THE REDUCTION OF CHROMIUM AND CHEMICAL OXYGEN DEMAND OF BATIK EFFLUENT BY UNCALCINED AND CALCINED Mg/Al HYDROTALCITE ON VARIOUS pH TREATMENTS

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ABSTRACT

The increasing Batik industry in Indonesia has an impact on wastewater production. The chemical compound in Batik wastewater such as dyes will contaminate the environment when it does not correctly treat, especially for a small-scale industry that usually does not have proper treatment before discharge to the environment. Adsorption is a simple and efficient method of reducing dyes. Hydrotalcite is an adsorbent material with rehydration properties. Hydrotalcite has been synthesized by the co-precipitation method. Rehydration properties improve Batik wastewater quality through Cr reduction and Chemical Oxygen Demand (COD) degradation with pH three as the optimum condition for adsorption. Ability to improve adsorption capacity after rehydration makes hydrotalcite possible as reusable material.

Keywords: Batik Wastewater, Adsorption, Hydrotalcite, Calcination, COD

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INTRODUCTION

The population of the batik industry in Indonesia increased due to the announcement from UNESCO in 2009 that Batik was one of Indonesian cultural heritage. It has an impact on a higher volume of Batik wastewater discharge. Some compound has been mixed to get batik colors such as dyes (anionic or cationic dyes), resin, wax, and other chemicals in the dyeing process.¹ Some industries, tiny scale industries, sometimes discharge their effluent directly to the environment without further treatment that will affect environmental conditions in negative ways, apart from its chemical compounds that sometimes are carcinogens. For example, the color of batik wastewater made an aesthetic problem and reduced the amount of oxygen dissolved in water. Some methods already offered to treat batik wastewater include membrane nanofiltration,¹ electrocoagulation,² adsorption,³ and photocatalytic degradation.⁴ Adsorption is one alternative treatment that is easily in preparation and low cost. Furthermore, specific material could be used several times with enhanced absorption capability after being used, like hydrotalcite.

Hydrotalcite is anionic clay that contains divalent and trivalent cations, and anion works as the counterion. Stawiński *et al.*⁵ reported that Mg/Al Hydrotalcite (Mg/Al HT) after calcination enhanced its adsorption capability because of the reconstruction process.⁵ Mg/Al HT reported widely used as an adsorbent for dye,^{5,6,7} and metal.^{8,9} Even though some research has been conducted using Mg/Al HT as an adsorbent for dyes, few studies reported it used in sample effluent.

We previously reported the use of magnetite-hydrotalcite materials for dyes adsorption.¹⁰ Herein, we presented the influence of calcined and uncalcined Mg/Al HT as an adsorbent for batik wastewater treatment. Calcined and uncalcined Mg/Al HT performance was evaluated in terms of its function in Chromium (Cr) reduction and COD degradation from batik wastewater under various pH.

EXPERIMENTAL

All reagents were an analytical grade (Merck Co. Inc. Germany), and Batik wastewater was collected from a small-scale Batik industry in Sleman District, Yogyakarta, Indonesia. Batik wastewater is

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collected in a closed container with simple treatment (carbon active and coconut fiber placed at the bottom of the container as sorbent material). The sample was taken from the container using a glass bottle and stored in an icebox for further experiments.

Mg/Al HT Synthesis

Mg/Al HT was synthesis through the co-precipitation method.¹¹ Dissolved $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; 12.8 g and 9.4 g each in 100 mL DI water at the closed container. Add dropwise NaOH 1.65 M to the solution until it reaches the base condition (pH 10). The prepared solution was then hydrothermally heated at 120 °C for 5 hours. Prepared Mg/Al HT was filtered, washed until it reached neutral pH (7.0-7.4), and left to dry at 100 °C. Then ground Mg/Al HT with mortar.

Adsorption Experiments

Pretreatment was used before the adsorption of Batik wastewater using the filtration process to remove impurities then diluted until reach required concentration.

The adsorption process was carried out in batch condition with 12.5 mg of Mg/Al HT and HCl and NaOH were prepared each at 0.1 M. 12.5 mL of Batik wastewater to adjust a solution. The mixture was then stirred for 2 hours, then filtered. The same procedure was applied to calcined Mg/Al HT. Optimum adsorption condition was getting with adjusted solution pH at 3, 5, 7 and 9. Mg/Al HT was calcined at 500 °C for 3 hours to get Calcined Mg/Al Hydrotalcite.¹²

Characterization

The adsorbent materials were characterized using X-ray diffraction (XRD) by Shimadzu and Scanning Electron Microscope (SEM) by Phenom Thermo Scientific.

RESULTS AND DISCUSSION

Characterization of Materials

The diffractogram of synthesized materials through co-precipitation is shown in Fig.-1. From diffractogram, it has been shown that it has a similar peak with Mg/Al HT from Stawiński *et al.*⁵ with peak characteristic at 11° (d003); 22° (d006); 34.8° (d012); 38-39° (d015); 46° (d018); 60° (d110) and 61° (d113). Calcined Mg/Al HT has a similar peak with uncalcined Mg/Al HT. This diffractogram reported that the calcination process in this research did not destroy its structure.

Fig.-1: XRD Patterns of Materials: (a) Uncalcined, (b) Uncalcined after adsorption, (c) Calcined, and (d) Calcined after adsorption

SEM was used to characterize morphologies of Mg/Al HT synthesize. From Fig.-2, morphologies of Mg/Al HT synthesized have nanosheets structure that similar to hydrotalcite reported by Huang *et al.*⁸ and Navajas *et al.*¹³

Fig.-2: SEM Image of Materials: (a) Uncalcined and (b) calcined

Adsorption Experiments

The composition of Batik wastewater would be affected by a chemical used in the processing step. Process production of Batik in the small-scale industry in Sleman categorizes as hand-written Batik (or 'batik tulis') that used pen-like tools called 'canthing' when applying wax. There are several steps used in Batik production. The early step is to draw molten wax using traditional tools (a pen-like tool called 'canthing') or a metallic stamp. The next step is the coloring process with dipping the cloth in the dye bath (sometimes they used salt to brighten up Batik's colour). The final process was rinsing, which eliminates wax using hot water (called 'pelorodan'). Based on this process, there are three main chemical compounds in Batik wastewater: wax (paraffin as dominant compound), dyes (vat and reactive dyes), and salt. Batik wastewater in small-scale industries is usually collected before further treatment in a closed container.

COD parameter used to represent various chemical compounds in Batik wastewaters. The color of Batik wastewater sample was yellowish black with pH 8, COD 3500 mgL⁻¹ and Cr concentration at 17 mgL⁻¹. For the adsorption process, the sample was filtered to reduce the particulate and insoluble materials of Batik components; furthermore, it was diluted with DI water. Since pH conditions will affect the adsorption process, such as changing the surface charge of the adsorbent and adsorbate,¹⁴ adsorption processes in this research were conducted under different pH that describes acid, neutral and base conditions.

After the adsorption process, the COD parameter seems to reduce for both adsorbents, with calcined Mg/Al HT giving more significant degradation (Fig.-3). The higher capability of calcined Mg/Al HT in the adsorption process was predicted because the disappearance of some water and ionic compounds that interact at the surface and functional groups of materials after the calcination process made some space for another compound to interact with the material.

The optimum condition of COD degradation for both adsorbents happen at pH 3, similar results with Birgani *et al.*¹⁵ The explanation is, at acid condition, the surface of Mg/Al HT contains hydroxyl groups in a protonated form. Since the surface charge of the adsorbent was affected by pH conditions, when increasing pH value, functional groups of the adsorbent will be deprotonated. Since the sample of Batik wastewater contains dominant organic materials (dyes), there are possible interactions between adsorbent and adsorbate through electrostatic interaction between hydroxyl groups of hydrotalcite layers and functional groups adsorbate.^{7,10,14,16} Since acid is the optimum condition of the adsorption process; anionic dyes are the dominant compound in the sample.¹⁴

Some references said that Mg/Al HT would reconstruct its structure after destruction after calcination, affecting its capability on adsorption.⁷ While, Fig.-1, the calcination process does not seem to destroy the Mg/Al HT structure, it still impacts a higher adsorption process than uncalcined hydrotalcite. It is proven from the diffractogram that the intensity of peaks is increased after the adsorption process.

Similar to an optimum condition for COD degradation, the optimum condition for Cr reduction of both adsorbents is at pH 3 (Fig.-4). Possibility explanation from this process was an interaction between functional groups adsorbent, and Cr speciation was electrostatic interaction.^{9,20,21,22} Cr speciation was dominantly affected by Cr(VI) that was anionic. At acidic conditions, functional groups of adsorbents are

a protonated form, then Cr speciation happens at anion condition. The adsorption of Cr speciation decreases with increasing pH. While, at base condition, the adsorption process for Cr seems to increase because usually, metals are in precipitated form. An indication that Cr was precipitate is the addition of total dissolved solids at the base condition in this research: approximately 1400 mgL⁻¹.

Fig.-3: COD Degradation (mgL⁻¹) of (a) Mg/Al HT and (b) Calcined Mg/Al HT

Even though the COD reduction showed a lower value than biosorbent materials by Patel and Vashi¹⁷ (Table-1), it can be used several times.¹⁰ Based on government regulation in Indonesia for textile effluent, COD and Cr parameters have limitation values at 150 mgL⁻¹ and 1 mgL⁻¹. The result of this research is still above the permissible limit by the government. Then, for direct application, this method needs to enhance parameter experiment such as temperature and contact time or additional method for complement process so it could fulfill the requirement.

Fig.-4: Cr Reduction of (a) Uncalcined and (b) Calcined Mg/Al HT Material

Table-1: Comparison of COD Degradation from Textile Wastewater

Adsorbent	COD degradation	References
Activated of natural materials	1400 - 1600 mgL ⁻¹	Patel and Vashi ¹⁷
Plastic Sheet coated by TiO ₂ nanoparticles	97 mgL ⁻¹	Sutisna <i>et al.</i> ¹⁸
Bioequalization-electrocatalytic	178 mgL ⁻¹	Mukimin <i>et al.</i> ¹⁹
Calcined and Uncalcined Mg/Al HT	250 – 400 mgL ⁻¹	this research result

CONCLUSION

Mg/Al HT can enhance batik wastewater quality by reducing COD and Cr; each was 256.7 mgL⁻¹ and 13.5 mgL⁻¹. Calcined material has better adsorption capability than uncalcined with almost double the amount of COD that can be reduced (the adsorption capacity was 398.3 and 256.7 mgL⁻¹).

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