Magnetic Nanocomposite-Chitosan Based on North Sulawesi Iron Sand as Heavy Metal Adsorbent and Synthetic Dyes in Textile Industry Waste

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Magnetic Nanocomposite-Chitosan Based on North Sulawesi Iron Sand as Heavy Metal Adsorbent and Synthetic Dyes in Textile Industry Waste

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Abstract. Incorporation of chitosan-magnetic nanocomposite based on iron sand from North Sulawesi combined with chitosan as an adsorbent was recently carried out to improve the adsorbent ability. This study aims to synthesis of magnetic nanoparticles from iron sands of North Sulawesi and combined with chitosan in a chitosan-magnetic nanocomposite. Furthermore, analyzed the ability of the nanocomposites as heavy metal adsorbents and synthetic dyes in textile industry waste, especially batik. The metal and oxide content in iron sand was analyzed by XRF, magnetic-chitosan nanocomposite was analyzed by ICP-OES and magnetic-chitosan nanocomposite was analyzed by XRF after being tested as an adsorbent. The results showed that Fe metal and Fe_2O_3 oxide were the most abundant in iron sand with 87.25% and 84.43%, respectively. Fe content also remained dominant in the magnetic-chitosan nanocomposite with a concentration of 27000 mg/kg. The nanocomposite was able to adsorb the metal molybdenum (Mo) contained in the batik industrial waste with a concentration of 4.7% along with the waste dye. The results of this study indicate that the chitosan-magnetic nanocomposite can be used as an adsorbent for heavy metals and synthetic dyes, especially in batik industry waste and other industrial wastes.

INTRODUCTION

Signs of industrial development are the various industries that produce various human needs, like the paper industry, textile industry, and leather tanning. Because the industry increases, more and more waste is generated. Many industrial wastes contain heavy metals. Some heavy metals which will pollute the environment and are toxic are lead [Pb], chromium [Cr], iron [Fe], cadmium [Cd], nickel [Ni] [1]. If not managed properly, waste can become an environmental problem, especially heavy metal waste and synthetic dyes. Heavy metal ions, such as Pb^{2+}, Cd^{2+}, Hg^{2+} are very toxic and can cause cancer. The higher the level of industrialization, the greater the negative impact on the environment. The textile industry contributes to the production of synthetic dyes and heavy metals contained in the waste generated [2]. To reduce or even eliminate the presence of toxic waste, adsorbents can be used. Due to the advantages of being able to adsorb organic and inorganic waste, adsorption technology has been widely used in industry.

Since the discovery that adsorption technology is one of the most convenient ways to treat wastewater, researchers have been committed to developing inexpensive, effective, environmentally friendly and reproducible adsorbents. An interesting adsorbent, because it is obtained from natural ingredients and abundant raw materials in Indonesia, is chitosan. It is reported that chitosan can be used as an adsorbent because chitosan is a natural polysaccharide produced by deacetylation of chitin. Chitin is the second most abundant biopolymer in nature, extracted from cellulose from insects and marine crustaceans. Chitin makes chitosan has great potential as an adsorbent [3]. However, the adsorption capacity of pure chitosan is still very low because it is difficult to separate it from the solution after the adsorption

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process during the adsorption process [4], so it is necessary to modify chitosan. Chitosan modification can be done by adding other ingredients to produce complexes and increase the adsorption capacity of the complexes.

Iron sands can contain magnetite (Fe_3O_4), hematite (αFe_2O_3), maghemite (γFe_2O_3) and other magnetic minerals [5]. Magnetic minerals contained in iron sand are very useful, but not all minerals contained can be used optimally [6]. The iron sand ore currently being developed and used is nanoparticle-sized iron sand. And moves in the presence of an external magnetic field. Fe_3O_4 is a type of iron oxide which due to its biocompatibility and biodegradability, is often used in biomedical applications and has a surface that can be easily modified. One of the surface modifications of Fe_3O_4 nanoparticles is to coat the nanoparticles with polymer. According to [7], polyethylene glycol (PEG), dextran, polyvinylamine (PEI), phospholipids, and chitosan are some of the polymers commonly used to coat Fe_3O_4 nanoparticles.

The iron sand used in this study came from beach sand in the North Sulawesi region, East Bolaang Mongondow Regency. North Sulawesi is an area rich in mineral resources, especially iron sands, which are widely distributed in the western and eastern coastal areas of North Sulawesi. In some places, iron sand has been widely used as a raw material for the steel industry, making concrete [8], magnetic ceramics, and the basic material for the permanent magnet industry [9]. In several studies, iron sand has been used as an adsorbent by mixing it with other materials in a nanocomposite. Iron sand-based nanocomposites have been used as adsorbents for heavy metals and dyes such as Fe_3O_4/Bentonite nanocomposites from iron sands as adsorbents [10], adsorption of Co(II) by Fe_3O_4/bentonite nanocomposite [11]. The addition of Fe_3O_4 to bentonite increases the adsorption capacity. The use of iron sand combined with polymer materials is considered more effective as an adsorbent for heavy metals and synthetic dyes [11]. According to research reported by [12], the use of magnetic-chitosan nanocomposite as an adsorbent proved effective to adsorb Au(III) from aqueous solution, this is because the magnetic-chitosan nanocomposite has magnetic properties so that the adsorbent can be easily separated from the solution by using a magnetic field.

Previous research [13], has carried out a study to make a magnetic chitosan adsorbent that can be recycled and regenerated to absorb methylene blue from a layer of magnetic polyethyleneimine nanoparticles with chitosan sulfonate, which is intercalated with Fe_3O_4 and then crosslinked with glutaraldehyde. The Fe_3O_4 used in [13] study, is commercial Fe_3O_4, while Fe_3O_4 can also be found in iron sands which are very abundant in Indonesia, especially in North Sulawesi. Several coastal areas in North Sulawesi were identified as containing iron sand deposits. This area is spread from the east and west coasts of Minahasa as well as several areas in the Bolaang Mongondow region [14]. The use of chitosan-magnetic nanocomposite offers significant advantages over other adsorbents in terms of the ability to separate heavy metals from wastewater. This is also because the basic ingredients of chitosan-magnetic nanocomposites, namely iron sand and chitosan, are abundant in nature. Thus, the use of magnetic-chitosan based on iron sand can be an adsorbent for heavy metals and synthetic dyes that have a great effect on environmental sustainability but require low production costs. [15,4] The use of magnetic-chitosan nanocomposites based on iron sand is more effective because the two materials used are abundant in nature and do not require a lot of time and money to make.

Based on the explanation above, it is necessary to do research to make a magnetic adsorbent used in the dye adsorption process to make a magnetic adsorbent used in the adsorption process of heavy metals and textile dyes in the batik industry. However, until now the use of iron sand from North Sulawesi is still very rare, and for its use as a chitosan magnetic nanocomposite there has been no research reporting it. Based on this, it was studied the potential use of iron sand from North Sulawesi as an adsorbent combined with chitosan, to form magnetic-chitosan nanocomposites to adsorb Molybdenum contained in industrial textile waste, especially in the batik industry.

METHODOLOGY

General

Material used in study, aquadest, iron sand was obtained from the Lolak Beach, North Sulawesi, NaOH 500g (Merck), Glutaraldehyde 100 mL (Merck), Glacial acetic acid (Merck) 100 mL, Chitosan 50 g (Merck) and textile industry waste (batik industry).

Iron Sand Preparation

The sample used in this study was iron sand taken from Bolaang Mongondow Timur district, precisely on Lolak beach. Preparation of iron sand begins with pounding iron sand to make it smoother, then filtered using a 200 mesh sieve. The iron sand that has been sifted is then pulled using a permanent magnet.

Preparation of Chitosan Solution

A total of 0.35 grams of chitosan was dissolved in 20 mL of 2% acetic acid and stirred with the help of a stirrer for 2 hours. Into this chitosan solution, 5 mL of glutaraldehyde was added and stirred again for 2 hours.

Magnetic-chitosan Preparation

Magnetic preparation of chitosan was carried out according to the procedure reported [10] with some modifications. A total of 0.5 grams of magnetic (iron sand) was put into the solution and stirred again for 2 hours. 3M NaOH solution was dropped into the mixture until a precipitate was formed and the precipitate formed was filtered and washed several times until the pH of the solution becomes neutral. Magnetic-chitosan was dried in an oven overnight at 40 °C.

Test as Adsorbent

A total of 0.1 grams of magnetic-chitosan was put into an Erlenmeyer flask, which already contained 10 mL of batik textile industry waste solution. The solution was stirred at 250 rpm for 2 hours. The heavy metal measured to test the adsorbent capacity of the metal chitosan magnetic nanocomposite is Mo, which is contained in batik industrial waste. After the adsorption process (stirring) was completed, the chitosan-type was separated from the solution using a permanent magnet.

Characterization

The characterization will be carried out on samples of iron sand and magnetic-chitosan products using X-ray Fluorescence (XRF) and Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES).

RESULTS AND DISCUSSION

Iron Sand Preparation

The sand used to obtain iron sand comes from Lolak Beach, East Bolaang Mongondow Regency, North Sulawesi Province. The sand obtained was first washed and dried in the sun and the dry sand was used in this study, as shown in Fig. 1.

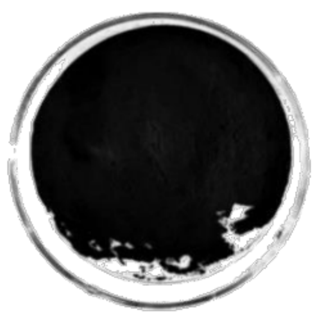


FIGURE 1. The iron sand of Lolak Beach, East Bolaang Mongondow Regency.

The dried iron sand was sifted through a 200 mesh sieve. The sieving process is shown in Fig. 2.

FIGURE 2. The iron sand sieving process uses a 200 mesh sieve.

The sifted iron sand was characterized by X-ray Fluorescence (XRF) to determine the content of elements and oxides contained in it, as shown in Fig. 3 and 4.

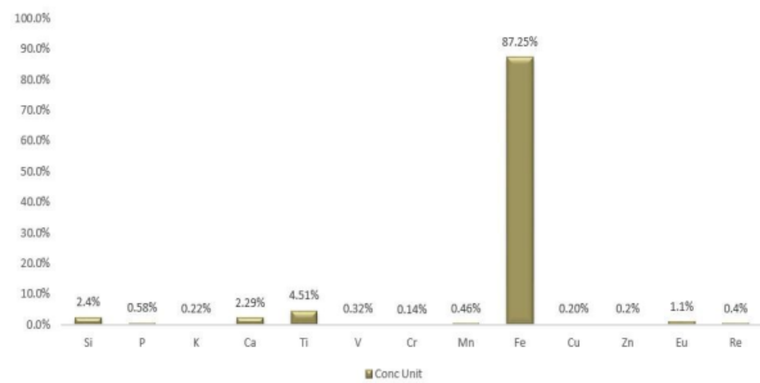


FIGURE 3. XRF data for the concentration of iron sand on Lolak beach, East Bolaang Mongondow Regency, North Sulawesi.

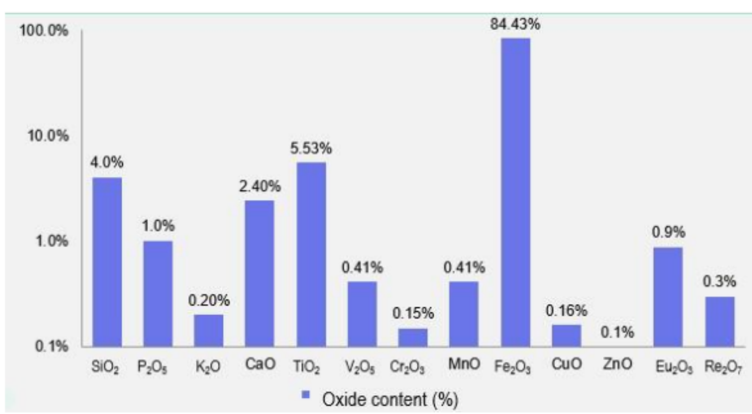


FIGURE 4. XRF data for the concentration of iron oxide content in Lolak beach, Bolaang Mongondow Timur Regency, North Sulawesi

Fig. 3 and 4 above show that the most abundant element in the iron sand sample from Lolak Beach, Bolaang Mongondow Timur Regency is iron (Fe) reaching 87.25 %, followed by Titanium (Ti) at 4.51%. Furthermore, the highest oxide content in the iron sand sample was also dominated by iron oxide (Fe_2O_3) as much as 84.43% and also Titanium oxide (TiO2) as much as 5.53%.

Magnetic-chitosan Preparation

The sifted iron sand was dissolved in a chitosan solution and followed by the addition of NaOH solution to produce magnetic-chitosan. The resulting magnetic-chitosan product is dark brown in color and is shown in Fig. 5.

FIGURE 5. Magnetic-chitosan products.

Furthermore, the magnetic-chitosan produced was characterized by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) to see the content of elements (5 elements) in it. The content of these elements is presented in Fig. 6.

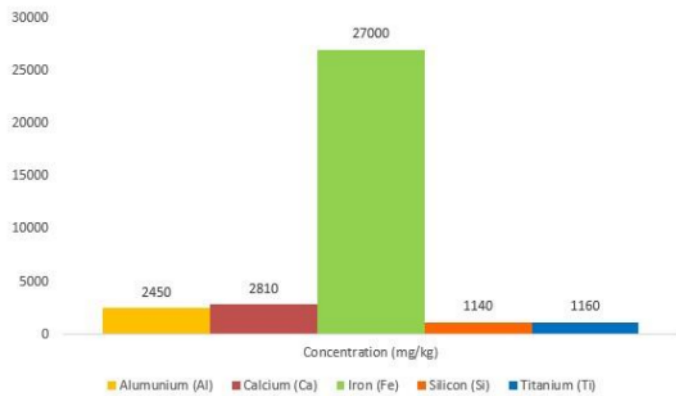


FIGURE 6. The content of elements contained in magnetic-chitosan based on ICP-OES analysis.

The picture above shows that Fe is the most dominant element in the magnetic-chitosan sample (27000 mg/kg) and the lowest is Si (1140 mg/kg). Based on data from Fig. 3 and Fig. 4, the iron element contained in the magnetic-chitosan sample is an iron oxide compound sourced from Fe_2O_3, which means that this iron oxide is dominant in the magnetic-chitosan sample.

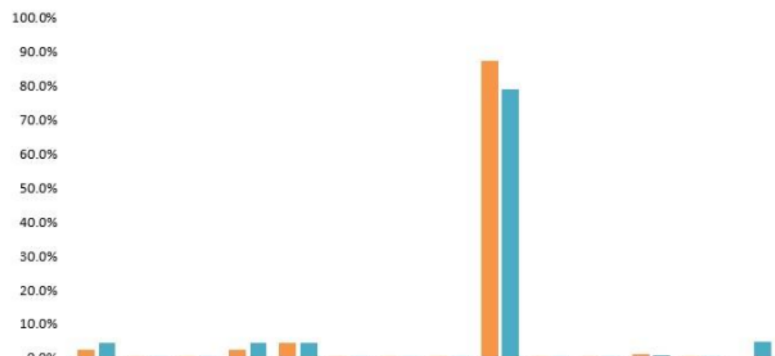
Test as Adsorbent

The magnetic-chitosan that has been produced was then tested as an adsorbent for batik industrial waste. The process is carried out by immersing the magnetic-chitosan into a sample of batik textile industry waste for 2 hours by stirring at a speed of 250 rpm and then filtering. The results are shown in Fig. 7.

(a) (b) (c) (d)

FIGURE 7. (a) Magnetic-chitosan immersion process in batik industrial waste samples, (b) Stirring process of magnetic-chitosan products in batik industrial waste samples for 2 hours, (c) Magnetic-chitosan products after immersion in waste samples, (d) Magnetic product-chitosan after grinding.

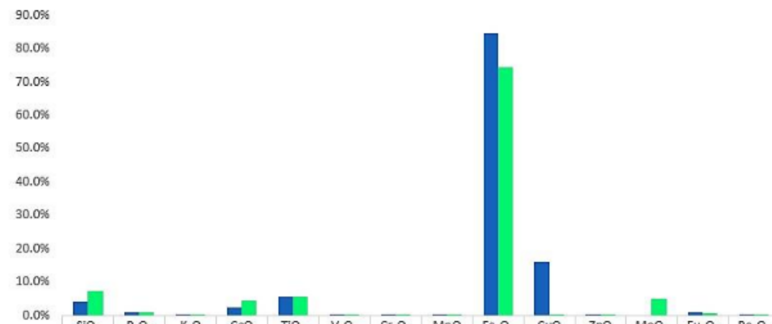
The image above shows that the magnetic-chitosan product changes color from dark brown (Fig. 5, before soaking in batik waste) to reddish brown (light brown, Fig. 7c). The image above shows that the magnetic-chitosan product changes color from dark brown (Fig. 5, before soaking in batik waste) to reddish brown (light brown, Fig. 7c). The color change that occurs is due to the binding of metal ions to the iron sand-based magnetic-chitosan nanocomposite, which generally binds to the available functional groups (hydroxyl, carboxyl, thiol, and amine groups) in the composite [16]. This information shows that magnetic-chitosan can adsorb dyes from batik waste. The magnetic-chitosan product that has been tested as an adsorbent is further characterized by XRF. The characterization results are presented in Fig. 8 and Fig. 9.



	Si	P	K	Ca	Ti	V	Cr	Mn	Fe	Cu	Zn	Eu	Re	Mo
Before	2.4%	0.58%	0.22%	2.29%	4.51%	0.32%	0.14%	0.46%	87.25%	0.20%	0.2%	1.1%	0.4%	
After	4.5%	0.47%	0.23%	4.30%	4.56%	0.44%	0.13%	0.43%	78.81%	0.15%	0.09%	0.82%	0.4%	4.7%

FIGURE 8. Comparison of the content of elements contained in iron sand that has been attracted by magnets and magnetic-chitosan products after testing as an adsorbent.

In Fig. 8 above, it can be seen that after testing as an adsorbent for batik industrial waste, there is a new element that is read, namely the element Mo with a content of 4.7%. This shows that after being tested as an adsorbent, a magnetic-chitosan nanocomposite based on iron sand is able to absorb 4.7% of heavy metal Mo contained in batik industry waste, and for Fe elements after testing on batik waste it has decreased from 87.25% to 78.8%. And for the comparison of the oxides can be seen in Fig. 9 below.



	SiO_2	P_2O_5	K_2O	CaO	TiO_2	V_2O_5	Cr_2O_5	MnO	Fe_2O_3	CuO	ZnO	MoO_3	Eu_2O_3	Re_2O_7
Before	4.0%	1.0%	0.20%	2.40%	5.53%	0.41%	0.15%	0.41%	84.43%	16.00%	0.1%		0.9%	0.3%
After	7.3%	0.87%	0.21%	4.36%	5.47%	0.46%	0.14%	0.35%	74.38%	0.12%	0.06%	5.1%	0.75%	0.4%

FIGURE 9. Comparison of the oxide content contained in the iron sand that has been attracted by magnets and the magnetic chitosan product after testing as an adsorbent.

CONCLUSION

From the research data, it can be seen that the most abundant element in the iron sand samples from Lolak Beach, East Bolaang Mongondow Regency is iron (Fe) reaching 87.25 %, followed by Titanium (Ti) as much as 4.51%. Furthermore, the highest oxide content in the iron sand sample was also dominated by iron oxide (Fe_2O_3) as much as 84.43% and also Titanium oxide (TiO_2) as much as 5.53%. The chitosan-magnetic nanocomposite product was dark brown in color and after being tested as an adsorbent for batik industrial waste, the chitosan-magnetic nanocomposite which was initially dark brown in color, changed to reddish brown. This proves that chitosan-magnetic nanocomposite based on iron sand in North Sulawesi can be used as an adsorbent for heavy metals and synthetic dyes from textile industry waste and has the potential to be an alternative method in processing textile industrial waste, especially batik.

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