Study of Adsorption-Desorption on Batik Industrial Dyes (Naphthol Blue Black) on Magnetite Modified Humic Acid (HA-Fe₃O₄)

Maya Rahmayanti [a,1,*], Erni Yunita [a,2], Nunung Faizah Yosi Putri [a,3]

[a] Department of Chemistry, Faculty of Science and Technology, Universitas Islam Negeri Sunan Kalijaga, Yogyakarta, Indonesia

* Author's email: (1,*) maya.rahmayanti@uin-suka.ac.id; (2) erniyunita859@gmail.com; (3) yosiputri1712@gmail.com

Article Info

Abstract

The rapid development of the batik industry can pollute water resources and become an increasingly severe problem. This research studies the adsorption-desorption of naphthol blue-black (one of the dyes in batik liquid waste) by magnetite modified humic acid (HA-Fe₃O₄). The adsorption isotherm was studied using the Langmuir and Freundlich isotherm models. Meanwhile, desorption agents used in this study were distilled water and hydrochloric acid. The results show that the adsorption isotherm followed the Langmuir adsorption model with a maximum adsorption capacity of 2.41 mmol/g. Desorption studies show that the desorption efficiency of naphthol blue-black on HA-Fe₃O₄ is 0.058% and 5.86% in the desorption agent of distilled water and HCl (1 M)

1. Introduction

Naphthol blue-black is two typical dyes that are widely used by batik artisans in Indonesia. These dyes are non-biodegradable organic compounds, so it is complicated to degrade in nature. In batik coloring, the dye is only used around 45%, while the remaining 55% will be disposed of as liquid waste. The existence of these compounds in nature can cause environmental pollution, especially the aquatic environment. Therefore, it is necessary to process dyes contained in batik liquid waste before batik waste is discharged into the waters.

Currently, wastewater treatment techniques in the batik industry are being developed, including photocatalysis, electrolysis, nanofiltration, ultrafiltration, and adsorption [1, 2, 3, 4]. Photocatalysis and electrolysis methods are less effective because they require high costs and are difficult to apply. Meanwhile, the nanofiltration method can cause new problems because the adsorbed dyes will accumulate on the adsorbent's surface. The adsorption method is reported to be quite useful in removing dyes from batik liquid waste. The advantages of the adsorption method are economical and straightforward. It is just that the dye will accumulate on the surface of the adsorbent and become new waste. Thus, it is necessary to conduct further treatment of the adsorbent post adsorption so that the adsorbent does not become waste and cause new problems.

This study reports the use of economical materials and based on natural resources and local minerals in Indonesia to overcome the naphthol blue-black dyes. The material used in this study is humic acid (HA), which is isolated from peat soils originating from Riau, Sumatra. Humic acid has been widely developed and reported as a successful adsorbent for heavy metals [5, 6, 7] and textile dye compounds [8]. Chemically, HA is a macromolecule that is rich in active groups such as carboxylate (-COOH) and hydroxyl (OH) groups, both phenolics and alcoholates, and quinones [9, 10]. Hence humic acid is thought to have high absorptivity, including naphthol blue-black dyes. To the author's knowledge, humic acid isolated from Riau's peat soils in Sumatra has not been much studied as an adsorbent for naphthol blue-black dyes. The selection of humic acid from the isolation of peatlands in Riau, Sumatra, is based on Rahmayanti *et al.* [10], who reported that the humic acid from the isolation of Riau peatlands in Sumatra has a higher -OH group content than humic acid from Kalimantan peatlands.

Humic acid has stability at low pH (pH <3) and dissolves at pH> 3 [9] so that the pH range of adsorption is limited. HA coating on magnetite compounds (Fe₃O₄)

can be done so that HA, as an adsorbent, can work over a wider pH range. Another benefit of AH coating on magnetite compounds is that the desorption process can be carried out without filtration and centrifugation because separation can use external magnetic fields to be more environmentally friendly [11, 12]. The coating on Fe_3O_4 is expected to reduce the particle size of the adsorbent produced so that it can increase the adsorption ability of naphthol blue-black dyes.

2. Methodology

2.1. Equipment and Materials

In this study, the humic acid was humic acid from the isolation of peat soils in Riau, Sumatra. The humic acid coating on magnetite was carried out using iron chloride hexahydrate ($FeCl_3.6H_2O$), iron sulfate hexahydrate ($FeSO_4.7H_2O$) and sodium hydroxide. The desorption agents used were distilled water and hydrochloric acid. All of these chemicals came from Merck Darmstadt, Germany. The naphthol blue-black dye used was special in the batik industry.

The equipment used in this study was a set of standard laboratory glassware, vacuum pumps, 4800 Thermolyne oven/furnace, BP 110 Sartorius analytical balance, desiccator, Leistungsfreq type sonicator, 70VA generator, Orion 920A pH meter, shaker (Osk), Shimadzu-8201 PC Fourier Transform Infrared (FTIR) spectrophotometer, and Double Beam 1601 PC Shimadzu UV-VIS Spectrophotometer.

2.2. Preparation of magnetite-modified humic acid (HA-Fe₃O₄)

The magnetite modified humic acid preparation was carried out following the method of Rahmayanti *et al.* [6] with a slight change. 5.56 g (0.01 mol) of $FeSO_4.7H_2O$ was dissolved in 200 mL of distilled water and added to 11.12 g (0.02 mole) of $FeCl_3.6H_2O$, which was dissolved in 200 mL of distilled water. The solution was heated at 90°C while stirring, then the mixture was added to the NaOH solution set at a pH of 13 and then added with 2 g of humic acid resulting from the isolation of peat soils. The mixture was stirred at 90°C for 60 minutes. Then the mixture was allowed to stand at the same temperature for 60 minutes. The mixture was cooled at room temperature, then filtered, and the precipitate obtained was washed with 100 mL of distilled water six times (with the help of an external magnetic field). Washing precipitates were heated using an oven at 90°C then characterized using XRD and FTIR spectrophotometers.

2.3. Absorption of naphthol blue-black on HA-Fe₃O₄

Ten mg of HA-Fe₃O₄ was mixed with 10 mL of naphthol blue-black dye solution at pH 2 with varying concentrations of 100, 200, 300, 400, and 500 ppm. The mixture was shaken for 60 minutes then filtered using Whatman filter paper (with the help of an external magnetic field at the bottom of the bottle). The filtrate obtained was then measured for pH, then analyzed using a UV-Vis spectrophotometer.

2.4. Study of adsorption isotherms

The adsorption isotherm models used to explain the pattern of adsorption isotherms in this study are Langmuir and Freundlich isotherm models. The Langmuir adsorption isotherm model can be expressed by equation (1).

$$\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}} \tag{1}$$

The amount of metal adsorbed at the equilibrium state (mg/g) is expressed as q_e. C_e is the concentration of free metal ions in solution at equilibrium (mg/L). q_{max} is the maximum adsorption capacity (mg/g), and KL is the Langmuir constant (L/mol) related to the adsorption energy [13].

The Freundlich isotherm model is expressed by equation (2).

$$\log q_e = \log KF + \frac{1}{n} \log C_e \tag{2}$$

The number of species adsorbed per gram of adsorbent at equilibrium (mg/g) is referred to as q_e. C_e is the concentration of free metal ions in solution at a state of equilibrium capacity (mg/g). KF is the Freundlich constant, which is related to adsorption capacity, and 1/n is a factor of heterogeneity [14].

2.5. Desorption of Naphthol Blue Black Dyes

The post-adsorption HA-Fe₃O₄ adsorbent was put into distilled water and added by HCl desorption agent with a variation of 0.5 M; 1 M; 1.5 M, and 2 M. The mixture was shaken at 125 rpm for 60 minutes. The solution was filtered for the filtrate then analyzed using a UV-Vis spectrophotometer according to the naphthol blue-black dye wavenumber. Post desorption adsorbents were characterized using FTIR. The percentage of desorption was calculated using the formula presented in Equation 3.

$$desorption\ (\%) = \frac{\text{naphthol blue−black dye}_{initial} - \text{naphthol blue−black dye}_{remain}}{\text{naphthol blue−black dye}_{initial}} \times 100\% \tag{3}$$

3. Results and Discussion

3.1. Modification of Humic Acid with Magnetite (HA-Fe₃O₄)

The success of modification of humic acid with Fe_3O_4 was studied using FTIR, and the spectra are presented in Figure 1. The presence of magnetite in humic acid is characterized by absorption at a wavelength of 580 cm⁻¹, which is the stretching vibration of Fe-O. Meanwhile, the loss of absorption of the carboxylic group C=O at wavelengths of 1700 cm⁻¹ and 1500 cm⁻¹ indicates that the organic compound's anion binds to the surface of the magnetite through chemical bonds. The possibility is through a carboxylic group that is symmetrically bonded to the magnetite surface, as indicated by the absorption only in the region of 1400 cm⁻¹. Absorption, which shows functional groups of HA, also appears (Figure 1. (c)) even with lower intensity. Thus, it can be said that the modification of humic acid with Fe₃O₄ has been successfully carried out. Evidence of HA-Fe₃O₄ adsorbent having magnetic properties is presented in Figure 2. (a).
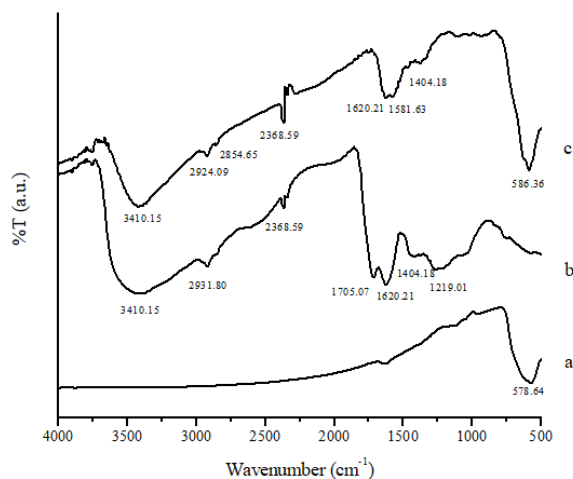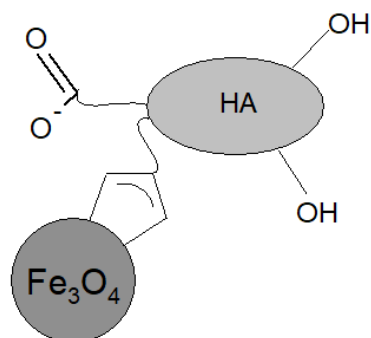
Figure 1. FTIR spectra (a). Fe_3O_4; (b) HA; (c) HA–Fe_3O_4

a.

b.

Figure 2. (a). The HA–Fe_3O_4 adsorbent is attracted by the external magnetic field (b). Illustration of interaction between magnetite and humic acid through the formation of chelate -COO-Fe

The alleged interaction between Fe_3O_4 and HA is through the formation of chelate -COO-Fe (Figure 2) because the modification of HA with Fe_3O_4 is carried out in an alkaline atmosphere (pH 9-10). In this condition, the surface of Fe_3O_4 tends to be negative because the pH > point of zero charges (pHpzc) of Fe_3O_4. Meanwhile, at this pH, the carboxylic and phenolate HA groups have been deprotonated so that interaction between the Fe_3O_4 surface with -COO- and -O- is not possible to occur through electrostatic interactions.

3.2. Study of Naphthol Blue Black Adsorption Isotherms on HA-Fe_3O_4

In this study, the naphthol blue-black adsorption isotherm on HA-Fe_3O_4 was studied through the Langmuir and Freundlich adsorption isotherm models. The Langmuir adsorption isotherm model was determined by making a graph of C_e/q_e versus C_e, as presented in Figure 3b. Based on the graph, on the naphthol blue-black adsorption on HA-Fe_3O_4, the correlation coefficient (R^2) obtained is 0.996, an adsorption capacity of 0.00241 mol g^{-1} adsorbent, adsorption equilibrium constant (K_L) of 5.9 $\times 10^4$ L mol^{-1} and adsorption energy (E_{ads} = 26.64 kJ mol^{-1}). Whereas, the Freundlich isotherm model for naphthol blue-black adsorption on HA-Fe_3O_4 was determined by graphing log q_e versus log C_e, as presented in Figure 3a. Based on the graph, the correlation coefficient (R^2) obtained is 0.906, and the Freundlich (K_F) constant is 5.77 x 10^{-2} mol g^{-1}.
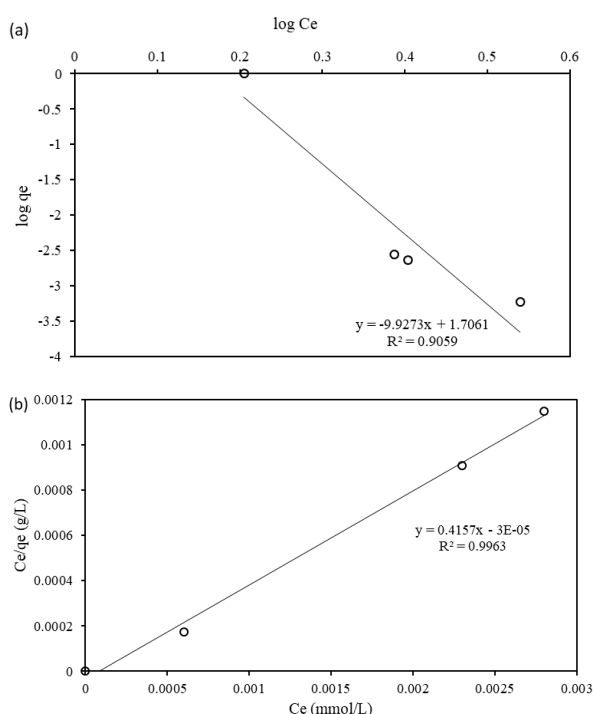

Figure 3. Isotherm adsorption of Naphthol Blue Black on HA-Fe_3O_4 which is fitted to the (a) Freundlich equation and (b) Langmuir equation; (adsorbent dose 0.01 g, reaction time 15 min, reaction temperature 30°C, pH 2.0)

From Table 2, it can be seen that the adsorption of naphthol blue-black on HA-Fe_3O_4 follows the Langmuir isotherm model with a correlation coefficient (R^2) of 0.996. Thus, the active site on the surface of HA-Fe_3O_4 can be considered homogeneous. There is no interaction between naphthol blue-black molecules, so it can be said that naphthol blue-black on HA-Fe_3O_4 only forms one layer (monolayer). When viewed from the adsorption energy (E_{ads} = 26.64 kJ/mol), the interaction between naphthol blue-black and HA-Fe_3O_4 adsorbent is physisorption. The activation energy in physisorption is in the range of 5-40 kJ/mol, while chemisorption is 40-800 kJ/mol [15]. Compared with some of the results of previous studies (Table 2), it appears that naphthol blue-

black dyes can be better adsorbed on HA–Fe$_3$O$_4$ compared to methylene blue and gold dyes in aqueous solutions.

Table 2. Calculated values of parameters in Langmuir and Freundlich equations

Adsorbents	Adsorbates	Langmuir equation				Freundlich equation		
		q_{max} (mol/g)	KL (L/mol)	Eads (kJ/mol)	R²	KF (mol/g)	n	R²
HA–Fe$_3$O$_4$	Naphthol Blue Black	0.00241	5.9 x 10⁴	26.64	0.996	0.0577	-0.101	0.906
HA– Fe$_3$O$_4$ [6]	HAuCl$_4$	0.00062	1608	18.6	0.992	1.02 x 10⁻⁴	4.695	0.956
HA– Fe$_3$O$_4$ [14]	Methylene blue	0.00034	–	–	0.997	–	–	–
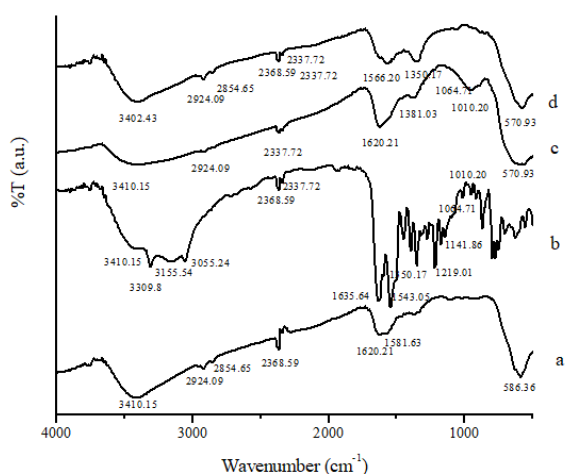
Figure 4. FTIR spectra (a). HA–Fe$_3$O$_4$; (b) naphthol blue black (c) HA–Fe$_3$O$_4$ after adsorption; (d) HA–Fe$_3$O$_4$ after desorption

FTIR data after adsorption (Figure 4) shows that there are differences in uptake that appear before and after naphthol blue-black is adsorbed on HA–Fe$_3$O$_4$. The difference is seen in the absorption that appears in the region of 3500-3200 cm⁻¹ and the region of 1000-1100 cm⁻¹ (Figure 4c). The absorption that appears in the area of 3400 cm⁻¹ has decreased intensity after adsorption. This is presumed because the HA–Fe$_3$O$_4$ phenolate group plays a role in the naphthol blue-black adsorption process on HA–Fe$_3$O$_4$. Interactions that occur are suspected through electrostatic interactions because the adsorption of naphthol blue-black on HA–Fe$_3$O$_4$ is carried out at pH 2. At this pH, the phenolate -OH group protonates to -OH$_2^+$, while the naphthol blue-black group is anionic because it has a -SO$_3^-$ group, so that electrostatic interactions between the adsorbent surfaces and the adsorbate are possible. The second suspicion, interactions occur through hydrogen bonds between the hydrogen atom of the -OH phenolate adsorbent group and the oxygen atom of the naphthol blue-black sulfonate group. The appearance of uptake in the 1010 cm⁻¹ and 1066 cm⁻¹ regions (Figure 4c) shows the S-O group stretch vibrations and the asymmetric strain S=O groups originating from the sulfonate groups.

3.3. Desorption Study on Naphthol Blue Black Dyes

Desorption studies can be studied using thermal and chemical regeneration methods [16]. In this study, the desorption of naphthol blue-black from HA–Fe$_3$O$_4$ adsorbent was studied using chemical methods with desorption agents as distilled water and HCl. The mechanism of the naphthol blue-black (adsorbate) desorption reaction from HA–Fe$_3$O$_4$ (adsorbent) using an HCl desorption agent is thought to be through an ion exchange reaction. The HCl desorption agent in the solution ionized into H⁺ and Cl⁻. The Cl⁻ ion replaces the adsorbate (which is negatively charged) to bind to the adsorbent, and or the H⁺ ion replaces the protonated adsorbate (positively charged) to bind to the adsorbate.

Figure 4 shows that the distilled water desorption agent only succeeded in absorbing naphthol blue-black by 0.058%. Meanwhile, the HCl desorption agent succeeded in absorbing the optimum naphthol blue-black at 5.86% at 1 M HCl concentration. Figure 4 shows that if the concentration of HCl> 1 M, desorption decreases. This is presumably because the naphthol blue-black dye is damaged in a solution that is too acidic. The low ability of distilled water and HCl in the absorption of naphthol blue-black from HA–Fe$_3$O$_4$ is suspected because HCl (H⁺ and Cl⁻ ions) do not sufficiently break the bonds formed between naphthol blue-black and the surface of the adsorbent HA–Fe$_3$O$_4$. As previously explained, the bond energy formed between naphthol blue-black and the surface of the HA–Fe$_3$O$_4$ adsorbent is 26.64 kJ mol⁻¹.
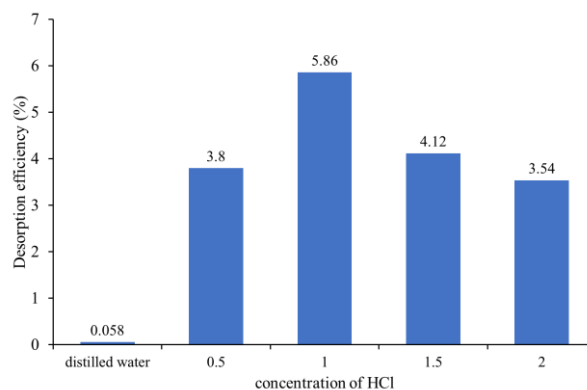

Figure 4. The effect of HCl concentration on desorption efficiency (reaction time 60 min, reaction temperature 30°C)

4. Conclusions

Magnetic modified humic acid (HA–Fe$_3$O$_4$) can be used as an adsorbent for dyes in the batik industry liquid waste (naphthol blue-black). The adsorption isotherm study showed that the adsorption of naphthol blue-black on HA–Fe$_3$O$_4$ followed the Langmuir isotherm model with adsorption capacity (q_{max}) = 0.00241 mol/g. Desorption studies show that naphthol blue-black does not succeed in deporting well enough from HA–Fe$_3$O$_4$. The efficiency of desorption using distilled water desorption agents is 0.058% while using HCl desorption agents (1 M) is 5.86%.

Acknowledgement

References

[1] Payam Moradi Birgani, Navid Ranjbar, Rosniah Che Abdullah, Kien Tiek Wong, Gooyong Lee, Shaliza Ibrahim, Chulhwan Park, Yeomin Yoon, Min Jang, An efficient and economical treatment for batik textile wastewater containing high levels of silicate and organic pollutants using a sequential process of acidification, magnesium oxide, and palm shell-based activated carbon application, *Journal of Environmental Management*, 184, (2016), 229-239 https://doi.org/10.1016/j.jenvman.2016.09.066

[2] Saidah Malihah Binti Mansor, Batik wastewater treatment using membrane bioreactor (MBR), undergraduate thesis, Faculty of Civil Engineering and Earth Resources, Universiti Malaysia Pahang, Pahang, Malaysia

[3] Tri Murniati, Inayati Inayati, Sri Budiastuti, Pengelolaan Limbah Cair Industri Batik dengan Metode Elektrolisis sebagai Upaya Penurunan Tingkat Konsentrasi Logam Berat di Sungai Jenes, Laweyan, Surakarta, *Ekosains*, 7, 1, (2015), 77-83

[4] Sushanta Debnath, Niladri Ballav, Hlengilizwe Nyoni, Arjun Maity, Kriveshini Pillay, Optimization and mechanism elucidation of the catalytic photo-degradation of the dyes Eosin Yellow (EY) and Naphthol blue black (NBB) by a polyaniline-coated titanium dioxide nanocomposite, *Applied Catalysis B: Environmental*, 163, (2015), 330-342 https://doi.org/10.1016/j.apcatb.2014.08.011

[5] Fande Meng, Guodong Yuan, Steven L. Larson, John H. Ballard, Charles A. Waggoner, Zikri Arslan, Fengxiang X. Han, Removing Uranium (VI) from Aqueous Solution with Insoluble Humic Acid Derived from Leonardite, *Journal of Environmental Radioactivity*, 180, (2017), 1-8 https://doi.org/10.1016/j.jenvrad.2017.09.019

[6] Maya Rahmayanti, Guliston Abdillah, Sri Juari Santosa, Sutarno Sutarno, Application of Humic Acid Isolated From Kalimatan Peat Soil Modifying Magnetite for Recovery of Gold, *Jurnal Bahan Alam Terbarukan*, 8, 2, (2020), 77-83 https://doi.org/10.15294/jbat.v8i2.20392

[7] Syarifatul Muniroh, Maya Rahmayanti, Kinetika Adsorpsi Kromium (VI) yang Terkandung dalam Limbah Batik pada Asam Humat Termodifikasi Magnetit (AH-Fe$_3$O$_4$), *Integrated Lab Journal*, 7, 2, (2019), 42-46

[8] Gita Citra Santi, Maya Rahmayanti, Effect of Solution pH to Indigosol Blue Adsorption on Humic Acid Isolated from Kalimantan Peat Oil, Proceeding International Conference on Science and Engineering, Yogyakarta, (2019)

[9] George R. Aiken, Diene M. McKnight, Robert L. Wershaw, Patrick MacCarthy, *Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization*, Krieger Publishing Company, 1991

[10] Maya Rahmayanti, Erni Yunita, Masyithah Nisvi Prandini, Isolasi Asam Humat dari Tanah Gambut Sumatera dan Kalimantan dan Analisis Kandungan Gugus Fungsionalnya, *Integrated Lab Journal*, 7, 2, (2019), 132-139

[11] Maya Rahmayanti, Sri Juari Santosa, Sutarno Sutarno, Comparative Study on the Adsorption of [AuCl$_4$]$^-$ onto Salicylic Acid and Gallic Acid Modified Magnetite Particles, *Indonesian Journal of Chemistry*, 16, 3, (2016), 329-337 https://doi.org/10.22146/ijc.21150

[12] Maya Rahmayanti, Sri Juari Santosa, Sutarno, Sonochemical Co-Precipitation Synthesis of Gallic Acid-Modified Magnetite, *Advanced Materials Research*, 1101, (2015), 286-289 https://doi.org/10.4028/www.scientific.net/AMR.1101.286

[13] Irving Langmuir, The Constitution and Fundamental Properties of Solids and Liquids. Part I. Solids, *Journal of the American Chemical Society*, 38, 11, (1916), 2221-2295 https://doi.org/10.1021/ja02268a002

[14] Herbert Freundlich, Über die Adsorption in Lösungen, *Zeitschrift für Physikalische Chemie*, 57U, 1, (1907), 385-470 https://doi.org/10.1515/zpch-1907-5723

[15] Stavros G. Poulopoulos, Vassilis J. Inglezakis, *Adsorption, Ion Exchange and Catalysis: Design of Operations and Environmental Applications*, Elsevier Science, 2006

[16] Liang Peng, Pufeng Qin, Ming Lei, Qingru Zeng, Huijuan Song, Jiao Yang, Jihai Shao, Bohan Liao, Jidong Gu, Modifying Fe$_3$O$_4$ nanoparticles with humic acid for removal of Rhodamine B in water, *Journal of Hazardous Materials*, 209-210, (2012), 193-198 https://doi.org/10.1016/j.jhazmat.2012.01.011