of 1050 cm⁻¹. C=O or -COO- absorption is a typical spectrum of CMC. Chitosan vibrations in the materials portable adsorbant can be observed at an absorption of 3423 cm⁻¹, where the N-H vibrations overlap with the O-H vibrations. In addition, chitosan with specific absorption of the N-H group is found at a wave number of 1546 cm⁻¹ according to [28]. The FT-IR spectrum of the materials composite proves the existence of electrostatic interactions. Apart from that, it has bonds that match the polysaccharide framework such as the absorptions of 1631 cm⁻¹ and 1546 cm⁻¹ which belong to the COOH and NH³⁺ groups respectively. This vibration is caused by the formation of intermolecular complexes through electrostatic interactions between the cationic groups of chitosan and the anionic groups of CMC. In these composites, it can be assumed that the stability of the complex is also maintained by hydrogen bonds [29]. Meanwhile, the functional groups Fe – O and Ti – O are at wave numbers 600-400 cm⁻¹. Based on the interpretation of the existing spectrum, it can be concluded that the materials adsorbant portable composition has been successfully synthesized. Manuscripts must be submitted online with the following procedure:

3.3. Characterization SEM

The surface morphology of the resulting material has a rough surface, thereby increasing the formation of pores which function as a binding matrix for Fe³⁺ ions. The morphological results of the addition of Fe ions prove that the role of the Fe formed provides a characteristic characteristic of the formation of the number of pores in the composite and the emergence of the formation of nanorod structures. This is in accordance with research conducted by [39] that the formation of nanorods is caused by FeCl₃ forming Fe₃O₄ crystals to increase pore formation and electron and ion transfer efficiency (Figure 3a). Figure 3b shows the surface morphology results after adding TiO₂ which appears to be inserted into the porous material and has an effect on the composite surface, thereby reducing the pores formed. Thus, it can be concluded that the addition of TiO₂ affects the number of pores in the adsorbent material

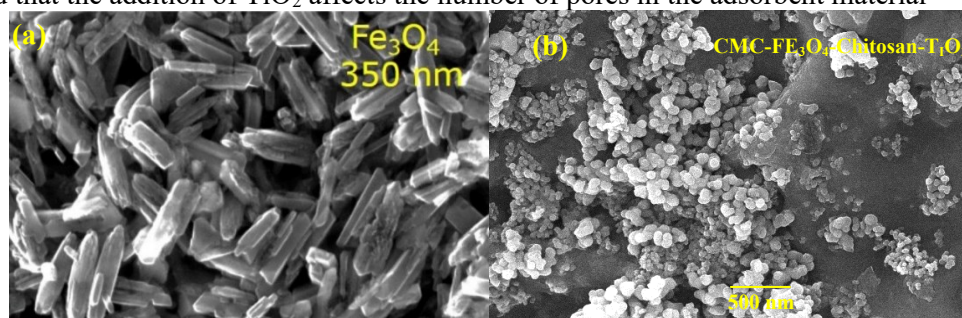


Figure 3. Characterization SEM (a) Nanorod Fe₃O₄ (b) Material Adsorbent

3.4. Comparison Adsorpsi ion Metal (Hg) and Dye (Rh B)

When viewed from the adsorption time for dyes and Hg (II) metal ions, based on the research results it appears that the optimum adsorption time is shown by dyes to be faster, namely 50 minutes compared to Hg (II) metal ions, namely 60 minutes with a maximum capacity of 24.25 mg/g. This is not much different from [31] namely 31 mg/g which uses chitosan-TiO₂ composite for the adsorption of Cu(II) metal ions, but is different from [32] which reaches 229 mg/g for the adsorption of Ni(II) ions by modifying alginate-chitosan-TiO₂. This occurs assuming a difference in molecular size, where the dye is larger than the Hg (II) metal ion. This means that with a smaller size of metal ions and a greater number in solution, it takes a long time to reach equilibrium. Shows Figure 4(a) and 4(b).

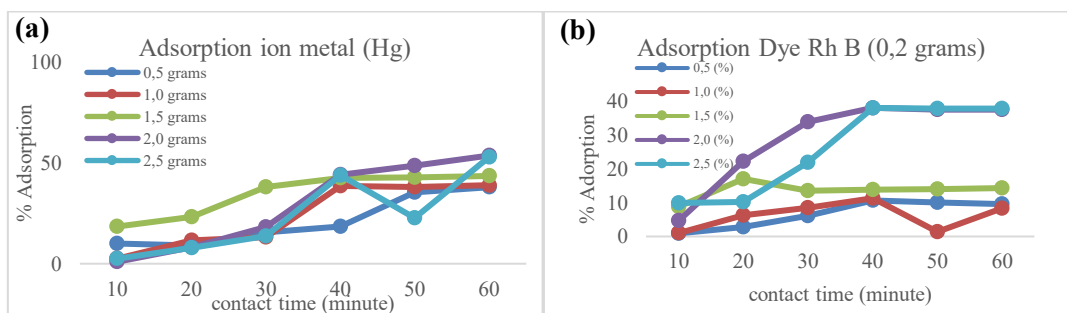


Figure 4. (a) Adsorption ion metal Hg (II) (b) Adsorption dye (Rh B)

Based on the soft hard acid base concept, the metal ion Hg(II) is in the soft acid group, meaning that its outer electrons are easily distorted and provide great polarizability. Apart from that, it also has a large ionization energy, so that the complex formed is more stable. Complexes are formed when the adsorbent is assumed to be a ligand, as in figure 5(a) dan 5(b) [33].

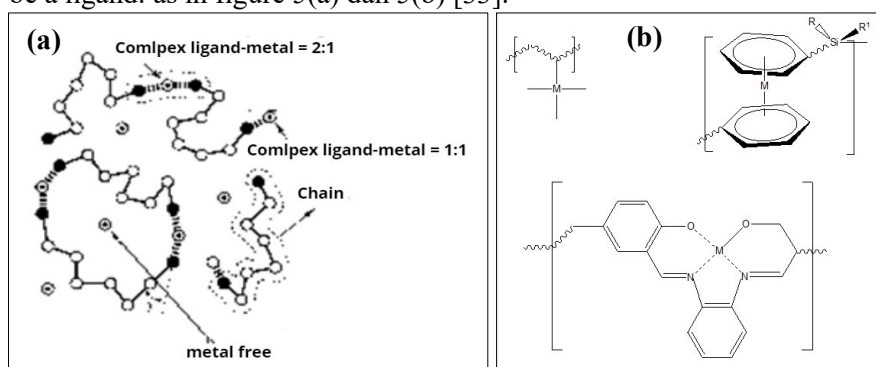


Figure 5. (a) complex formation at varying constants (b) polymeric structures bond metal ions

4. Conclusion

Portable adsorbent material CMC-Fe₃O₄-Chitosan- TiO₂ can be synthesized. FT-IR results show the presence of functional groups from CMC, Fe₃O₄, Chitosan and TiO₂ which make up the material. The presence of Fe₃O₄ and TiO₂ is also shown in SEM characterization showing surfaces that are very clearly different from each other. The results of the adsorption test in this study showed that it was more effective against Hg (II) metal ions with a capacity of 53% in 60 minutes compared to 38% for dyes in 40 minutes. Further research needs to be carried out in various conditions, for example pH variations and testing on metals and other dyes or even by designing adsorption reactor path designs so that they are easy to apply.

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