Overview of the Impact of Different Concentration of Acid Solutions in the Production of Adsorbents from Shrimp Waste and the Capacity to Eliminate Textile Colours

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Abstract. Textile dyes are a combination of organic compounds, chromophores, and auxochromes as activators of chromophore work and binders between colors and fibers. In the industry, a large amount of waste of textile dye is produced daily. Before discharge into the environment, the waste must be processed so does it contain less amount of dyes. Removal of textile dye can be carried out using an adsorption process, one of which uses adsorbents derived from chitin and chitosan. This study aims to provide an overview of the impact of different concentrations of acid solutions used in the manufacture of adsorbents from shrimp waste and their capacity as textile dye adsorbents. The method used in this study is the article review method by comparing the results of the published articles. The gathered result showed that several dyes could be eliminated using chitin and chitosan, such as rhodamine B, methylene orange, methylene blue, direct black 38, procion red, methylene violet, reactive red, direct blue 78, indigo carmine dye. This overview might provide a platform to prepare better chitin-based adsorbent to eliminate dyes used in the industry.

1. Introduction
The textile industry is an industry that processes fiber into yarn, continues into fabrics, and finally becomes textiles [1]. The process that exists in the textile industry cannot be separated from the dyeing process that, unfortunately, uses harmful dyes [2]. Textile dyes are a combination of unsaturated organic compounds, chromophores, and auxochromes as activators of chromophore work and binders between colors and fibers [3].

The dye enters the water stream and becomes waste with the main issue, such as changing the water's color, which is harmful to aquatic organisms. The changes in the water color can be observed due to an increase in the chemical oxygen demand (COD) value, resulting in an imbalance in the environment. An increase in the COD value causes the aquatic environment to lack oxygen and disrupt the water biota. There are three types of waste treatment methods, such as biological, chemical treatment (oxidative degradation, use of allophane soil added with NaOH activator, chemical oxidation, UV light with the addition of H₂O₂), and physical (adsorption and coagulation). Among these three, adsorption is considered the best method to eliminate the textile dye from the water stream [4].

Chitosan is one of the materials used as an adsorbent to remove textile dyes from the water stream for several reasons. First, it is abundant in nature [5]. Second, chitosan has good characteristics, such
as biodegradation and biocompatibility, that make chitosan an environmentally friendly adsorbent. Thus, these characteristics make chitosan as good material to be used as an adsorbent. The presence of amino (NH₂) and hydroxyl (-OH) groups is responsible for chitosan adsorption performance. In this context, these two groups play a role in forming coordination bonds with metal ions [6]. Based on this background, this study aims to provide an overview of the impact of different concentrations of acid solutions used in the manufacture of adsorbents from shrimp waste and their capacity as textile dye adsorbents.

2. Material and methods

Methods used in this study was the article review by a systematic investigation. A systematic review is a way of collecting, critically evaluating, integrating, and presenting the primary research data obtained to present more comprehensive and balanced facts [7].

3. Result and discussion

3.1. Results

Several acids have been used to prepare adsorbent from shrimp, such as CH₃COOH and HCl. Also, chitin's performance as adsorbent not only depends on the type of acid but also its concentration. For example, the CH₃COOH used for a 1% concentration produces a maximum adsorption value ranging from 2.74 - 341.43, as can be seen in Table 1. While at a concentration of 2%, the maximum adsorption value ranges from 12.5 - 40.69, as shown in Table 2. When compared with a 1% concentration, the maximum adsorption yield at a concentration of 2% has a lower adsorption value. The adsorbent in Table 2 shows the significant value of procion red with a maximum adsorption value of 40.69. The chitosan has been modified, namely microcapsules of chitosan gel beads crosslinked with ethylene glycol diglycidyl ether (PSF-EGDE-CTS) were prepared to improve adsorption capacity and mechanical stability of chitosan at acidic condition [8].

Based on the type of textile dye adsorbent, maximum effective adsorption on methylene blue dyes. The elementary analysis of all chitosans, the viscosity molecular weight, and their weight losses are calculated by mass differences between neat and oxidized chitosans. The degree of oxidation dissolved oxygen (DO) and aldehyde content [9]. The chitosan used was mixed with zeolite nanocomposite in the methylene blue study by Javad and Vahid (2019). The results show that the synthesized bio-nano composite adsorbent is not disposable, and they still show the ability to dye adsorption after being used in successive adsorption cycles [10].

| Table 1. The Results of Acid Concentration 1% |
|---------------------------------------------|
| Type of Acid | Type of Dye           | Adsorption Max. (mg/g) | References       |
| CH₃COOH     | Methylene Blue        | 341.43                 | Orietta et al., 2018 |
| CH₃COOH     | Methylene Orange      | 52.5                   | Orietta et al., 2018 |
| CH₃COOH     | Methylene Blue        | 2.74                   | Javad and Vahid, 2019 |
| CH₃COOH     | Acid Blue 113         | 255.5                  | Rodrigo et al., 2020 |

| Table 2. The Results of Acid Concentration 2% |
|---------------------------------------------|
| Type of Acid | Type of Dye           | Adsorption Max. (mg/g) | References       |
| CH₃COOH     | Procion Red           | 40.69                  | Triana et al., 2012 |
| CH₃COOH     | Acid Orange 7         | 26.37                  | Corneliu et al., 2018 |
| CH₃COOH     | Crystal Violet        | 12.5                   | H. Jayasantha et al., 2016 |
| CH₃COOH     | Direct Blue 78        | 12.30                  | Ainoa et al., 2019 |

Another thing that affects the maximum adsorption is the optimum time and optimum pH. The application of the optimum conditions of chitin and chitosan showed a higher absorption rate than the standard solution [5]. The determination of the maximum adsorption was carried out using the Freundlich adsorption isotherm model. Freundlich's isotherm model explains that the adsorption process on the surface is heterogeneous, not all surfaces have adsorption power [2].
3.2. Discussion

Making chitosan as an adsorbent can be done in various ways, such as being formed in the form of powder, gel, or beads. The aim is to increase the adsorption ability of chitosan. Several factors can influence absorption, such as an acid used in the adsorbent preparation, contact time, and pH. The adsorption test on procion red color was carried out under optimum pH and optimum contact time [5].

One of the variables that can determine the amount of adsorbate that can be absorbed by the adsorbent is the contact time between the adsorbent and the adsorbate. One example of the effect of chitin and chitosan contact time is the absorption of procion red. The absorption of chitin to procion red continued to increase from 0 minutes contact time to 90 minutes contact time then decreased. At 90 minutes, contact time and the most considerable amount of procion absorbed by chitin was 2,317 mg, with a significant absorption rate of 92.66%. The optimum contact time was 150 minutes in chitosan, with the amount of absorbed procion of 1.986 mg [5].

The effect of pH of the procion red solution showed that the most considerable absorption of chitin was 2.188 mg at pH 8, with absorption effectiveness of 87.52%. Chitin absorbs the procion red at an alkaline pH. It is due to the N atom in the acetamide group in chitin is delocalized to the O atom or divides the negative charge into the O atom, which causes chitin to be more alkaline than chitosan. At pH 6, chitosan has an absorption capacity of 2.20 mg with absorption effectiveness of 88.02%. It is because the N atom in chitosan in the amine group is not delocalized, which causes the atom to be more electronegative than the N atom in chitin [5].

The use of different acids and in different concentrations shows an effect on the adsorption yield. This shows that it is essential to determine the type of acid used to absorb the type of textile dye [11]. Based on Tables 1 and 2, the different textile dyes show a significant difference in the adsorption results. The use of CH₃COOH is more appropriate for blue dyes such as methylene blue and acid blue 13.

The characterization that can be done to determine the effectiveness of absorption is Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). Based on studies from Triana et al. (2012) showed that the uptake of both chitosan and chitosan gel (CTS) was the same, only the 3400 cm⁻¹ uptake experienced a widening, which is thought to be due to the presence of acid trapped in the CTS, but could be lost in the next process. The spectra indicate this on the subsequent crosslink results that are not wide. Figure 1 shows a peak in the 1650 cm⁻¹ area, which shows the N-H bending in -NH₂ of CTS is weakening because in CTS N-H is in the form of NH³⁺, which is supported by increased absorption in the 1450 cm⁻¹ region.

![Figure 1. Chitosan and CTS IR Spectra (Triana et al., 2012).](image_url)
SEM results are shown in Figure 3. Figure 3 (a) shows that there is a kind of wall covering the core material. It is evident in Figure 5 (b) after experiencing a 500x magnification. Based on Figure 3 (b), it can be calculated the thickness of the overlying wall, which is about 25 μm. The presence of this layered wall indicates that the PSF-EGDE-CTS has been formed [8].

![Figure 2. SEM of EDGE-CTS](image)

![Figure 3. SEM of PDF-EDGE-CTS at different magnifications (Triana et al., 2012).](image)

Based on the study regarding the optimum conditions' role, it is concluded that the optimum pH and time affect the absorption capacity of the adsorbent. Meanwhile, FTIR characterization shows that the N-H bending in -NH$_2$ of CTS is weakening because in CTS N-H is in the form of NH$^+$ which is supported by increased absorption. Morphological characterization shows that not all adsorbent surfaces can absorb dyes.

4. Conclusion

Herein, we report the impact of acid and its concentration in chitosan manufacturing with cationic removal capacity and anionic dye from a water medium. The use of weak acids serves to activate the active site on chitosan, and the difference in concentration affects the adsorption value. The obtained result can be a guideline to select appropriate acid to prepare chitin and chitosan-based adsorbent.

5. References

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