Effect of pH CaCl$_2$ solution on graphene oxide encapsulated alginate (GO-AL) for removing methylene blue dyes

Syahna Febrianastuti$^{1*}$, Ganjar Fadillah$^{2*}$, Elsa Ninda Karlinda Putri$^{1}$, Uly Wulan Apriani, Sayekti Wahyuningsih$^{1}$

$^1$Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret, Indonesia
$^2$Department of Chemical Analysis, Faculty of Mathematics and Natural Sciences, Universitas Islam Indonesia, Indonesia

* Corresponding author: a syahnafebr97@gmail.com, b ganjar.fadillah@uii.ac.id

Abstract. The industry waste pollution is unseparated issue in era of globalization. It’s caused in industry didn’t apply Green Chemistry principle in their production process, so that they still use hazardous chemicals that can pollute the environment, one of them is a methylene blue dye (MB) waste. The remove dyes by the combination technique of electrochemistry and adsorption appeared to be an efficient and simple. This study aims to determine the pH optimum characterization of graphene oxide-alginate composite to degradation of methylene blue in liquid waste. Graphene oxide-alginate was prepared by encapsulation method at 2% CaCl$_2$ (b/v) solution. The material was characterized by X-Ray Diffraction (XRD) and Fourier Transform Infra-Red (FTIR). The XRD characterization results indicated a high 2θ peak at 10.7703 and increased d-spacing of graphite to graphene oxide. The FTIR spectra of graphene oxide-alginate shows the presence of combined adsorption of graphene oxide and alginate. This indicates that the composite GO-AL was successful synthesized. Calcium chloride solubility varies with the changes in the pH of the solution and so will be the cross-linking ability of alginate with calcium ions. The optimum value of GO-AL composite with Eco-Bio method on MB degradation was obtained in CaCl$_2$ solution pH 3 and gave MB degradation of 93.78%

Keywords: Graphene oxide, Alginate, Methylene blue, Bioadsorption-electrochemical

1. Introduction
Industrial growth is one of the rapid factors in the global era today. However, rapid industrial growth has led to the environmental pollution. One of pollution from industrial process is dye contamination. Dye contamination can be produced from leather factories, metal plating plants, food companies, paint industries, pulp, and textile industry. One of the most widely used dyes in the industry is methylene blue (MB). Methylene blue (MB) is widely used because MB is a basic dye and has good solubility. But in the colouring process, the amount MB adsorb is only about 5% while the remaining 95% released into the environment and causing pollution of water [1]. This compound has complex aromatic molecular structure so the compound is stable and difficult to biodegradation in nature and dangerous for the environment [2, 3]. Besides, the contamination of MB dyes is dangerous to the environment, the dye contaminants are also dangerous to human life. It can cause irritation of the gastrointestinal tract if ingested, causing cyanosis if inhaled, and irritation of the skin if touched by skin [4]. Therefore, it is necessary to remove the MB dyes from the industrial wastes.
Several research such as filtration, reverse osmosis, precipitation, membrane separation, and sedimentation to remove methylene blue dye (MB) in water has been done. But the conventional techniques are reportedly expensive and less effective [5]. One of the most successful, efficient, and effective wastewater removal techniques to decrease the concentration of methylene blue dye (MB) is bioadsorption-electrochemical combined (Eco-Bio) technique on waste. Nowadays the development of research on the Eco-Bio technique is using materials such as graphene oxide. Graphene oxide (GO) express good adsorption property it has a two-dimensional layer structure, large surface area, large pore volume, and presence of functional groups on its surface [6]. Nevertheless, GO has low physical resistance so that limit its application in wastewater treatment. To overcome these disadvantages, another material must be added to GO [1]. Alginate is recent interesting material that can be developed as a composite [7]. Its largely source in Indonesia and potential of alginate as an adsorbent material make this material become an interesting research. Added alginate can protect graphene oxide from environmental damage so that the physical endurance of the adsorbent material can be increased [8]. In this work focuses on the utilization of graphene oxide-alginate (GO-AL) composites in MB degrades with bioadsorption-electrochemical adsorption (Eco-Bio). Utilization of graphene oxide-alginate (GO-AL) composite is expected to decrease environmental pollution MB dye concentration effectively and efficiently.

2. Method

2.1. Materials

Materials used in this study include graphite, alginate, 1M NaOH, 1M HCl, 2M HNO₃, CaCl₂ 2%, standard solution of methylene blue 1000 ppm, and distilled water. While the instrument used include pH meters, thermometers, shakers, balance sheets, UV-Vis spectrophotometer, and a set of glass instrument.

2.2. Experimental section

2.2.1. Synthesis and Characterizations Graphene Oxide-Alginate. The method used to synthesize graphite oxide in this study is modification of Hummer Method, 2 g graphite dissolved in 150 ml 98% H₂SO₄ and stirred in ice bath to keep the temperature around 0-20°C for 1 hour. Then add 4 g of NaNO₃ and 8 g of KMnO₄ gradually with 5 min intervals in each addition then stirred for 2 hours. After 24 hours, stirring is switched off and H₂O₂ added to the solution. The solution of graphite oxide then washed with distilled water removed dissolved ions. The solid then neutralized to pH 5 (distilled water pH). Graphite oxide solution is in sonic bath for 30 minutes, then settled to settle. Then washed 2 times with 100 mL distilled water. The precipitate obtained in freeze drying and will be obtained by brown graphene oxide powder [1]. 0.2 g of graphene oxide and 0.2 g of alginate were dissolved in 10 mL of distilled water and stirred to homogeneous solution. The mixed solution of graphene oxide-alginate was encapsulated in 100 mL CaCl₂ 2% with pH variations 1, 3, 5, and 7 to form GO-AL composite (Graphene Oxide-Alginate). The GO-AL composite (Graphene Oxide-Alginate) then washed several times with distilled water and oven at 60°C for 8 hours. Graphene oxide, alginate, and Graphene Oxide-Alginate composites then characterized using FTIR and XRD instruments.

2.2.2. Combination Technique of Bioadsorption-Electrochemical on Synthetic Methylene Blue Dye. The combination of bioadsorption-electrochemical technique is combination of adsorption and electrochemical technique to decrease the concentration of methylene blue dye. A synthetic solution of methylene blue dye is prepared into a 10 mL beaker. Then the solution is added in the electrochemical. 0.1 g of graphene oxide-alginate composite with pH variation of CaCl₂ solution is added into the electrochemical and stirred in cell system. The combination of bioadsorption-electrochemical technique on synthetic methylene blue dye was carried out with variations of pH of CaCl₂ solution. The solution then filtered, the remain concentration of methylene blue was measured using a UV-Vis, at wavelengths of 300-750 nm. The result were converted into blue methylene dyestuff concentrations using a
calibration curve. Then calculated % degradation of residual concentration of MB and initial concentration of MB.

3. Result and Discussion
The synthesized graphene oxide-alginate (GO-AL) composite is characterized using X-Ray Diffraction (XRD) and FTIR (Fourier Transform Infra-Red). XRD test aims to determine the changes that occur because of the treatment given to the sample. The XRD test was performed using x-ray diffraction at angle of 2θ=5°-70° and λ Cu-Kα 1.54060 Å. The results of X-Ray Diffraction (XRD) analysis for graphite and graphene oxide are depicted in the form of diffraction patterns which can be seen in Fig. 1.

![Graphene Oxide and Graphite XRD Analysis](image)

Fig. 1 show that graphite give a high 2θ peak at 26.4237 d-spacing 3.3497 Å while on graphene oxide shows a high 2θ peak at 10.7703 d-spacing 8.214 Å [9]. This shows that graphite successfully oxidized. In addition, the increased d-spacing value of graphite to graphene oxide is due to the addition of water and oxygen molecules between the layers in graphene oxide [10]. The Fourier Transform Infra-Red (FTIR) qualitative analysis is performed to identify the presence of major functional groups within the graphite and graphene oxide structure show seen in Fig. 2.

Fig. 2 show in graphite and graphene oxide FTIR results show a stretching OH bond vibration at 3442 cm⁻¹ wavenumbers for graphite and 3418 cm⁻¹ for graphene oxide. The absorption of CH stretching functional groups is also present in graphite on wavenumbers 2879 cm⁻¹ and graphene oxide at 2890 cm⁻¹ wave numbers [1]. The other functional group bonds between graphite and graphene oxides are aromatic C=C bond at wavenumbers 1670 cm⁻¹ in graphene oxide and 1631 cm⁻¹ in graphite. C-H group absorption is getting stronger in graphene oxide due to the shifting vibration at wavenumber 1218 cm⁻¹ identified as functional group of C-OH which means oxidation process from graphite to graphene oxide goes well. It shows that graphene oxide was successfully synthesized from graphite by modified Hummer method where the exfoliation process was assisted by ultrasonic waves that made the intensity of absorption in graphene oxide stronger [11].
Figure 2. Analysis result on FTIR graphene and graphene oxide.

Fig. 3 shows the presence of group combined absorption of graphene oxide and alginate in the GO-AL composite. In addition, there is no shift in the graphene oxide waves in the FTIR GO-AL spectra. This suggests that in composite formation on the main ingredients graphene oxide and alginate can increase functional groups and increase degradation of MB dye.

Figure 3. Analysis result on FTIR graphene oxide, alginate, and graphene oxide-alginate.

Fig. 4 show in FTIR analysis result of composite graphene oxide alginate with pH various of CaCl₂ solution. Calcium chloride solubility varies with the changes in the pH of the solution and so will be the
cross-linking ability of alginate with calcium ions. With the variation in pH, the concentration of available calcium ion would be different too. Therefore, a formation of an intermolecular network of alginate molecules in the presence of calcium ions could be different with different pH. Similarly, \(-\text{COO}^–\) and \(-\text{OH}\) groups along the alginate chain can attain different charge densities depending on the pH. Alginate can induce the formation of hydrogels and acid gels in aqueous solution only when a pH value is less than the pKa value of uronic acid residues of alginate. Encapsulation efficiency of alginate has been attributed to the degree of cross-linking. The mechanical properties of formed hydrogels are affected as well and subsequently, there can be distinct differences in cell growth, differentiation, and tissue formation [12].

The pH conditions of CaCl$_2$ solution in the encapsulation process may affect the MB degradation process. This is due to the influence of the amount of H$^+$ ions from CaCl$_2$ solution which can affect the dyestuff degradation process of MB. Based on Fig. 5 the pH of CaCl$_2$ for MB degradation at pH 3 with MB degradation value of 93.79%. This is because if the pH is too low (pH < 3) CaCl$_2$ solution will increase binding to H$^+$ in the active site on the composite during the encapsulation process and caused decrease MB degradation process. While, at high pH (pH > 3) CaCl$_2$ solution condition causes precipitate of Ca(OH)$_2$ in MB degradation so the process is not maximal [1].
4. Conclusion
Calcium chloride solubility varies with the changes in the pH of the solution and so will be the cross-linking ability of alginate with calcium ions. The biosorbtent performance test on the degradation of methylene blue substances showed that graphene oxide-alginate composites (GO-AL) with biosorption-electrochemical (Eco-Bio) technique had 93.79% degradation of under optimum conditions of pH CaCl$_2$ solution 3 and voltage cell at 4.5 V during contact time 30 min.

Acknowledgement
The acknowledgement is dedicated to the RISTEKDIKTI (Ministry of Research, Technology and Higher Education of the Republic of Indonesia) which has provided funding of this research through Research Student Creativity Program (PKM-PE) 2018.

References
[1] Li Y, Du Q, Liu T, Sun J, Wang Y, Wu S, Wang Z, Xia Y and Xia L 2013 Methylene blue adsorption on graphene oxide/calcium alginate composites Carbohydr. Polym. 95 1 501-7
[2] Kornaros M and Lyberatos G 2006 Biological treatment of wastewaters from a dye manufacturing company using a trickling filter J. Hazard. Mater. 136 1 95-102
[3] Chen M, Chen Y and Diao G 2010 Adsorption kinetics and thermodynamics of methylene blue onto p-tert-butyl-calix [4, 6, 8] arene-bonded silica gel J. Chem. Eng. Data 55 11 5109-16
[4] Sheng J, Xie Y and Zhou Y 2009 Adsorption of methylene blue from aqueous solution on pyrophyllite Appl. Clay Sci. 46 4 422-4
[5] Popuri S R, Vijaya Y, Boddu V M and Abburi K 2009 Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads Bioresour. Technol. 100 1 194-9
[6] Kemp K C, Seema H, Saleh M, Le N H, Mahesh K, Chandra V and Kim K S 2013 Environmental applications using graphene composites: water remediation and gas adsorption Nanoscale 5 8 3149-71
[7] Fadillah G, Putri E, Febrianaustiti S, Maylinda E and Purnawan C 2018 Adsorption of Fe Ions from Aqueous Solution Using α-Keratin-Coated Alginate Biosorbent Int. J. Environ. Sci. Dev. 9 82-5
[8] Fadillah G, Putri E, Febrianaustiti S, Munawaroh H, Purnawan C and Wahyuningsih S 2018 α-keratin/Alginate Biosorbent for Removal of Methylene Blue on Aqueous Solution in a Batch System IOP Conf. Ser. Mater. Sci. Eng. 333 1 012052
[9] Shahriary L and Athawale A A 2014 Graphene oxide synthesized by using modified hummers
approach Int. J. Renew. Energy Environ. Eng. 2 01 58-63

[10] Castro K, Oliveira S, Curti R, Araújo J, Sassi L, Almeida C, Ferreira E, Archambo B, Cabral M and Kuznetsov A 2018 Electrochemical Response of Glassy Carbon Electrodes Modified using Graphene Sheets of Different Sizes Int. J. Electrochem. Sci. 13 1 71-87

[11] Ilhami M R and Susanti D 2014 Pengaruh Massa Zn Dan Temperatur Hydrotermal Terhadap Struktur Dan Sifat Elektrik Material Graphene Jurnal Teknik ITS 3 2 F185-F90

[12] Zhang Z, Zhang R, Zou L and McClements D J 2016 Protein encapsulation in alginate hydrogel beads: Effect of pH on microgel stability, protein retention and protein release Food Hydrocoll. 58 308-15