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The fast and of low-cost-adsorbent to the removal of cationic and anionic dye using chicken eggshell with its membrane

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Abstract: The use of the **c**hicken eggshell with its membrane as low-cost adsorbent had been done to the removal of synthetic dyes in aqueous solution. Adsorption method in the batch system was done to adsorb Methylene Blue and Indigo Carmine as the cationic and anionic dyes. Some parameters were studied such as pH, contact time, initial concentration of dyes and mass of ES+M to find the optimum adsorption. The functional group of ES+M like hydroxyl, amine, carboxyl and thiol were used to binding the dyes. The characteristics of ES+M were determined by FTIR and XRF to analyzed functional group and elements composition before and after adsorption. The adsorption capacity optimum of ES+M to adsorb Methylene Blue was 11.54 mg/g with % RE 92.34% in 30 minutes, and Indigo Carmine was 8.04 mg/g with % RE 64.34% in 15 minutes.

Keywords: Adsorption; eggshell; Methylene blue; Indigo carmine; wastewater treatment.

1. Introduction

Increasing population growth and rapid industry, has increased the amount of waste that enters the environment. The waste-water like synthetic dyes come from the textile industry, printing, plastic, coloring household and other materials. The synthetic dyes can be coloring the water even in small concentrations. The presence of dyes in waste-water reduces sunlight penetration to photosynthesis and acute toxicity to aquatic life [1].

These dyes adversely affect human health, such as eye irritation, skin irritation, mutagenic, and carcinogenic [2,3].

Various ways in overcoming the problem of dye waste both physically and chemically have been widely reported, such as chemical coagulation [4], activated sludge [5], biodegradation [6], photocatalysis [7], photocatalysis and magnetically separation [8], oxidation [9], membrane technologies of reverse osmosis and nanofiltration [10].

One of those methods was adsorption that is currently being developed due to easy and environmentally friendly to adsorb wastewater [11]. Adsorption used geomaterials such as natural zeolite to remove nutrients from livestock wastewater [12], Thai bentonite to adsorb aflatoxin B1 [13], ZnO to adsorb aliphatic dicarboxylic acids [14] and polymers to adsorb methylene blue [15]. Meanwhile, adsorption used natural adsorbents derived from plants and animals (biomaterials) that are more environmentally friendly, high efficiency, easily obtained while reducing organic solid waste. This method is the most widely used because it is safe, does not give side effects that endanger health, does not require complicated and expensive equipment [16].

Several studies on the use of biomaterials from plants have been carried out, such as apricot stone [17], activated carbon cocoa [18], mango seeds [19], pine fruits [20], orange peels [21], gherkin leaves powder [21], melon peels [22], Tunisian palm [23], okra seeds [24], several plants bark [25] and from animals like chitosan modified to adsorb metal ion [26,27,28] and eggshell. Eggshells are waste by-products of eggs that produced several tons per day that sent to the landfill with high management cost. Eggshells mostly contain calcium carbonate [29,30] which is often used as a calcium supplement, fertilizer, cosmetic from the membrane of eggshell, dental preparation, and other uses [31].

Several studies have made eggshells as adsorbents, such as fluoride absorption [32], removal of Ni [33], and H_2S [34]. The ability of the eggshell to adsorb pollutant

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due to it has many pores, and the membrane of eggshells have a functional group that could be binding with cation or anion compound [35]. The eggshell was used as low-cost adsorbent [36] to adsorb dyes in textile and batik [37] industry in Indonesia as a developing country to removal dyes in wastewater. The membrane of the eggshell has an amino acid that has functional group such as amine that contacted with anionic dyes. In contrast, hydroxyl, carboxyl and a sulfonic group can interact with cationic dyes. Even though of membrane eggshell higher adsorption capacity, but Pramanpol and Nitayapat report that eggshell without membrane and eggshell with the membrane in the difference of absorption capacity is not too significant [38].

The aim of this research to utilize eggshells with its membrane (ES+M) to adsorb synthetic dyes, and comparison of adsorption capacity and % Removal of efficiency of ES+M to adsorb Methylene Blue and Indigo Carmine as representative of cationic and anionic dyes. The study was conducted with a batch method by finding the optimum conditions of adsorption with parameter variations: pH, contact time, initial concentration, and mass of eggshells in small particle size of 36 µm to expand the surface area to interact between ES+M and dyes. Characterization of the ES+M with FTIR and XRF analyzed to know which part of the functional group was actively adsorbing dyes, and the elements contained in the ES+M before and after adsorption.

2. Experimental section

2.1. Adsorbent preparation

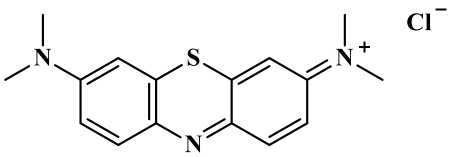
The adsorbent of the eggshell with its membrane (ES+M) is collected from Bukittinggi, West Sumatera, Indonesia. The physically treated of ES+M was cleaned with water, air-dried, ground by (Turbo 8099) in processed temperature ≤ 60ºC and sifted with particle size ≤ 425 µm.

2.2. Activation adsorbent

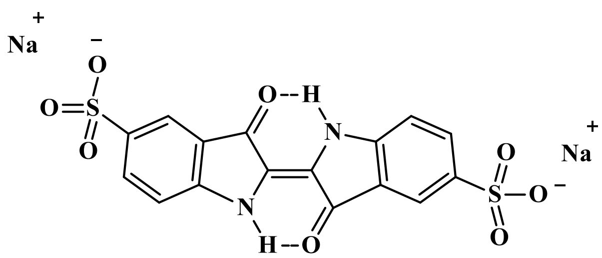
The chemically-treated of ES+M was soaked as much as 25 g in 75 mL 0.01 N HNO_3 for 2 hours, then neutralized by added aqua dest [39,40]. The aimed of adding HNO_3 was to remove the impurity and opened the pore of eggshell. Furthermore, the ES+M was dried, ground and sifted with particle size ≤ 36 µm and ready to used.

2.3. Preparation of Solution

0.250 g Methylene Blue (MB) dissolved with 250 mL distilled water in a volumetric flask. Then a variation of the concentration of Methylene Blue dye was made with multilevel dilution to create a calibration curve for a standard solution with differences in concentrations of 0, 2, 4, 6, 8, 10 mg/L. The same thing was done to make Indigo Carmine (IC) dye solution.



a. Methylene Blue



b. Indigo Carmine

Figure 1. Structure of Methylene Blue (cationic dye) and Indigo Carmine (anionic dye)

2.4. Determination of Optimum Adsorption of dyes by biosorbents

Several parameters such as pH, contact time, initial concentration of dyes and mass of adsorbent were done. 0.1 – 1 g eggshell was added into 25 mL of Methylene Blue and Indigo carmine (10 - 50 mg/L) with adding HNO_3 and NaOH to adjust pH ranging from 2 – 10. The agitation time was done ranging from 15 - 60 minutes on 100 rpm. The solution of Methylene Blue and Indigo carmine after contacted on ES+M were filtered and analyzed by Spectrophotometry UV-vis (Shimadzu).

The adsorption capacity of removal dye (Eq. 1) was calculated as follows:

$$qe = \frac{(Co - Ce)V}{m} \tag{1}$$

The % removal efficiency (RE) of removal dye (Eq. 2) were calculated as follows:

$$\%\ RE = \frac{(Co - Ce)\ 100\ \%}{Co} \tag{2}$$

Where Co and Ce were the initial and equilibrium dye concentrations (mg/L), m was the mass of ES+M (g), and V was the volume of IC dye solution (L).

3. Results and discussion

3.1. Effect of pH solution

Adsorption is a complex process depending on several interactions such as electrostatic and non-electrostatic interactions. The pH effects were investigated by varying the pH from 2 to 10 were presented in Figure 2. The optimum adsorption of Methylene Blue has occurred at pH 8 and Indigo carmine at pH 10. Comparison of adsorption cationic and anionic by ES+M in Figure 2 showed that adsorption capacity and % RE of Methylene blue higher than Indigo carmine.

Generally, the surface area of adsorbent will be positive at low pH and can adsorb anionic dyes [41,42]. But the existence of $CaCO_3$ the solution will be slightly alkaline. The low adsorption capacity of methylene blue at acidic pH might increase due to the presence of excess H^+ ions competing with positively charged cationic dye for the available adsorption sites [43]. So the optimum ES+M to adsorb Methylene Blue at pH 8. Another literature report that the adsorption of Brillian green as the cationic dye was optimum to pH 9 onto eggshell [44].

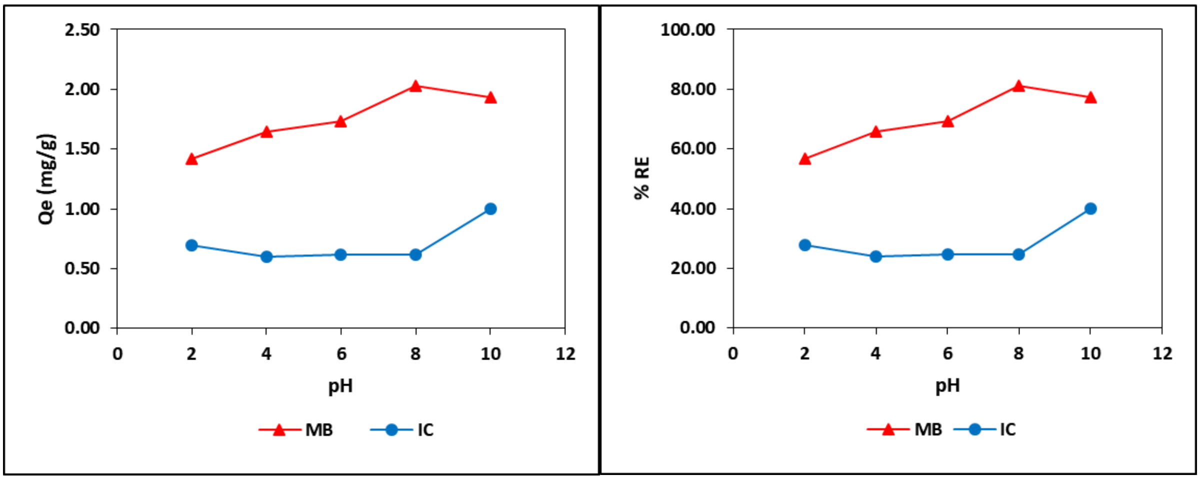


Figure 2. Effect of pH solution to adsorption capacity and % RE to removal Methylene Blue and Indigo Carmine

Meanwhile, the adsorption capacity for ES+M to adsorb Indigo carmine has occurred at pH 10. The present of HNO3 may cause it in low pH make the $CaCO_3$ will be release CO_2 [45] with reaction equation 1, so the binding could not occur, at the acid condition. Besides that, the present of $CaCO_3$ in different initial pH can influence the solution of ES+M in alkaline condition [38].

$$CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2 \quad (1)$$

The increase adsorption capacity equal with the increase of the pH. It caused of the electrostatic force of attractions between the indigo carmine dye and calcium hydroxide with mechanism reaction in Figure 3. Ramesh et al. also reported that adsorption Indigo carmine by calcium hydroxide was effective at pH 12 [46].

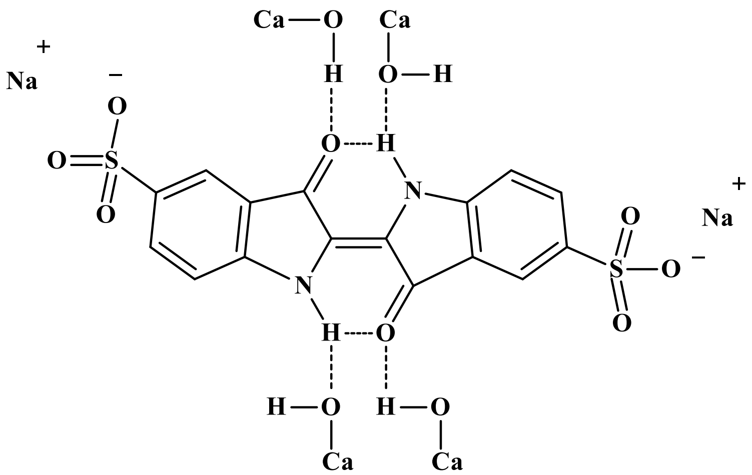


Figure 3. Mechanism of interaction of Indigo carmine and Calcium hydroxide

3.2. Effect of contact time

The adsorption capacity and % RE of Methylene Blue in Figure 4. was 30 minutes similar to Ngadi et al. in 30 minutes [43]. The optimum contact time of ES+M to adsorb Indigo carmine occurred in 15 minutes. It caused of the two ions from sulfonate group at Indigo carmine easier to bind with ES+M compare with Methylene blue that have one ion. Meanwhile, the longer of contact time after the equilibrium phase, the easer Indigo carmine to loose from ES+M. However, the decreased adsorption was not too significant.

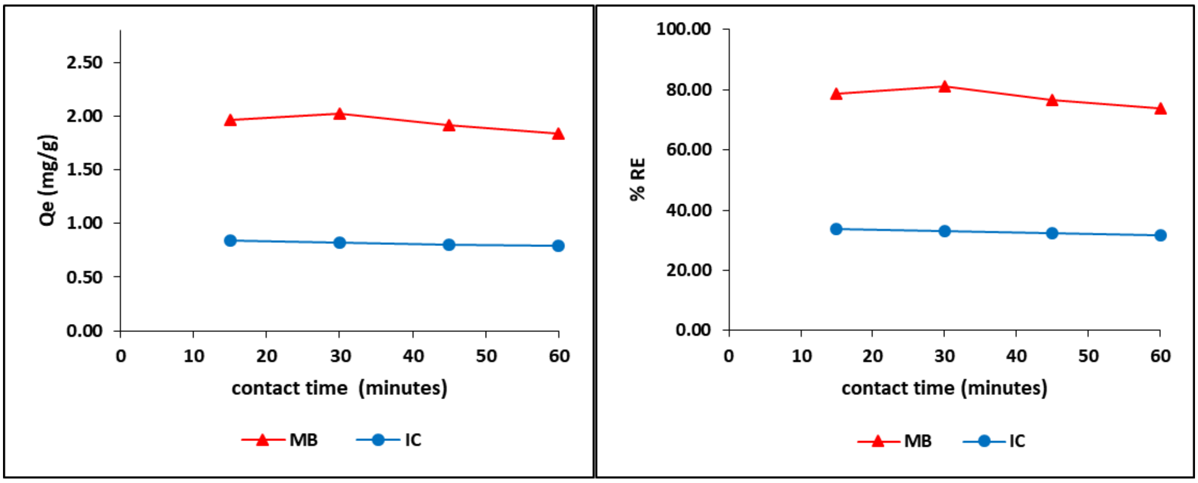


Figure 4. Effect of contact time to adsorption capacity and % RE to removal Methylene Blue and Indigo Carmine

3.3. Effect initial concentration of dye

The effect of the initial concentration of dyes was studied in the range of 10-50 mg/L. Increasing of Methylene Blue and Indigo Carmine concentration increased the adsorption capacity of ES+M until equilibrium and saturated. Figure 5 showed that the optimum adsorption capacity of Methylene Blue onto ES+M was 9.03 mg/L, and Indigo carmine was 5.79 mg/L. Its adsorption capacity high enough comparing with eggshell adsorb fluoride [32]. Meanwhile, the more top of initial concentration, the lower removal efficiency of methylene blue and indigo carmine. It occurred that higher concentration of dyes could be saturated of the active site of ES+M, so that removal efficiency both of them would be decreased.

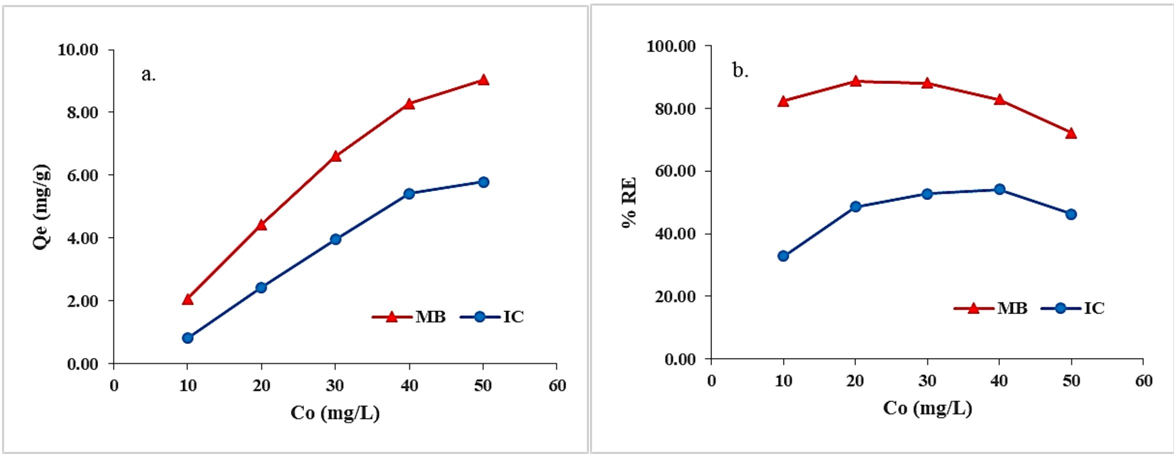


Figure 5. Effect of the initial concentration of dyes on adsorption capacity and % RE to removal Methylene Blue and Indigo Carmine by ES+M

3.4. Effect mass of adsorbent

In Figure 6 showed the greater mass of adsorbent, the higher the adsorption capacity and % RE Methylene Blue by ES+M. In this case the optimum mass of adsorption of Methylene Blue at 1 g of adsorbent. This phenomenon refers to increasing the surface area of ES+M and the availability of more adsorption sites to interact with the dye. Whereas Indigo Carmine, the more adsorbent mass does not always increase the adsorption capacity and % RE. The optimum mass of adsorbent to adsorb Indigo carmine is 0.5 g. If more than it, the interaction of Indigo Carmine and adsorbent will be released due to the collision between adsorbents, thereby disrupting the adsorption of indigo carmine.

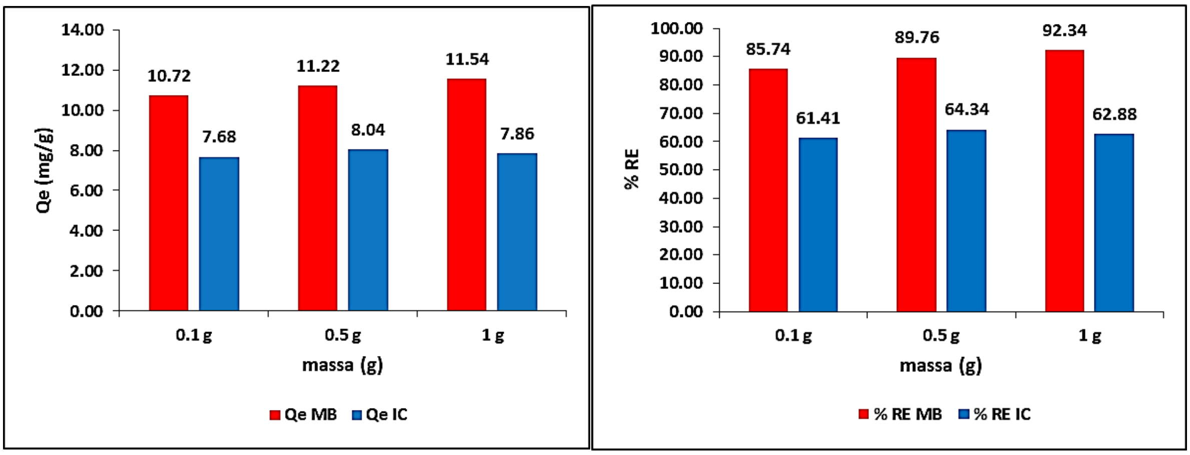


Figure 6. Effect mass of adsorbent to adsorption capacity and % RE to removal Methylene Blue and Indigo Carmine

3.5. FTIR Analysis

Characterization of ES+M to adsorb dyes shown the presence of $CaCO_3$ and proteins that have amino acids to binding with the dyes [47]. In Figure 7 could be seen that the shift of wavenumber of ES+M before and after adsorbing Methylene Blue and Indigo Carmine. There is a shift in the wavenumber such as at 675 - 1000 cm^{-1} the existence of -C=H bending, N-H at 867 cm^{-1}, C-C vibration at 710 cm^{-1} [48], S=O at 1075 cm^{-1} after adsorbing Methylene Blue and S=O at 1077 cm^{-1} after adsorbing Indigo Carmine, 1400 - 1600 cm^{-1} indicating the presence of the CH bending group C=C alkene. The presence of the C=O group at 1795 cm^{-1} and carbonate group 1400 cm^{-1}, C-H vibration organic layers with an amino acid in eggshell at 2978 cm^{-1}, S-H thiols at 2510 – 2600. The present of O-H from the carboxylic acid and H_2O as a result of the reaction of $CaCO_3$ with HNO_3 at 3670 and 3669 cm^{-1} [45, 49].

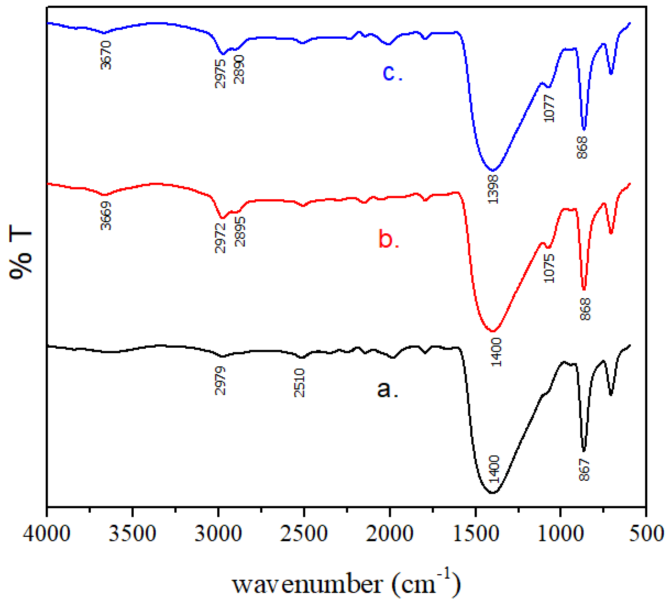


Figure 7. FTIR of ES+M before adsorbing MB and IC (a), after adsorbing MB (b), and after adsorbing IC (c)

3.6. XRF Analysis

Most of ES+M containing $CaCO_3$ from with 97.563 % and a small number of other minerals. In Table 1 could be seen that several elements in ES+M would be decreased and increased before and after adsorption. It means that occurred the interaction between ES+M and dyes. After adsorbing Methylene Blue as cationic dye increased the composition of Ag, P_2O_5 and after adsorbing Indigo Carmine as an anionic dye, the composition of S increased caused of Indigo Carmine consist S element in its structure. From data can be seen that the amount of the protein from membrane eggshell to interact with dyes only small. It also effects the adsorption capacity of ES+M in binding with the dyes.

Table 1. XRF analysis of ES+M before and after adsorb Methylene Blue and Indigo Carmine.

Element in compound	Before adsorption (%)	After adsorbing MB (%)	After adsorbing IC (%)
CaO	97.563	97.468	97.591
P_2O_5	0.943	0.978	0.81
SO_3	0.299	0.211	0.547
Ag	0.679	0.717	0.719
Al	0.244	0.27	0.219

4. Conclusions

In this study reported that the optimum adsorption MB and IC used ES+M occurred at pH 8 and 10, contact time 30 and 15 minutes, in 50 mg.L^{-1} and mass adsorbent 1 g and 0.5 g respectively.

For all treatment indicated that Methylene Blue as cationic dye higher adsorption capacity and higher % Removal efficiency than Indigo carmine as an anionic dye. The phenomenon caused of the presence of the membrane of the eggshell has more functional group such as hydroxyl, carboxyl and sulfhydryl to interacted with Methylene blue, whereas amine group and the $Ca(OH)_2$ in solution only interact with Indigo Carmine. However, we can conclude that ES+M could be used to remove Methylene Blue and Indigo Carmine as a low-cost adsorbent that easy to obtain, inexpensive, and the process was so fast.

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