

Biocomposite Materials of *Eleocharis dulcis* Fibers with Iron (III) Nanoparticles and Its Potential for Sasirangan Textile Wastewater Treatment

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Abstract— *Eleocharis dulcis* (Chinese water chestnut), locally Kalimantan named Purun Tikus, is a plant that grows in highly acidic swamps areas in South Kalimantan. *Eleocharis dulcis*(ED), was usually used as a material for traditional handicrafts. Therefore it is necessary for develop and innovate to convert the material becomes valuables. This research focuses on the study of biocomposite nanoparticles of ED and its potentials as an adsorbent to reduce the concentration of Pb^{2+} ions, Total Suspended Solid (TSS) and color from Sasirangan textile industry wastewater. The synthesis of the biocomposite nanocomposite was made by solvothermal synthesis. Firstly, ED stems dried was cut to small size (250 microns), then through the de-lignification process to eliminate lignin by 1% w/v NaOH solution. ED de-lignification put into a hydrothermal reactor, right afterward was carried out by one-pot solvothermal reaction of 1,6-diaminohexane, iron (III) chloride hexahydrate, and ethylene glycol at 200 °C for 6 h. The process was produced two types of biocomposites, without the amino group (EDB-M) and the amino group (EDB-MH). The characterization results shown by SEM, magnetic nanoparticles have been formed on the surface of ED fiber. The ED biocomposite nanoparticles (EDB) with diameter size around 30–50 nm could be obtained. X-Ray Diffraction (XRD) analysis showed treatment of ED delignification was increased the porosity of the fiber, shown by increased Crystallinity Index (CrI) about 72.75%. The biocomposites adsorbent, EDB-M, and EDB-MH had adsorption capacity for Pb^{2+} ions about 44.21 mg/g and 55.62 mg/g at equilibrium pH (pH_e) of 6 and equilibrium time of 2 hours. The effectiveness of reduced TSS was about of 91.9% and 98.1%. Besides that, the colour intensity of color was decreased about 96.7% and 97.8% for the EDB-M and EDB-MH, respectively.

Keywords— adsorption; biocomposite; *Eleocharis dulcis*; iron (III) nanoparticle; Pb^{2+} ion; TSS; color

I. INTRODUCTION

Eleocharis dulcis (Chinese water chestnut), locally Kalimantan named Purun Tikus, is an aquatic plant that grows in highly acidic swamps areas in South Kalimantan. ED Stems are hollow, have an average diameter of 5 mm and growth almost to 2 m tall and having heavy metal uptake capacity in wetland filtration system [1]. ED is highly renewable material, abundant resources in South Kalimantan among almost of 70 acres are grown in a swamp area and it takes a few months to grow toward maturity. ED has also been customarily used to living handicrafts, such as bag, floor mat, kitchen tools, etc.

The textile industry is very flourishing in their process. It is causing a large amount of highly polluted effluent wastewater including detergents, oils, dyes, suspended solids and dissolved solids, harmful, biodegradable and non-biodegradable substances, and alkalines substance that poses an environmental problem [2]-[4]. Considering a traditional

textile in South Kalimantan, Indonesia called Sasirangan, the process including pretreatment, dyeing, printing, and finishing operation that using different types of dyes, such as: disperse, reactive, insoluble dye, etc. in the presence of additional dyeing and chemicals. Dyeing effluents from Sasirangan textile industry are highly toxic as same as other textiles industry contain a number of metal complex dyes (e.g. Pb, Cu, Cd, etc), a high concentration of suspended solid (e.g TSS) and color into the receiving waters. Lead (Pb^{2+}) is considered detected in sasirangan textile wastewater even from dyestuff and printing process [5]. It is one of those heavy metal that toxic to humans at low concentration. It is therefore important to reduce the concentration of metal, TSS, and color in textile wastewater to meet the standard regulation before charging it into surface water and river.

Adsorption process is commonly used to eliminate color, suspended solids and metal pollutant from textile wastewater compares to other technologies such as coagulation-flocculation, filtration, chemical precipitation, membrane-

filtration, oxidation, sedimentation, biological process, etc. [2]-[6]. Activated carbon is commonly used as an adsorbent in adsorption process, however commercial activated carbon is becoming more expensive, then there is a need to find low-cost adsorbent from renewable sources. Using low-cost biosorbents such as biomass, agricultural wastes, organic and seafood processing wastes, and clay materials can be as an alternative adsorbent for textile wastewater treatment because they are inexpensive and remarkable of reducing trace levels of color, suspended solids, and heavy metal ions. However, to improve their adsorption density and enhance the adsorption kinetic, the design of and research of innovative adsorbents are still required [7].

Potential environmental impact of ED fibers utilization will be studied in this work. Since there is no information on using biocomposite of ED fibers with iron (III) nanoparticle as an adsorbent to remove Pb^{2+} ion, TSS, and color from textile wastewater, this research will focus on the study of a biocomposite of ED fibers with iron (III) nanoparticle as a possible alternative adsorbent for Sasirangan textile wastewater treatment. Modified of ED is promising to this alternative adsorbent for textile wastewater treatment due to abundant, renewable, potentially less expensive and readily available. Develop and converting of the ED to become a value-added product will be studied in this research. Iron and its compounds were reported can be used to chemically modify the adsorbent concerning to improve the adsorption density of metal ions and easily to separated it from the solution using magnetic [8]. Magnetic nanoparticles are well-known and prepared for their ability and can be conveniently separated to generate heat when exposed to alternating magnetic fields [9]. It has been also found that the chemical and physical properties of the ED adsorbent can be enchanted even by chemical or physical modifications treatment to make the adsorbent become effective and high capacity adsorption in composites.

This research will focus on the study of a biocomposite of ED with iron (III) nanoparticles and its potentials as an adsorbent to reduce the concentration of Pb^{2+} ions, TSS, and color from Sasirangan textile wastewater.

II. MATERIALS AND METHOD

A. Materials

Sasirangan textile wastewater was obtained directly from the factory discharge point without any treatment in Banjarmasin, South Borneo. The samples were kept stored at below 4°C. Pure grade analysis chemicals of anhydrous sodium acetate ($C_2H_3NaO_2$), ethylene glycol anhydrous, 99.8% ($C_6H_6O_2$), 1,6-diaminohexane ($C_6H_{16}N_2$), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), D-Glucose anhydrous ($C_6H_{12}O_6$), lead (II) nitrate, 99.9% ($Pb(NO_3)_2$) was used as artificial Pb^{2+} solution, hydrochloric acid (HCl), and sodium hydroxide (NaOH) were obtained from MERCK. All others chemicals directly used in this work were of analytical grade without further treatment.

B. Preparation of ED Biocomposites with Iron (III) Nanoparticles

The synthesis of ED biocomposites with iron (III) nanoparticles (EDB-M) was carried out by one-pot

solvothermal synthesis. Firstly, ED stem (approximately 75 cm) was dried and be cut into small size (± 25 mm), then placed in a conical flask. The delignification process by adding 1% w/v of NaOH solution into the flask and allowed at 80°C for 2 h on a hot plate magnetic stirrer for eliminating the lignin. After 2 h, the flask and its content were allowed to cool to ambient temperature. The delignified fibers (ED fibers) were filtered in a Buchner funnel and washed with warm distilled water until the pH of filtrate become neutral. Finally, the ED fibers were dried in an oven at 80°C for 6 h.

Briefly, anhydrous sodium acetate (1.6 g) and iron (III) chloride hexahydrate (0.8 g) were dissolved in ethylene glycol anhydrous (24 mL) with vigorous stirring at 50 °C using magnetic stirrer with temperature control to give an orange solution. Surface amine-functionalized of iron (III) nanoparticles were synthesized adapting to the method used by [8]. The iron (III) nanoparticles composites were reacted by soaking of 0.5 g ED fibers into the solution, and then solvothermal was carried out at 200 °C for 6 h (EDB-M). When 1,6-diaminohexane (7 mL) was added, the mixed solution will turn into dark-orange for EDB-MH. After cooling to ambient temperature, the ED biocomposites were collected from the mixed solution by applying a magnet and was rinsed with deionized water (DI water) followed by ethanol of 70% v/v each for three times to eliminate the remaining chemicals. The obtained of ED biocomposites with iron (III) nanoparticles were kept in DI water for forthcoming use.

There are two types of ED biocomposites material, added and without the addition of amino group using 1,6-diaminohexane. The processes were produced two types of ED biocomposites, without the amino group (EDB-M) and with the amino group (EDB-MH).

C. Characterization of EDB-M and EDB-MH

Surface morphology of EDB-M and EDB-MH were characterized by field-emission scanning electron microscopy (FESEM, JOEL JSM-6500F) with energy-dispersive X-ray spectroscopy (EDS). The samples were coated with platinum by sputtering before the examination.

The X-ray diffraction (XRD) analysis was carried out on Rigaku n D/MAX-BX-ray diffractometer by using Copper K-alpha ($CuK\alpha$) radiation. The operating voltage and current were kept at 40 kV and 100 mA, respectively. Fourier transform infrared spectrometry (Bio-rad, Digilab FTS-3500) was used to identify the surface functional groups of the EDB-M and EDB-MH nanocomposites.

C. Batch Mode Experiment of Sasirangan Textile Wastewater Treatment

Batch adsorption experiments were performed by putting 50 mL solution of a certain amount of lead into 100 mL glass bottle and adjusting its pH value using 1M NaOH or HCl. Afterward, weighed the amount of the adsorbent (EDB-M and EDB-MH, respectively) was added into a glass bottle. The mixture was then placed in a shaker with a water bath (Firstek Scientific) at a pre-determined temperature for certain contact time. The adsorption process was carried out while shaking at ambient temperature for 6 hours. At the end of the running experiment, the mixed solution was

centrifuged and filtered by using a 0.2 μm PVDF membrane (Advantec). Then, the filtrates were analysed for residual Pb^{2+} concentration using Inductively Coupled Plasma Optical Emission Spectrophotometer (ICP-OES, Horiba Jobin-Yvon Ultimate II). TSS values were measured by APHA standard method 2540-D [9]. The filtrates were also used for color concentration analysis using UV-Vis spectrophotometer (Shimadzu UV-2600) at the maximum absorption wavelength of ($\lambda_{\text{max}} = 402 \text{ nm}$). Adsorbed Pb^{2+} ion, TSS, and color were calculated from the difference between initial and equilibrium the adsorbate concentrations. The adsorption capacity of Pb^{2+} ion onto the adsorbent in the equilibrium, q_e was calculated as follows:

$$q_e = \frac{(C_o - C_e)V}{m} \quad (1)$$

where V is the volume of sample solution (mL), m is the amount of adsorbent used in this batch experiment (mg) and C_o (mg/L) and C_e (mg/L) are initial and the equilibrium concentration of Pb^{2+} ion, respectively

The adsorbent was also used to investigate the pH equilibrium factor that affecting Pb^{2+} , TSS, and color adsorption capacity. The others, EDB-M and EDB-MH, were separately used to finding out the correlation of amine content that has an important role in the adsorption phenomenon. The adsorption experiments were done in triplicate samples and the average value was taken.

In order to regenerate the adsorbent for repeated uses, the EDB-M and EDB-MH loaded metal ions were desorbed by shaking into 0.1 M HCl for 24 hours. After washing completely using DI water, the regenerated adsorbent was loaded for the next cycle of Pb^{2+} , TSS and color adsorption processes. The cycles of such adsorbent were repeated for three times in triplicate analysis.

III. RESULTS AND DISCUSSION

A. Characterization of EDB-M and EDB-MH

The characterization of EDB-M and EDB-MH were done by SEM, XRD, TGA, and FTIR analysis. Fig. 1 presents SEM images indicating the changes in the surface properties of the ED fibers after the treatments.

Fig. 1a shows the physical features of ED fibre structure are roughness with the lamellar shape. It is indicated ED fibres contain lignin, hemicelluloses, and other components that binding with cellulose. After delignification (Fig. 1b), the ED fibres morphology of the surface of alkaline treated ED fibres using 1% NaOH solution shows the formation of the scratches by cause of the discharge of the lignin, hemicelluloses, and other components changed the characteristics of the surface morphology. It is noted that the alkaline treatment discharges the waxy and gummy substances observed in the fibers before treated [11]-[12].

This characteristic might be increased the adhesion between fibres and matrix when it is used in reinforcing composites material [10]. The ED fibers change their morphology after alkaline treatment. It's exposed for the composite easy to attach the matrix site of the ED fiber. A typical biomass from organic plants is composed of 30–50% cellulose, 20–40% hemicelluloses and 15–30% lignin [13].

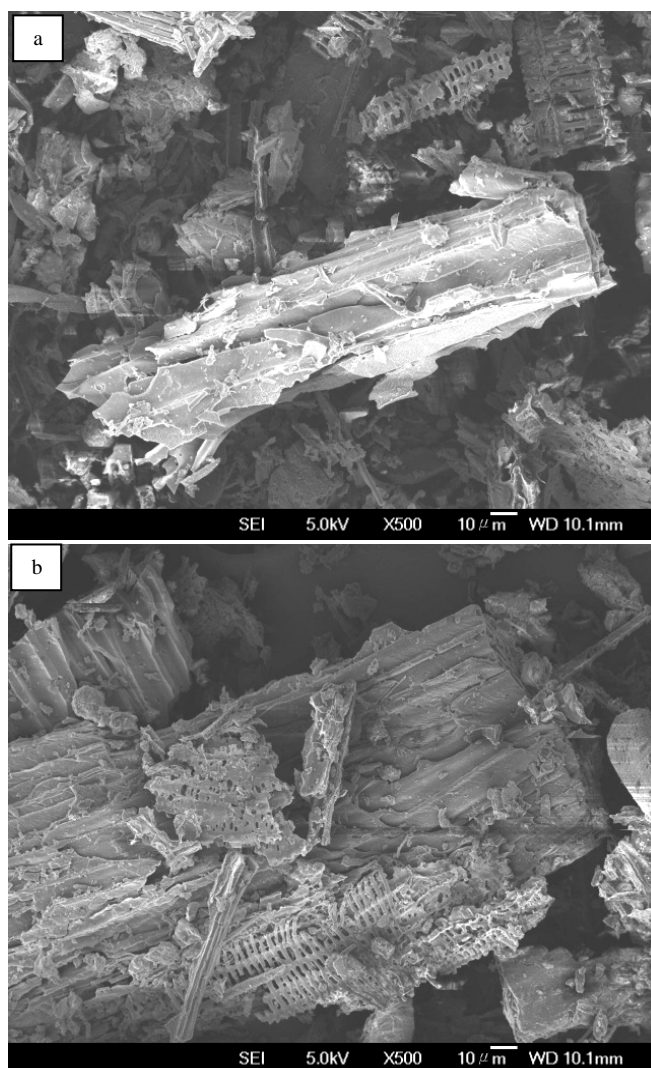


Fig. 1 FESEM image of a. ED fibers, b. ED fibers after delignification

Fig. 2 shows the surface texture of the treated ED fibers, ED biocomposites material, without and with the addition of amino group using 1,6-hexanediamine. The processes were produced two types of ED biocomposites, without the amino group (EDB-M) in Fig. 2a, and with the amino group (EDB-MH) in Fig. 2b. Recognizing the photograph, monodispersed nanoparticles were aggregated positively, which was due to the nanoparticles size of the Fe_2O_3 . As shown, the surface of ED fibers is attached to iron (III) nanoparticles with diameter size around 30–50 nm, even for EDB-M and also EDB-MH. It is also confirmed by EDX analysis that the EDB-M and the EDB-MH contain the iron component. The iron content may affect the adsorbent by enhancing the high-adsorption of sorbent capacity for reactivity toward a wide range of organic pollutants [14]. This reactivity arises from the complexity of its chemical surface functional group compared to those other surfaces. Iron particles will also promote the adsorption of metal ions.

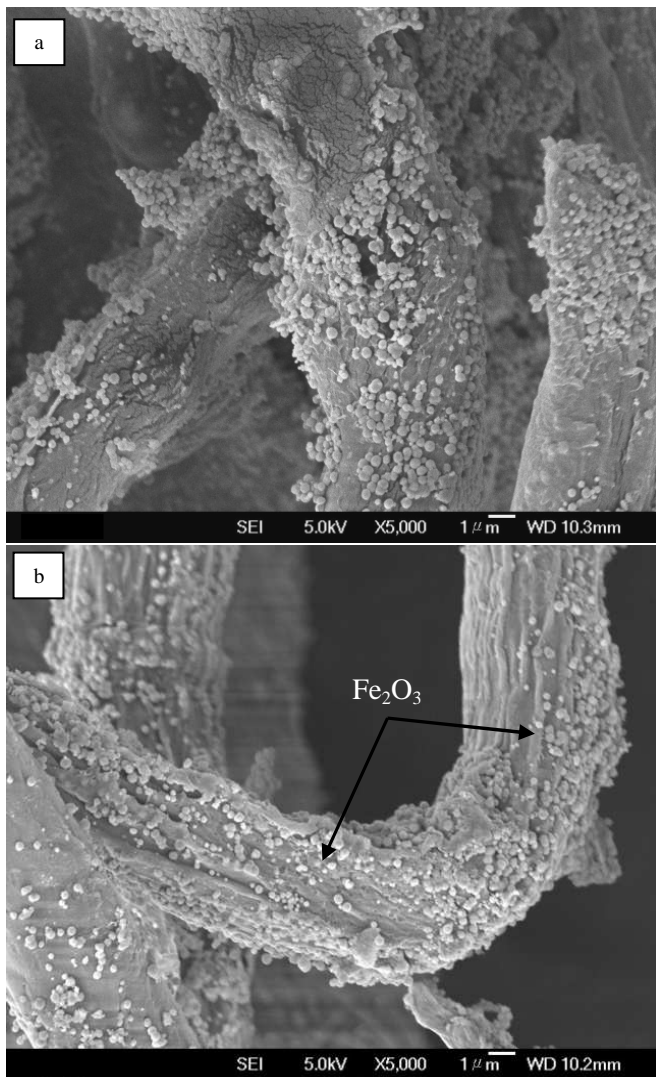


Fig. 2 FESEM image of biocomposites of a. EDB-M, b. EDB-MH

XRD analysis as shown in Fig. 3 are a pattern of ED fibers, ED after delignification, and biocomposites of EDB-M and EDB-MH. The crystallinity of the ED fibers before and after treatment was shown. The XRD pattern shows a typical spectrum of cellulosic crystalline material, having amorph peak amorph at $2\theta = 16,2$ and crystalline peak at $2\theta = 22.6$. The main crystalline peak is appropriated as indicative of highly organized crystalline cellulose, while the amorph peak determines of a minor organized polysaccharide structure and its assigned to broad peak with low angle [10]. The treatment of ED fibers with alkaline treatment, biocomposite using iron (III) nanoparticles, even by added and without the addition of amino group will change the crystalline structure.

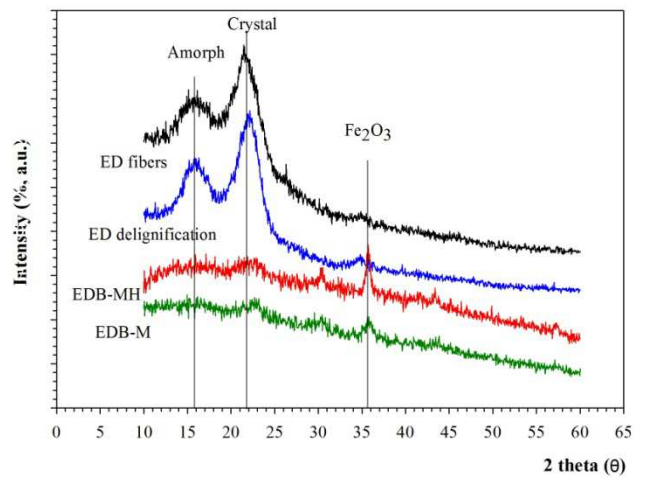


Fig. 3 XRD analysis of ED fibers, ED delignification, EDB-M, and EDB-MH

The alkaline treatment of ED fibers improves their crystalline structure. It is noted that enhances the crystallinity index to 72,75% using 1% of NaOH solution. This is due to the chemical reagents react to the chain ends on the surface of the crystalline structure and reducing the amorphous product like cellulose, hemicellulose and lignin [13]. The formation of the iron (III) can also be seen in the XRD peaks of Fe_2O_3 around at 36. These lines are characteristic for spinels Fe_2O_3 . Magnetic nanoparticles are adjacent to the standard pattern figure of crystalline hematite (JCPDS card 39-0664).

FT-IR spectra analysis of the ED fiber and modified ED fibers are shown in Fig. 4. The C-H stretching vibration of the ED fibre and modified ED fibres are manifested through a strong peak at 2930 cm^{-1} . The infrared spectra shown in this figure, revealed the absorption peaks at 580 cm^{-1} belonged to the stretching vibration mode of Fe-O bonds in Fe_2O_3 , even for EDB-M and EDB-MH, while at this peaks the stretching vibration did not appear for ED fibre and ED delignification, respectively. The present of amina on ED biocomposites is accordant with that of the band around 1540 cm^{-1} was due to the N-H bending vibration in $-NH_2$.

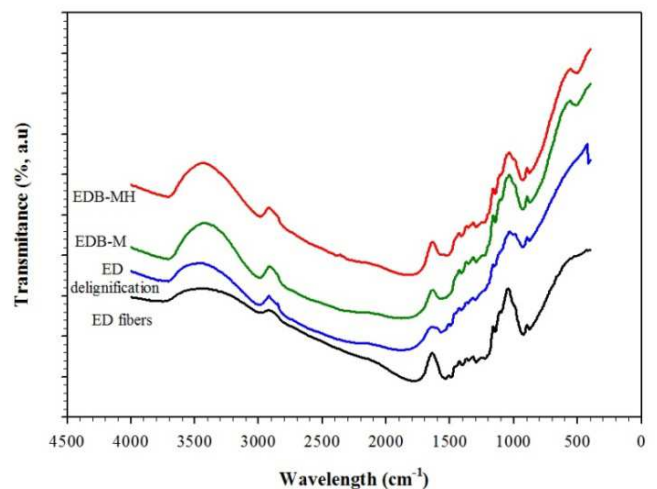


Fig. 4 FTIR analysis of ED fibers, ED delignification, EDB-M, and EDB-MH

B. Batch Adsorption Experiment of Sasirangan Textile Wastewater Treatment

1) The Contact Time Effect on Adsorption

Adsorption density mainly depends on the surface area available for adsorption and the composition of the adsorbent, whereas in this research modified by impregnating with iron (III) nanoparticles, without the amino group (EDB-M) and with the amino group (EDB-MH). Using the batch processes described in the experimental section, the dependencies of the adsorbed amounts of Pb^{2+} , TSS, and color on their equilibrium concentrations in solution were measured. The contact time effect on the amount of Pb^{2+} , TSS and color adsorbed onto adsorbent, EDB-M and EDB-MH, respectively were examined by conducting an experiment at ambient temperature, an adsorbent dose of 2.5 g/L, pH_e of 6 ± 0.2 , and shaking rate of 150 rpm.

Fig. 5 shows that during the first 30 minutes, Pb^{2+} uptake capacity increased significantly from 0 mg/g to 42.92 mg/g and 48.98 mg/g for EDB-M and EDB-MH, respectively. It was probably due to the diffusion taking place into the pores and/or adsorb onto the surface of the adsorbent. Initially, all sites on the surface of the adsorbents were vacant and the Pb^{2+} concentration gradient was relatively high diffusing into and through the pore of the adsorbent [14]. Afterward, the Pb^{2+} uptake capacity slightly increased to Pb^{2+} uptake capacity of 44.82 mg/g and 49.92 mg/g, respectively. Then finally to be attached to the adsorbent surface, caused by the decrease in the number of vacant sites on the surface of the adsorbent within 2 hours. It also maybe due to the availability of more adsorption sites with more functional groups resulting from the increase adsorption capacity for EDB-MH. The time beyond which no significant change in the adsorption takes places has been fixed as equilibrium time, then can be accepted as optimum contact time. The adsorption experiments were conducted in 2 hours reaction time to evaluate some parameter of Pb^{2+} removal.

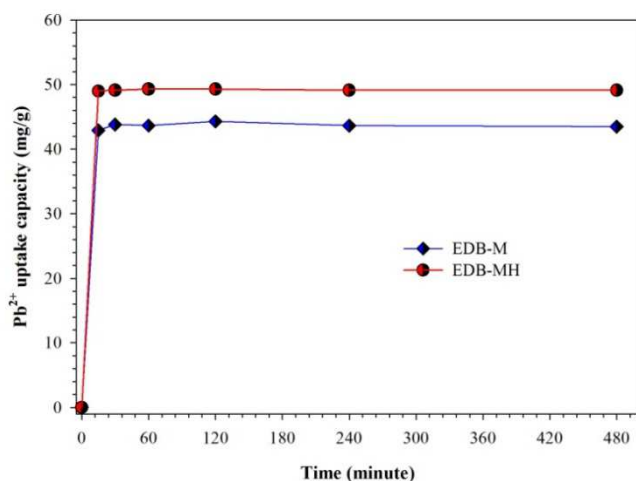


Fig. 5 Effect of contact time of Pb^{2+} adsorption onto EDB-M and EDB-MH, respectively at ambient temperature, adsorbent dose of 2.5 g/L, pH_e of 6 ± 0.2 , and shaking rate of 150 rpm

2) The Equilibrium pH Effect on Adsorption

The equilibrium pH effect on adsorption was investigated by conducting an experiment at ambient temperature, the initial Pb^{2+} concentration of ca. 100 mg/L, the adsorbent dose of 2.5 g/L, shaking rate of 150 rpm, and contact time of 4 h. Fig. 5 shows that pH affected Pb^{2+} adsorption density over a wide pH controlled range of $4.0-12.0 \pm 0.2$.

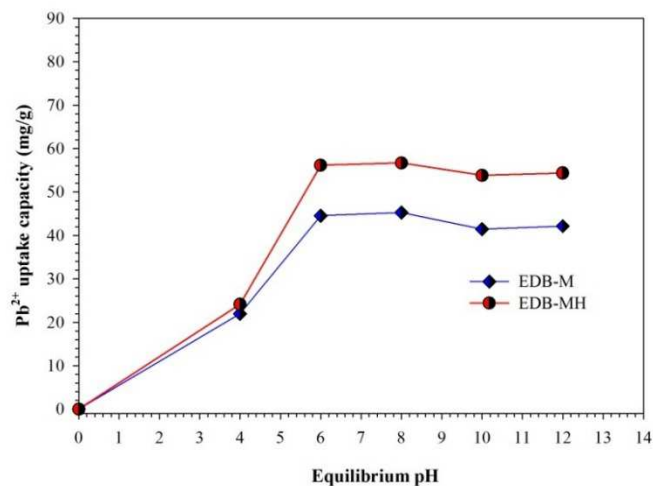


Fig. 6 The equilibrium pH effect on Pb^{2+} adsorption onto EDB-M and EDB-MH, respectively at ambient temperature, adsorbent dose of 2.5 g/L, and shaking rate of 150 rpm

Plotted in Fig. 6 shown that the Pb^{2+} adsorption envelopes for the adsorbent was bell-shaped like typical oxyanions sorption curves. The lower value of Pb^{2+} adsorption density when the pH was low (pH around 4) could be due to the excess of hydrogen ions surrounding the binding sites making adsorption process was unfavourable. Pb^{2+} and H^+ ions compete with the active adsorption site and account for the lower adsorption uptake capacity [15]. Thus, Pb^{2+} adsorption density will increase with increasing pH around 6–8 up to 44.21 mg/g and 55.62 mg/g for EDB-M and EDB-MH, respectively. The surface of the EDB-MH formation has many $-NH_2$ groups that can coordinate with Pb^{2+} ions [7], then increased adsorption capacity compared without an amino group. The increase in Pb^{2+} removal as pH increases can be explained on the basis of a decrease in competition between protons (H^+) and positively charged metal ions at the surface sites. At higher pH ($pH > 8$) due to metal solid hydroxide precipitation the Pb^{2+} ion seems remaining constant [15].

The equilibrium pH effect of the solution was also studied on TSS and color removal by EDB-M and EDB-MH, respectively at ambient temperature, an adsorbent dose of 2.5g/L, and shaking rate of 150 rpm. Initial TSS of Sasirangan textile wastewater was of 1159.5 mg/L. The solution pH was varied between 4 and 12. The result of this effect is as shown in Fig. 7. The maximum percentage of TSS removal was obtained at pH 6–8 around 91.9% and 98.1% removal, respectively for EDB-M and EDB-MH. Various groups such as carboxylic and phenolic group present in wastewater interact with metal cations at low pH,

while hydroxyl and aliphatic hydroxyl groups interact at the elevated value of pH [17].

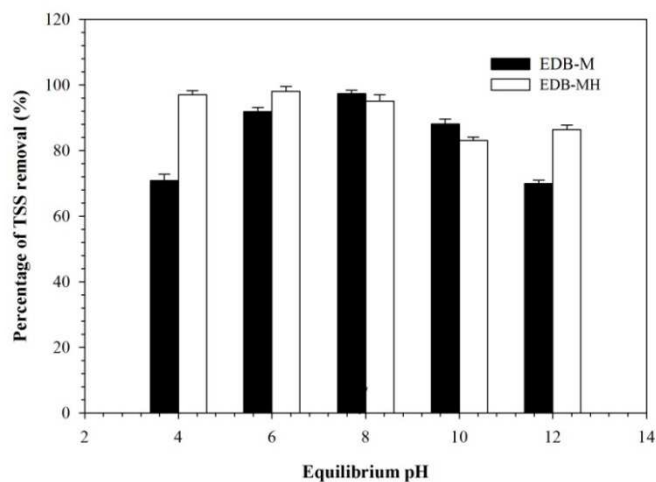


Fig. 7 The equilibrium pH effect on TSS removal using EDB-M and EDB-MH, respectively at ambient temperature, adsorbent dose of 2.5 g/L, and shaking rate of 150 rpm

The equilibrium pH effect of the solution was studied on color removal by EDB-M and EDB-MH, respectively shown in Fig.8. The initial color of Sasirangan textile wastewater was of 590 Pt/Co. The solution pH was varied between 4 and 12. The high color reduction obtained at pH of 6–8 around 96.7% and 97.86% removal, respectively for EDB-M and EDB-MH. This, in turn, neutralized the positively charged adsorbent surface with the existing iron oxide.

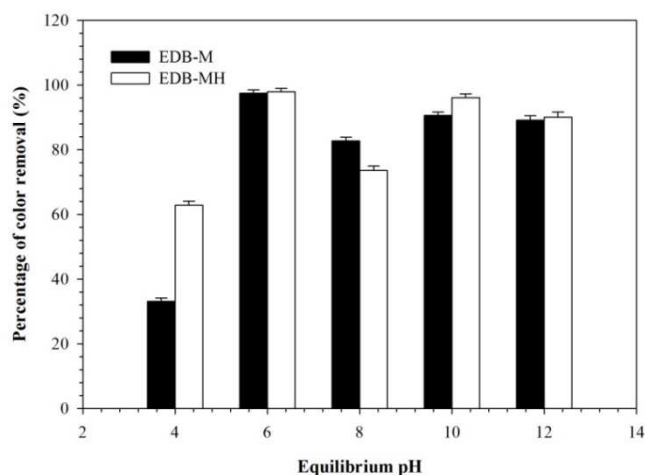


Fig. 8 The equilibrium pH effect on color removal using EDB-M and EDB-MH, respectively at ambient temperature, adsorbent dose of 2.5 g/L, and shaking rate of 150 rpm

The high color reduction at this range of pH is because of the abundance of OH^- ions and ionic interaction between the positively charged active sites of the adsorbent. The adsorption of the color of dye may be explained to proceed via the electrostatic attraction between the positively charged protonated amino groups on the adsorbent surface of EDB-MH ($-\text{NH}_3^+$) and the negatively charged sulfonate groups (SO_3^-) of the dye [18]. A lower adsorption values at low pH is maybe due to attributed to the presence of larger number

of H^+ ions, and ionic repulsion with the positive charged active sites of the adsorbent, then the adsorption capacity becomes decreases. There is no significant effect the adsorbent used for repeated uses. Regeneration of the adsorbents still reaching an efficiency of around 98% after 3 cycles.

IV. CONCLUSIONS

This research study revealed that *Eleocharis dulcis* (ED) is a promising alternate to be used in the preparation of biocomposite materials with iron (III) nanoparticles for the reduction of Pb^{2+} , TSS, and color from Sasirangan industrial textile wastewater. The characterization results shown by SEM, magnetic nanoparticles have been formed on the surface of ED fibre (EDB-M). The ED biocomposite with iron (III) nanoparticles (EDB-M) with diameter size around 30–50nm could be obtained. X-Ray Diffraction (XRD) analysis showed treatment of ED delignification was increased the porosity of the fibre, shown by increased Crystallinity Index (CrI) about 72.75%. The ED biocomposites adsorbent had adsorption capacity for Pb^{2+} ions about 44.21 mg/g and 55.62 mg/g. The effectiveness of reduced TSS was about of 91.9% and 98.1%. Besides that, the colour intensity of color was decreased about 96.7% and 97.8% for the EDB-M and EDB-MH, respectively at equilibrium pH (pH_e) of 6 and equilibrium time of 2 hours. The positive charges on the surface of amine-group of the EDB-MH can promote significant electrostatic interaction with negatively charged sites on the surface of dye to high performance efficient adsorptive density capacity. More research of ED biocomposites is needed with respect to certain modifications and its potential for contaminant removal of contaminated water or wastewater.

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