Journal of Environment and Earth Science
ISSN 2224-3216 (Paper) ISSN 2225-0948 (Online)
Vol.12, No.4, 2022

Study of Methylene Blue Adsorption with Silver Chloride Coagulants from Photographic Film Waste

Gunawan Gunawan*, Abdul Haris, Ela Uswatun, Sarahtrinita Glikeria Like M., Roni Adi Wijaya
Department of Chemistry, Diponegoro University, Tembalang Campus, Semarang, Indonesia, 50275

Abstract
Methylene blue is a dye that is widely used in industry. These dyes are hazardous and can pose a health risk if discharged directly into the environment. On the other hand, photographic waste containing Ag metal can be used as an AgCl coagulant. This study aims to determine the effectiveness of AgCl coagulant in the adsorption of methylene blue dye. Silver chloride was synthesized from photographic waste using the coagulation precipitation method. The results of the analysis showed that the AgCl coagulant was able to take 88.2% methylene blue dye at neutral pH 7 for 15 min with a stirring speed of 300 rpm for 10 mg/L methylene blue sample. The adsorption capacity of AgCl was 10.9 mg. g^{-1} and the adsorption kinetics model was pseudo-order 1 with an R^2 value of 0.9318.
Keywords: AgCl, coagulant, methylene blue
DOI: 10.7176/JEES/12-4-06
Publication date: April 30th 2022

1. Introduction

Recent information, more than 100 thousand commercial dye products have been discharged into the aquatic environment (Ghada *et al.* 2018), (Mosbah *et al*. 2019). The textile industry is the biggest contributor to water pollution followed by the paint, paper, leather, and printing industries (Vanitha *et al.* 2018), (Ponnusamy, *et al.* 2017). Disposal of dyes into the environment is harmful to the life of aquatic ecosystems and has a negative impact on human health. The risk of contamination of dyes in water for human health such as the emergence of skin diseases when in contact with polluted water and indigestion from drinking water can lead to a potential risk of cancer (Mustafa *et al.* 2014), (Vakili *et al.* 2014).

Methylene blue is a dye that is widely used in industry as a dye for paper, cotton, silk, wool, and other hair dye. Methylene blue is reported to cause several risks to human health, such as eye, respiratory, digestive, and mental disorders (Rafatullah *et al.* 2010), (Yuan, 2008). The removal of methylene blue from industrial effluents has been investigated using various methods such as enzymatic processes, photodegradation reactions, electrochemical discharges, chemical coagulation, membrane filtration, and physical adsorption methods (Rafatullah *et al.* 2010). Adsorption is the most studied method for methylene blue removal with the number of publications showing a more than twofold increase in the last 10 years. The adsorption method follows a simple procedure with the use of an inexpensive and abundant adsorbent and can maintain the high efficiency of methylene blue (MB) removal. The adsorption process also prevents the formation of secondary pollutants that can occur through the oxidation or degradation of MB blue (Vanitha *et al.* 2018), (Salleh, 2011).

Silver is a precious metal used in photo films because of its photosensitive properties. Film development causes photographic waste containing Ag in fixer solution and rinses water to be 1,000-10,000 and 50-200 mg/L in the form of the anionic thiosulfate complex $[Ag(S_2O_3)_2]_3^-$. Silver is a dangerous substance so it must be *recovered* completely, both from an economic point of view and for environmental reasons (Songkroah *et al.* 2004). Ag-thiosulfate is unstable and undergoes decomposition with the formation of colloidal sulfur and sulfur oxides according to the following reaction equation 1 (Songkroah *et al.* 2004):

$$2H^+ + Ag(S_2O_3)_2^{3-} \rightarrow Ag^+ + [HS_2O_3^-] \rightarrow Ag^+ + HSO_3^- + S \rightarrow Ag^+ + SO_2 + S + H_2O \quad (1)$$

Furthermore, the silver ions are reacted with chloride ions to form silver chloride precipitate which is used as a coagulant for adsorption of methylene blue in water. In this study, the use of silver from photographic waste was carried out for the preparation of AgCl coagulant as an adsorbent for methylene blue removal. The effect of variables, such as pH, contact time, stirring speed, chloride ion, and AgCl dose will be studied. This study contributes to an in-depth study of the preparation of AgCl coagulant and its characterization using XRD and FTIR. Furthermore, AgCl formed can be applied to take methylene blue dye.

2. Methods

2.1. Material and equipment

The materials used in this study included $AgNO_3$ pa (Merck), methylene blue, NaCl pa (Merck), HCl pa (Merck), HNO_3 pa (Merck), NH_3 pa (Merck), and NaOH pa (Merck), photographic film solution waste.

The equipment used in this study were a desiccator, beaker (Pyrex), Erlenmeyer (Herma), volumetric flask (Herma), dropper (Herma), funnel (Herma), watch glass (Herma), vial (Herma), burette (Herma), stands and clamps, oven (Kirin), analytical balance (Kern), filter paper (Whatman no. 42), UV-Vis spectrophotometer

(Genesys 10 S UV-Vis), X-Ray Diffractometers (XRD) (Shimadzu XRD-6100/7000), FTIR spectrophotometer, Spectrophotometer Atomic Absorption (Perkin Elmer PE 3110).

2.2. Recovery $AgNO_3$ from photographic film solution waste

Solution of 100 mL photographic film solution waste was reacted with 10 mL concentrated HNO_3, then the solution was heated until boiling and the process was stopped after the solution was dried 950 mg. The silver content was measured by AAS and found the percentage around 92%. For preparation of $AgNO_3$ solution we used dried $AgNO_3$ above by dissolving in aqua-DM.

2.3. Synthesis of silver chloride

Silver nitrate ($AgNO_3$) and sodium chloride (NaCl) are reacted to produce an AgCl precipitate. Furthermore, the precipitate obtained is washed to remove impurities. For photographic waste, nitric acid (HNO_3) is added to obtain silver ions (Ag^+) and then reacted with sodium chloride to form an AgCl precipitate. Variations in nitric acid affect the crystal size of AgCl. To obtain AgCl nanocrystals, a procedure for adding already formed ammonia was taken, and then nitric acid was added in a small concentration so that the crystals did not grow large.

2.4. Methylene blue adsorption with silver chloride coagulant

AgCl crystals were added in a silver ion beaker glass and the methylene blue solution was added and stirred. After some time, the solution was filtered, and the filtrate obtained was determined for the residual content of methylene blue using a UV-Vis spectrophotometer. The added silver was varied to see the effect of taking methylene blue. Besides that, try adding chloride ions instead of silver ions, also trying to vary the pH of the solution.

2.4.1 Effect of $AgNO_3$ in methylene blue uptake

Methylene blue (MB) 10 mg/L solution was contacted with AgCl prepared from 5 mL of NaCl 0.1M and varied concentration of $AgNO_3$ 0.1 M, namely 4.0; 4.5; 5.0; 5.5 and 6 mL, respectively, the final volume was 25 mL. Then the solution was stirred at 200 rpm for 10 min and filtered to get the filtrate of non-adsorbed MB. The filtrate was measured its concentration using UV-Vis spectrophotometer.

2.4.2 Effect of AgCl dosage

Each volume of 1.2; 2.2; 3.2; 4.2; 5.2; 6.2; 7.2 mL $AgNO_3$ 0.1M was reacted with 1; 2; 3; 4; 5; 6; 7 mL NaCl 0.1M, respectively, then each of which was added with 10 mg/L MB. The final volumes were made 25 mL. Each solution was stirred at 200 rpm for 10 min and filtered to get the filtrate of non-adsorbed MB. The filtrate was measured its concentration using UV-Vis spectrophotometer.

2.4.3 Effect of contact time and adsorption kinetics

In 25 mL volumetric flask was added with 5.2 mL $AgNO_3$ 0.1M, 5.0 mL NaCl 0.1M and MB and the volume was made 15 mL to get 10 mg/mL MB. The solution was stirred at 200 rpm for certain times (5, 10, 15, 20, 25, 30 min) and filtered to get the filtrate of non-adsorbed MB. The filtrate was measured its concentration using UV-Vis spectrophotometer.

2.4.4 Effect of stirring speed

In 25 mL volumetric flask was added with 5.2 mL $AgNO_3$ 0.1M, 5.0 mL NaCl 0.1M and MB and the volume was made 15 mL to get 10 mg/mL MB. The solution was stirred at certain speed (200, 300, 400 rpm) for 10 min and filtered to get the filtrate of non-adsorbed MB. The filtrate was measured its concentration using UV-Vis spectrophotometer.

2.4.5 Effect of pH

In 25 mL volumetric flask was added with 5.2 mL $AgNO_3$ 0.1M, 5.0 mL NaCl 0.1M and MB and the volume was made 15 mL to get 10 mg/mL MB at certain pH (3, 5, 7, 8, 9). The solution was stirred at 200 rpm for 10 min and filtered to get the filtrate of non-adsorbed MB. The filtrate was measured its concentration using UV-Vis spectrophotometer.

2.5. Testing and characterization

The dye concentration test after undergoing treatment was carried out using a UV-Vis spectrophotometer. AgCl characterization was carried out with X-Ray Diffractometers (XRD) and FTIR spectrophotometer.

3. Results and Discussion

3.1. Synthesis of silver chloride

The synthesis of silver chloride was carried out by reacting NaCl and $AgNO_3$ in equilibrium. The synthesis was carried out to determine the effect of pH on the resulting AgCl precipitate. The pH adjustment was carried out on the solution from pH 1 to pH 10 using HCl or NaOH.

In Figure 1, the curve of the effect of pH on the weight of AgCl produced shows that the precipitate produced at pH 7 has the same theoretical value as AgCl precipitate. AgCl weight decreased at pH > 7 due to the re-formation of NaCl which will dissolve in water.

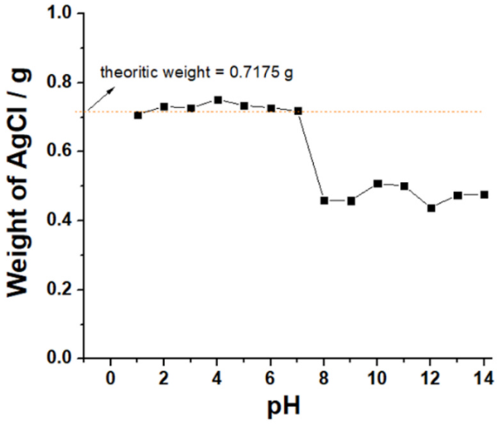


Figure 1. AgCl weight relationship curve to pH

3.2. Methylene blue adsorption with silver chloride coagulant

3.2.1 Effect of $AgNO_3$ in methylene blue uptake

The presence of other ions in the solution can affect the adsorption of methylene blue dye. Figure 2 showed the effect of the volume of $AgNO_3$ on the uptake of methylene blue with different initial volume variations from 4 to 6 mL. The absorption of methylene blue increases with the increase in the volume of $AgNO_3$ in the solution. This is because the NO_3^- ion in the solution causes the surface of the active site of the coagulant to be more negative so that methylene blue (cationic dye) is adsorbed there is competition. A large increase in methylene blue absorption occurs at a variation of 6 mL $AgNO_3$ which is 80.7%.

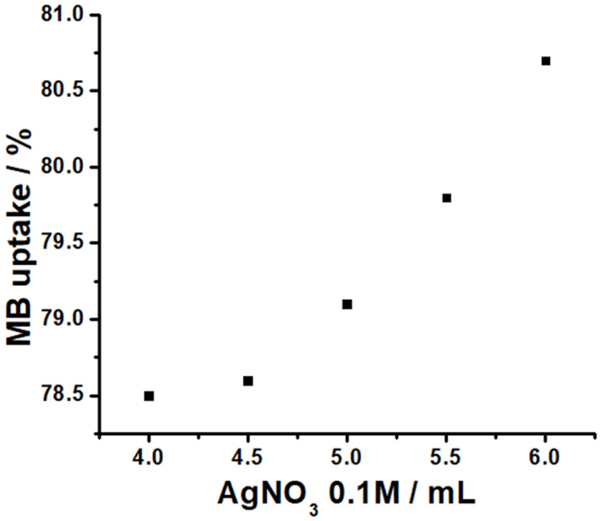
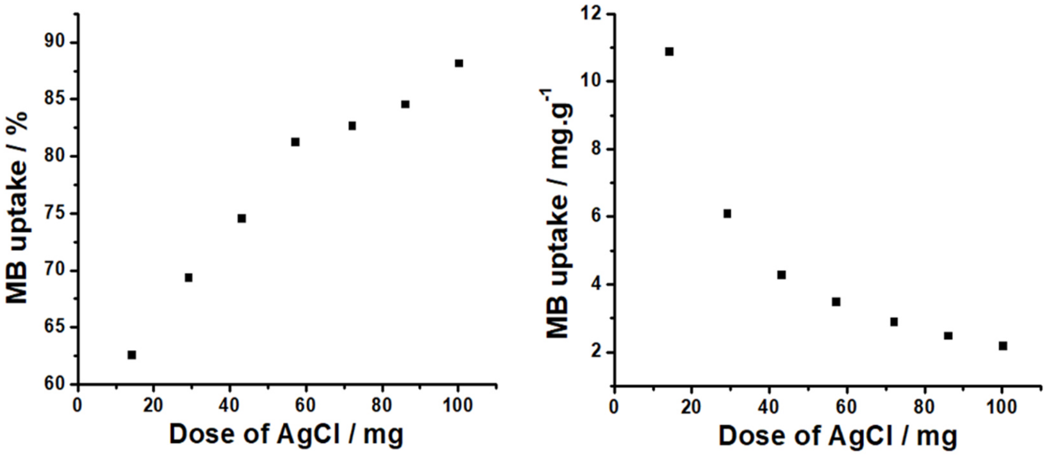


Figure 2. Relationship between MB adsorption and $AgNO_3$ volume.

3.2.2 Effect of AgCl dosage

Variations in the dose of AgCl have an important role in the adsorption process because they will produce different absorption efficiencies of methylene blue. The doses of AgCl that were varied were 14, 29, 43, 57, 72, 86, and 100 mg with a contact time of 15 minutes and at an optimum pH of 7.



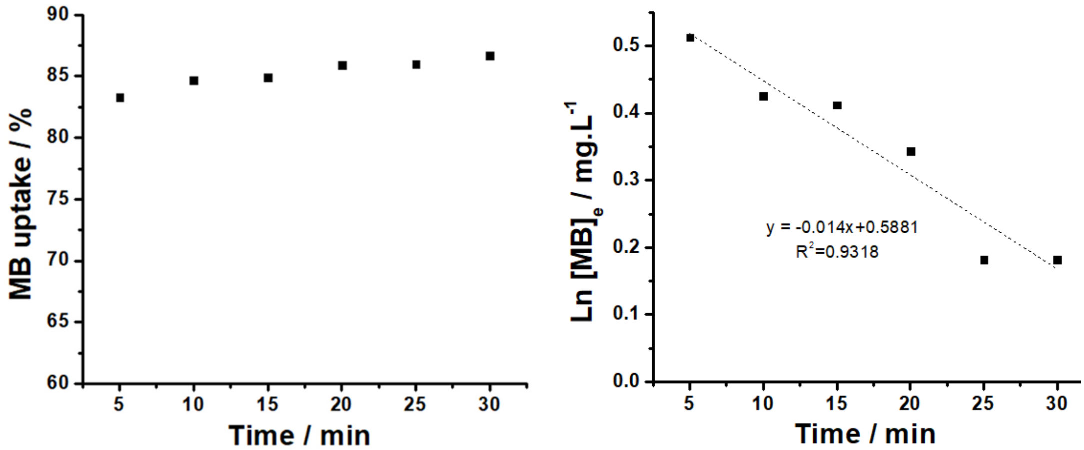
(a) (b)

Figure 3. Graph of relationship between AgCl dose and (a) % MB uptake (b) mg.g $^{-1}$ MB uptake.

Figure 3 showed that the percentage of methylene blue absorption increased with increasing adsorbent dose (Sakr *et al.* 2020). The absorption of 88.2% methylene blue occurred at a high dose of AgCl ie 100 mg. This is because compared to low doses of adsorbent, high doses of AgCl have a larger surface area so that the active side of the adsorbent on the absorption of methylene blue at a constant concentration will be more (He *et al.* 2019). Increasing the dose of AgCl was also accompanied by a decrease in adsorption capacity from 10.9 to 2.2 mg. g $^{-1}$ because high doses of AgCl caused agglomeration of AgCl particles to increase (Eltaweil *et al.* 2020).

3.2.3 Effect of contact time and adsorption kinetics

The effect of contact time and adsorption kinetics on methylene blue uptake was observed at different time intervals from 5 to 30 minutes. The effect of contact time is presented in figure 4 (a) which shows a slow and insignificant increase in the absorption of methylene blue with increasing adsorption time by AgCl coagulant. This is due to the binding process of methylene blue on the inside of the active site of AgCl particles and the adsorption that occurs is saturated (Kuang *et al.* 2020). The contact time for the next experiment was selected as 15 minutes. The adsorption kinetics of methylene blue on AgCl adsorbent in figure 4 (b) occurs with a pseudo-first-order kinetics model with an R^2 value of 0.9318.



(a) (b)

Figure 4. (a) Optimum contact time for MB uptake. (b) First order pseudo reaction kinetics.

3.2.4 Effect of stirring speed

The effect of stirring speed on the efficiency of methylene blue extraction was carried out using an AgCl coagulant at pH 7 for 15 minutes. Figure 6 shows an increase in the stirrer speed of 300 rpm which causes the collision between particles to increase so that the particles will be smaller in size and will more easily enter the pores of the adsorbent (Said *et al*. 2016) The absorption of methylene blue on a 400 rpm stirrer decreased due to a strong mechanical effect resulting in the adhesion force between methylene blue and AgCl not uniting them (Doan *et al.* 2020). The optimum stirrer speed at 300 rpm was selected during the study considering the high absorption of methylene blue.

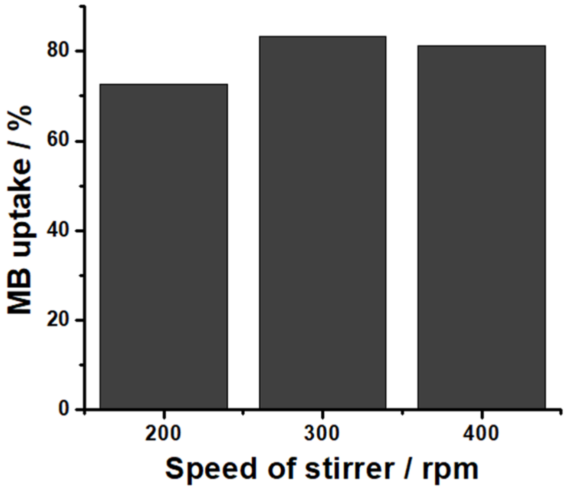


Figure 6. Optimum stirring speed curve for MB uptake.

3.2.5 Effect of pH

The effect of pH was carried out to determine the optimal pH in the uptake of methylene blue. Methylene blue was taken at various pH 3 to 9. Figure 7 showed the effect of pH on the uptake of methylene blue. The absorption of methylene blue increased at pH 7 which was 89% then decreased at pH > 7. Acid and neutral conditions in the solution changed the surface charge of AgCl. AgCl coagulant will be negatively charged thereby increasing the interaction with methylene blue (base dye) which is a positively charged dye (Yao et al. 2017). Increasing pH > 7 (alkaline) on methylene blue uptake resulted in the surface of AgCl not being maximal in methylene blue uptake so that methylene blue absorption decreased. In this study, pH 7 was chosen as the optimal pH for methylene blue extraction.

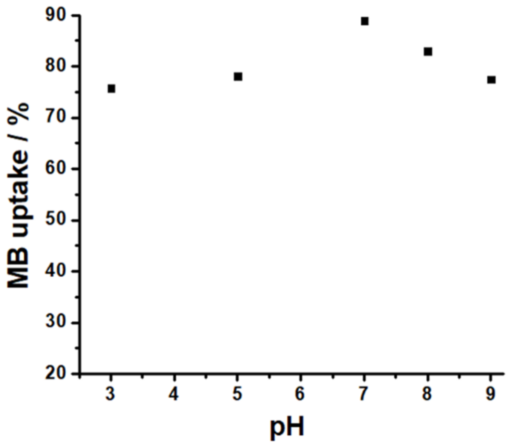


Figure 7. The Influence of MB adsorption curve on pH

3.3. Silver chloride precipitate characterization

3.3.1 XRD

The phase structure and crystallinity of the obtained nanoparticles were studied by XRD analysis. The diffraction pattern in Figure 8 reveals that the product corresponds to the AgCl phase (JCPDS No. 31-1238). The diffraction peaks at 2 of 27.28 °, 32.23°, 46.24°, 54.82°, 57.49°, and 67.46° can be assigned to (111), (200), (220), (311), (222) and (400) reflections of the face center cube structure (fcc) of AgCl crystals (Wang *et al.* 2012). AgCl particle size can be calculated by the Scherrer equation $d = K.\lambda/\beta.\cos\theta$, so that the peak sample particle size in the (200) AgCl plane is 4.53 nm.

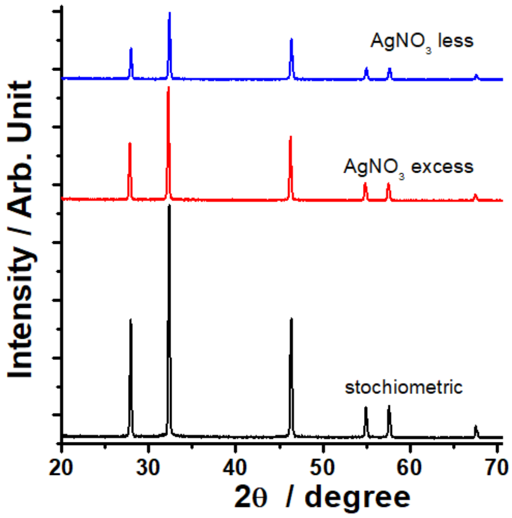


Figure 8. XRD pattern of AgCl synthesized Stoichiometric Variation of $AgNO_3$.

The sharp peaks indicate that the resulting AgCl nanoparticles have high crystallinity. There are no characteristic peaks belonging to other impurities in the diffraction pattern, providing evidence of the high purity of the AgCl phase. The variation of $AgNO_3$ stoichiometry used affects the intensity of the diffraction peaks. For samples synthesized under equilibrium stoichiometric conditions, the diffraction line was stronger than for samples obtained under conditions of less and excess $AgNO_3$.

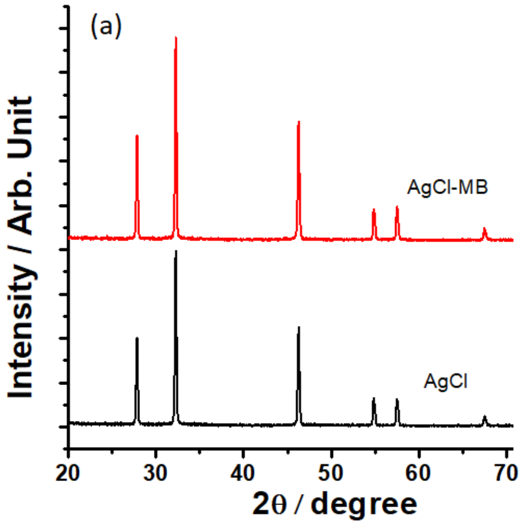


Figure 9. XRD pattern of AgCl bound to Methylene Blue

The diffraction pattern of the AgCl sample after taking methylene blue dye is shown in figure 9. This indicates that the MB adsorption process by AgCl occurs physically and does not involve chemical bonds. There were no other characteristic peaks indicating the purity of AgCl from other impurities.

3.3.2 FTIR

The FTIR spectral pattern of AgCl under equilibrium conditions, lack, and excess of $AgNO_3$ is shown in Figure 10. From this figure, AgCl gives similar IR spectral patterns both under equilibrium stoichiometric conditions, deficiency, and excess of $AgNO_3$.

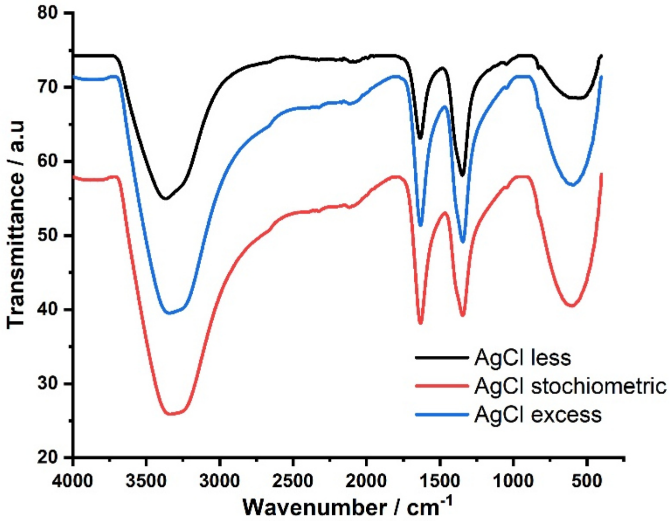


Figure 10. IR spectra of synthesized AgCl with Stoichiometric Variation of $AgNO_3$.

A strong broad peak at 3302 .92 cm^{-1} is associated with the strain vibration of the hydroxyl (OH) group. The peak at 1631.88 cm^{-1} represents the flexural vibration of adsorbed H_2O (Xie *et al.* 2013). The peak of 1347.58 cm^{-1} represents the aliphatic amine strain vibration. While the peak at 607.04 cm^{-1} could be ascribed to the hydrogen bonding of water and water (Chen *et al.* 2015).

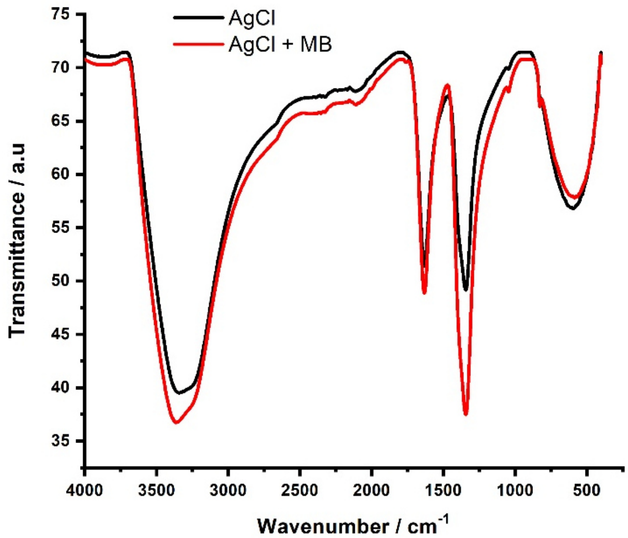


Figure 11. IR spectra of AgCl bonded to methylene blue.

While the possible interaction between methylene blue and AgCl was investigated by FTIR spectroscopy as shown in Figure 11 the IR spectral pattern of AgCl binding to methylene blue showed a similar pattern and there was no new bond between AgCl and methylene blue. FTIR analysis showed no significant chemical bond between methylene blue and AgCl only increased the intensity at 1631.88 cm^{-1} which represents the flexural vibration of the adsorbed H_2O.

4. Conclusion

The synthesis of AgCl coagulant has been successfully carried out using the precipitation method for the extraction of methylene blue dye. The results of UV-Vis spectrophotometry analysis showed that the AgCl coagulant succeeded in removing 88.2% methylene blue dye at pH 7 with an adsorption capacity of 10.9 mg. g^{-1}. Optimum methylene blue extraction at a contact time of 15 minutes with a stirring speed of 300 rpm. The adsorption kinetics model is Pseudo Order One with an R^2 value of 0,9318.

Acknowledgements

The authors are thankful to the Faculty of Science and Mathematics at Diponegoro University for supporting this work at the year of 2021.

References

Abdelazeem S. Eltaweil, Gehad S. Elgarhy, Gehan M. El-Subruiti, Ahmed M. Omer. (2020). Carboxymethyl cellulose/carboxylated graphene oxide composite microbeads for efficient adsorption of cationic methylene blue dye. *International Journal of Biological Macromolecules*. 154. 307–318. https://doi.org/10.1016/j.ijbiomac.2020.03 .122.

Amor Mosbah, Habib Chouchane, Soukaina Abdelwahed, Alaeddine Redissi, Manel Hamdi, Soumaya Kouidhi, Mohamed Neifar, Ahmed Slaheddine Masmoudi, Ameur Cherif, and Wissem Mnif. (2019). Peptides Fixing Industrial Textile Dyes: A New Biochemical Method in Wastewater Treatment. *Journal of Chemistry*. https://doi.org/10.1155/2019/5081807.

C. Songkroah, W. Nakbanpote, P. Thiravetyan, (2004). Recovery of silver-thiosulphate complexes with chitin. Process Biochemistry. 39. (11). 1553–1559. https://doi.org/10.1016/S0032-9592(03)00284-X.

F. Sakr, S. Alahiane, A. Sennaoui, M. Dinne, I. Bakas, Ali Assabbane, (2020). Removal of cationic dye (Methylene Blue) from aqueous solution by adsorption on two types of biomaterial of South Morocco. *Materials Today: Proceedings*. 22 (1), 93–96. https://doi.org/10.1016/j.matpr.2019.08.101.

Fangfang Xie, Joanna Borowiec, Jingdong Zhang. (2013). Synthesis of AgCl nanoparticles-loaded hydrotalcite as highly efficient adsorbent for removal of thiocyanate. *Chemical Engineering Journal*. 223. 584–591. http://dx.doi.org/10.1016/j .cej.2013.03.073.

Fei Chen, Qi Yang, Chenggang Niu, Xiaoming Li, Chang Zhang and Guangming Zeng. (2015). Plasmonic photocatalyst $Ag@AgCl/ZnSn(OH)_6$: synthesis, characterization and enhanced visiblelight photocatalytic activity in the decomposition of dyes and phenol. *RSC Adv*. 5. 63152–63164. https://doi.org/10.1039/c5ra10480g.

Ghada Eshaq, Ahmed E. Elmetwally. (2018). Bmim [OAc] -Cu 2 O / gC 3 N 4 as a multi-function catalyst for sonophotocatalytic degradation of methylene blue. *Ultrasonics – Sonochemistry*. 53, 99-109. https:/ /doi.org/10.1016/j.ultsonch.2018.12.037.

Jizhuang Wang, Changhua An, Meiyu Zhang, Chuan Qin, Xijuan Ming, Qinhui Zhang. (2012). Photochemical conversion of AgCl nanocubes to hybrid AgCl–Ag nanoparticles with high activity and long-term stability towards photocatalytic degradation of organic dyes. *Canadian Journal of Chemistry*. 90 (10). 858–864. https://doi.org/10.1139/v2012-079.

Kai He, Guangming Zeng, Anwei Chen, Zhenzhen Huang, Min Peng, Tiantian Huang, Guiqiu Chen. (2019). Graphene hybridized polydopamine-kaolin composite as effective adsorbent for methylene blue removal. *Composites Part Engineering*. 161. 141–149. https://doi.org/10.1016/j.compositesb.2018.10.063.

Lirong Yao, Xiaojuan Li, Guangyu Zhang, Shanqing Xu, Dehong Cheng, Yanhua Lu. (2017). Preparation of ag-containing ACF and its application for dye removal. *Journal of Engineered Fibers and Fabrics*. 12 (3). 39–47. https://doi.org/10.1177/155892501701200305.

Mohamad Amran Mohd Salleh, Dalia Khalid Mahmoud, Wan Azlina Wan Abdul Karim, Azni Idris. (2011). Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive review. *Desalination*. 280. (1–3). 1–13. https://doi.org/10.1016/j.desal.2011.07.019.

Mohammadtaghi Vakili, Mohd Rafatullah, Babak Salamatini, Ahmad Zuhairi Abdullah, Mahamad Hakimi Ibrahim, Kok Bing Tan, Zahra Gholami, Parisa Amouzgar. (2014). Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: A review. *Carbohydrate Polymers*. 113. 115–130. https://doi.org/10.1016/j.carbpol.2014.07. 007.

Mohd. Rafatullah, Othman Sulaiman, Rokiah Hashim, Anees Ahmad. (2010). Adsorption of methylene blue on low-cost adsorbents: a review. *Journal of Hazardous Materials*. 177 (1-3). 70-80. https://doi.org /https://doi.org/10.1016/j.jhazmat.2009.12.047.

Muhammad Said, Hassimi Abu Hasan, Mohd Tusirin Mohd Nor, Abdul Wahab Mohammad. (2016). Removal of COD, TSS and color from palm oil mill effluent (POME) using montmorillonite. *Desalination and Water Treatment.* 57. (23). 10490–10497. https://doi.org/10.1080/19443994.2015.1036778.

Mustafa T. Yagub, Tushar Kanti Sen, Sharmeen Afroze, H.M Ang. (2014). Dye and its removal from aqueous solution by adsorption. *Advances in Colloid and Interface Sci*. 209. https://doi.org/10.1016/j.cis.2014.04.002.

Ponnusamy Senthil Kumar, Sunita J. Varjani, Subburaj Suganya. (2018). Treatment of dye wastewater using an ultrasonic aided nanoparticle stacked activated carbon: Kinetic and isotherm modeling. *Bioresource Technology*. 250. 716–722. https://doi.org/10.1016/j.biortech.2017.11.097

Van Dat Doan, Thi Long Do, Thi Mong Thu Ho, Van Thuan Le, Hoai Thuong Nguyen. (2020). Utilization of waste plastic pet bottles to prepare copper-1,4-benzenedicarboxylate metal-organic framework for methylene blue removal. *Separation Science and Technology (Philadelphia).* 55 (3). 444–455. https://doi.org/10.1080/01496395.2019.1577266.

Vanitha Katheresan, Jibrail Kansedo, Sie Yon Lau. (2018). Efficiency of various recent wastewater dye removal methods: A review. *Journal of Environmental Chemical Engineering*. 6(4). 4676–4697. https://doi.org/10.1016/j.jece.2018.06.060.

Yang Zhi-yuan. (2008). Kinetics and mechanism of the adsorption of methylene blue onto ACFs. *Journal of China University of Mining and Technology*. 18(3). 437–440. https://doi.org/10.1016/S1006-1266(08)60090-5.

Yu Kuang, Xiaoping Zhang, Shaoqi Zhou. (2020). Adsorption of methylene blue in water onto activated carbon by surfactant modification, Water (Switzerland). 12. (2). 1–19. https://doi.org/10.3390 /w12020587.