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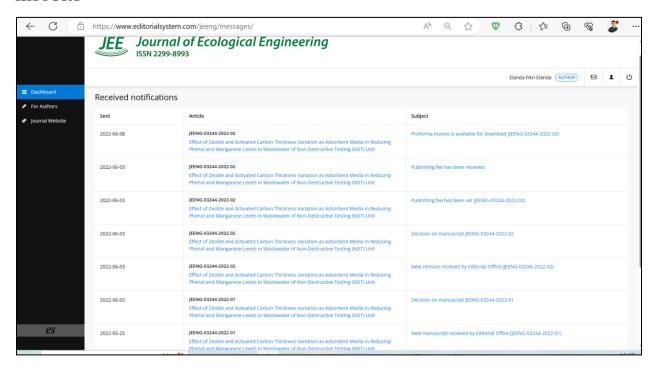
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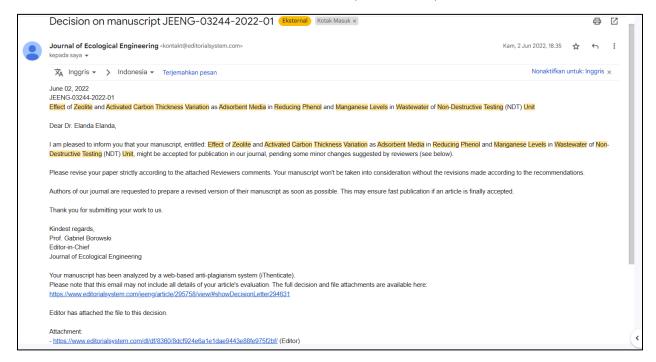
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Effect of Zeolite and Activated Carbon Thickness Variation as Adsorbent Media in Reducing Phenol and Manganese Levels in Wastewater of Non-Destructive Testing (NDT)-Unit

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ABSTRACT

The production wastewater contains phenol from the Non-Destructive Testing (NDT) unit because it uses solvents; meanwhile, the manganese originates from the metal material washing process. Based-On the basis of on the laboratory test results, the wastewater originating from the NDT unit of Y Industry, resulted in a phenol level of 2.33 mg/L, exceeding the quality standard of 0.5 mg/L and manganese level of 14.13 mg/L that exceeded the quality standard of 2 mg/L, based on the Regulation of the Minister of the Environment Number 5 of 2014 concerning Wastewater Quality Standards. This research used the pretest-posttest experimental research design without control. The sample in this study was wastewater from the NDT unit of the Y Industry. The average phenol level after passing through the adsorbent media at a thickness of 40 cm, 60 cm, and 80 cm resulted in 0.99 mg/L with 63% reduction, 0.60 mg/L with 77% reduction, and 0,28 mg/L with 89% reduction, respectively. The average manganese level after passing through the adsorbent media at a thickness of 40 cm, 60 cm, and 80 cm resulted in 0.10 mg/L with 61% reduction, 0.06 mg/L with 76% reduction, and 0,05 mg/L with 80% reduction, respectively. The most effective thickness variation in reducing the phenol and manganese levels of NDT wastewater is 80 cm thickness.

 $\textbf{Keywords} \hbox{: NDT was tewater, adsorption, zeolite, activated carbon, phenol, manganese.} \\$

INTRODUCTION

Industrial wastewater is all types of wastewater originating from the by-products of an industrial process. Based-Depending to on-the source, the liquid waste produced by the industry is an outcome of various industrial activities processes, such as materials processing, sanitation activities from the bathroom, cooling water-waste from the engine cooling system, waste from boilers (boiler), and waste originating from the material cleaning process (Siagian, 2016).

Based On the basis of on the laboratory examinations results, the quality outcome of the wastewater generated from The the NDT Waste Water Treatment Plant (WWTP), there are still several quality standard parameters that have not met the requirements. Several parameters in the NDT wastewater that did not meet the requirement were phenol with an initial level of 2.33 mg/L, while the quality standard was 0.5 mg/L and manganese with an initial concentration of 14.13 mg/L, while the quality standard was 2 mg/L.

The source of phenol in the NDT wastewater comes from the solvent used. This is according to the the fact that ethanol is a polar solvent, thus, this solvent is oftenly used to identify flavonoid compounds. Flavonoid compounds are one of the phenol derivative compounds, hence, there is a linkage between the use of solvents and phenol levels in wastewater (Suhendra et all, 2019). Meanwhile, the source of manganese in the NDT wastewater comes from the washing process of materials made of metal. This is because manganese is widely used in the iron-steel smelting and metal processing industries. Generally, manganese is used as an alloy for the manufacture manufacturing of stainless steel and alloys, In this case, the use of manganese aims to increase its strength, hardness, and resistance (Safitri, 2016).

Phenols are organic compounds found in the wastewater discharged from various industries such as petrochemical refineries, pharmaceuticals, coal processing, resins, polymers, pesticide industries and so on (Sun et all, 2019). Phenol in low concentrations can cause high toxicity and is considered as one of the most dangerous compounds. Phenol exposure can have serious effects on humans, be it through inhalation, ingestion, or absorption of the skin, it's its exposure can cause coma, convulsions, cyanosis, and can also cause liver, kidneys, lungs, and vascular system failures. Ingestion of 1 gram of phenol can

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be very lethal to humans (Zhang et al_x, 2016). Meanwhile, the presence of a small amount of manganese in the human body will not cause health problems, but in large quantities, it can accumulate in the liver and kidneys. It can also be toxic to the respiratory system. Exposure to high doses in a short time shows symptoms of obesity, skin disorders, skeletal disorders, changes in hair color, nervous system disorders, and digestive tract irritation. Water containing manganese will form deposits₂, hence_x it can cause stains on white objects, cause—odor and taste in drinking water, cause—low or high water turbidity, and cause—a brownish color on clothes (Sinambela, 2020). Hence, wastewater treatment is compulsory before discharging the wastewater to waterways or the sea.

Adsorption is one of the methods that can be applied to control the phenol and manganese pollution in wastewater. The adsorbent media used in the adsorption process are natural adsorbents, namely zeolite and activated carbon. Based_On the basis of theon research conducted by Khalid (in Ramirez et al. (2017)) regarding the removal of phenol using four types of zeolites as adsorbents and the comparison of its adsorption properties with activated carbon. In this study_diluted phenol solution was used as a contaminant and adsorption was carried out in batch and continuous streams. BEA zeolite contains silica with slightly higher adsorption capacity at low phenol concentration (1.6 g/L) compared to activated carbon. The BEA zeolites containing silica are proved to be efficient as adsorbents that can be easily regenerated (Ramirez et al_x, 2018). Another study conducted by Abustan et al_ (2017) said_reported that the use of activated carbon in granular form was more effective than the use of zeolite in eliminating manganese in water with a removal efficiency of 99.39 %. The highest manganese removal was achieved when the adsorbent dose was increased to 10 grams with a stirring speed of 200 rpm.

On the basis of Based on the above, the researchers are interested in conducting the research on the thickness variations effect of zeolite and activated carbon media adsorbent in reducing phenol and manganese levels of NDT wastewater.

MATERIALS AND METHODS

This study <u>uses used</u> experimental research with a pretest-posttest design without control. The sample in this study <u>is was</u> the effluent of wastewater produced at Y Industry. This study <u>aims aimed</u> to observe the process of eliminating phenol and manganese levels in production wastewater using zeolite and activated carbon as adsorbent media. The research tool design is as seen in Figure 1.

Figure 1. Filter reactor

Figure 2. Filter materials in detail

Figure 3. Experiment tool

The filter reactor contains zeolite and activated carbon media which are made in various media thicknesses, namely 40 cm, 60 cm, and 80 cm. The size of the zeolite used is 14-20 mesh and the activated carbon is 80 mesh.

In this study, 6 repetitions were carried out with 3 treatments. The pre_test was carried out by taking samples before the wastewater was contacted with the adsorbent media, while the post_test was carried out by taking samples that had been contacted with the adsorbent media. The test was carried out for 3 days with 2 repetitions each day. The number of samples in this study was 36-samples.

RESULTS AND DISCUSSION

pH measurement results of NDT wastewater

Based On the basis of on table 1, the media thickness variation of 40 cm, 60 cm, and 80 cm resulted in an average pH of 7.47 after the given treatment from 7.08 before treatment, average pH of 7.70 after the given treatment from 6.74 before treatment, and average pH of 7.70 after the given treatment from 6.70 before treatment, respectively.

Table 1. The pH measurement results of NDT wastewater before and after treatment using zeolite and activated carbon as adsorbent media at Y industry in June 2021

The pH is a measure to determine the nature of acid or base. The pH is one of the factors that affect the adsorption process. Based On the basis on this research, there is a change in the pH of the wastewater after passing through the adsorbent medium of zeolite and activated carbon. The wastewater pH after passing through the media tends to rise compared to the wastewater that has not been passed through zeolite and activated carbon as the absorbent media. This is because activated carbon is an effective

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absorbent material and binds metal ions in solution. In the adsorption process, the metal elements in wastewater will be broken down into metal ions and hydroxide ions (OH-). The metal ions will be attracted to the activated carbon by the Van der Waals force, thus leaving the (OH-) ion behind.

The interaction between metal ions and activated carbon is that metal ions exchanged for the acidic functional group on the surface of activated carbon causes cause the (H+) ions to reduce. In addition to the activated carbon effect, zeolite as a filtration media also affects the increasing pH of the adsorption results. The Wwastewater that passes through the zeolite will be bound to the cations because of zeolite's negatively charged properties of the zeolite to balance the ions, leaving the negative ions behind. The reduction of ions (H+) and the remaining ions left (OH-) in the adsorption results is the cause of the increase in pH level (Heriyani & and Dan, 2016).

The temperature measurement results of NDT wastewater

Based On the basis of on table 2, the media thickness variation of 40 cm, 60 cm, and 80 cm, resulted in an average temperature of 25°C after the given treatment from 25°C before treatment, an average temperature of 25°C after the given treatment from 24°C before treatment, and an average temperature of 25°C after the given treatment from 24°C before treatment, respectively.

On the basis of Based on the research, the researchers measured the temperature of the wastewater before and after passing through the zeolite and activated carbon adsorbent media as supporting data. Temperature is one of the factors affecting the adsorption energy. When adsorbate molecules are attached to the surface of the adsorbent, there is a certain amount of energy released, classified as exothermic adsorption. When the temperature is low, the adsorption ability increases, as so that does the adsorbate increases (Putri, 2019). The results of this study indicate that the wastewater temperature before and after passing through the adsorbent media of zeolite and activated carbon varies according to the surrounding environmental conditions.

Table 2. The temperature measurement results of NDT wastewater before and after treatment using zeolite and activated carbon as adsorbent media at Y industry in June 2021

The phenol level examinations results of NDT wastewater

Based-According to on-table 3, the media thickness variation of 40 cm, 60 cm, and 80 cm resulted in the average phenol level of 0, 98 mg/L after the given treatment from 2, 63 mg/L before treatment, phenol level average of 0, 59 mg/L after the given treatment from 2, 50 mg/L before treatment, and phenol level average of 0, 27 mg/L after the given treatment from 2, 52 mg/L before treatment, respectively.

Table 3. The <u>results of phenol level examinations results of NDT wastewater before and after treatment using zeolite and activated carbon as adsorbent media at Y industry in June 2021</u>

Based According toon table 4, the reduction difference of phenol levels in Industry Y-s NDT wastewater for media thickness variation of 40 cm, 60 cm, and 80 cm resulted in the average phenol levels reduction difference of 1_{5} 64 mg/L, 1_{5} 90 mg/L and, 2_{5} 24 mg/L, respectively.

Table 4. The phenol level reduction results of NDT wastewater before and after treatment using zeolite and activated carbon as adsorbent media at Y Industry in June 2021

The reduction of phenol levels happened due to the zeolite and activated carbon as the adsorbent media. According to Trisunaryanti, Zzeolites contain amorphous silica-alumina and crystalline mordenite that will have a good capability in absorbing wastewater pollutants when activated and modified. In addition, zeolite has a porous crystal structure with a large surface area (Atikah, 2016).

Activated carbon has a very large surface area of $1.95 \times 106 \text{ m}^2/\text{kg}$, with a total pore volume of $10.28 \times 10^{-4} \text{ m}^3/\text{kg}$ and an average of 21.6 Å pore diameter, enabling the activated carbon to absorb large amounts of the adsorbate (Achmad, 2018). Based On the basis of on the research conducted by Lorenc-Grabowska et al., (2016) has stated that the main mechanism that determines the phenol adsorption process is the activated carbon particle size ranging from $0.8 \times 1.4 \text{ nm}$.

Activation on zeolite and activated carbon adsorbent media was carried out to obtain a large surface area in order to maximally absorb pollutants in wastewater. The activation was done using chemical activation with NaOH activator, the use of NaOH is based on the research conducted by Bakalar Thomas et al. (2018) that which has stated that natural zeolites originating from the Manisa-Demirat area (Turkey) and their modifications using NaOH were also used For for manganese removal, the maximum adsorption

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capacity was obtained within the zeolite treated with 1.5 mol L^{-1} NaOH (Grabowska et al_z, 2016). The functional NaOH concentration not only caused a reduction in absorption capacity but also caused a significant deformation in the zeolite structure.

Researchers activated zeolite and activated carbon chemically, because based on the research by Suryani (2018), chemical activation has advantages over physical activation because the temperature used is lower than physical activation carbon time runs faster because the carbonization and activation processes can run simultaneously, and a wider activated carbon surface area is obtained. The activation process on activated carbon can increase the absorption capacity of phenol. 16. This is due to the surface of the active group on the activated carbon, the active groups include the oxide group, the oxide group is formed due to chemical adsorption between the surface of the activated carbon and oxygen in the air thus, it can bind phenol, within the existing hydroxyl group structure in the phenol that can be bound by the carbon surface (Mubarokah, 2010).

The <u>reduction of phenol</u> levels <u>reduction</u> was also caused by the adsorption process. Adsorption is a physical process and/or chemical process in which a substance accumulates on a surface. The substance that is transferred from the liquid phase to the surface is called the adsorbate and the solid phase in this process is known as the adsorbent. Physical adsorption is relatively non-specific and is caused by weak intermolecular forces. Chemical adsorption is also based on electrostatic forces, but with stronger forces in the process. In chemical adsorption, the attraction forces between the adsorbent and the adsorbate are caused by covalent bonds or electrostatic forces between atoms (Ramirez et al., 2018).

Among the three variations of the media thickness, the highest percentage reduction was obtained in the 80 cm variation thickness of zeolite adsorbent media and activated carbon activated by NaOH, with a contact time of 60 minutes, with an 89% of reduction. This is in accordance with the research conducted by Mubarokah (2010), the most optimum reduction in phenol levels were found in the adsorbent media zeolite and activated carbon thickness of 80 cm with a percentage reduction of 75.69%, which resulted in 2₇₂03 mg/L of phenol level after treatment from 8.37 mg/L. Besides, the research conducted by Arief (2014) using activated carbon from Kluwak shell with a mass of 1 gram and potassium oxide activator (KOH) is provenproved that it can to reduce the phenol levels in wastewater with an efficiency of 91₇₂97%. Similar to the research conducted by Siregar (2021), natural zeolite that has been activated by CTABr (Centhyl Trimethyl Ammonium Bromide) compound were able to adsorb phenol in wastewater with an initial concentration of 80 ppm and a contact time of 120 minutes, that which resulted in adsorption capacity of 3,424 g/mg. Dalang (2016) has also proven that zeolite can be used as an adsorbent, because it can adsorb phenol with an initial concentration of 282-658 ppm using 25 grams as the most optimum dose of zeolite, resulting in a percentage reduction of 68% in the phenol level.

The manganese level examinations results of the NDT wastewater

Table 5. The manganese level examinations results of the NDT wastewater before and after treatment using zeolite and activated carbon as adsorbent media at Y industry in June 2021

Based According to on table 3, the media thickness variation of 40 cm, 60 cm, and 80 cm, resulted in the average manganese level of $0_{\overline{a}}10$ mg/L after the given treatment from $0_{\overline{a}}26$ mg/L before treatment, average manganese level of $0_{\overline{a}}06$ mg/L after the given treatment from $0_{\overline{a}}26$ mg/L before treatment, and average manganese level of $0_{\overline{a}}05$ mg/L from $0_{\overline{a}}26$ mg/L before treatment, respectively.

Table 6. The manganese level reduction difference results of the NDT wastewater PT. Y before and after treatment using zeolite and activated carbon as adsorbent media at Y industry in June 2021

According to Based on table 4, the reduction difference of the manganese levels in Industry Y's NDT wastewater for media thickness variation of 40 cm, 60 cm, and 80 cm resulted in the average manganese level reduction difference of 0, 16 mg/L, 0, 20 mg/L, and, 0, 21 mg/L, respectively.

The reduction in manganese levels can be caused by the use of adsorbent media in the form of zeolite and activated carbon. Zeolite has a high capacity as an absorbent. This is because zeolites can separate molecules based on the size and configuration of the molecule. The Aadsorption mechanisms that may occur are physical adsorption (involving Van der Waals forces), chemical adsorption (involving electrostatic forces), hydrogen bonding, and the formation of coordination complexes (Tarigan, 2020).

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This is in line with the research conducted by Tarigan (2020) which has proven that phosphoric acid-activated zeolite can adsorb manganese in water with an adsorbent dose of 0.3 grams and a contact time of 30 minutes, which resulted in an adsorption capacity of 29.737 g/mg; thus, it has the reduction efficiency of 88,68%. Similarly to the research conducted by Fuad et al. (2018) which has proven that the effective reduction in the level of Mn(II) ion with the addition of 1.00% w/v Zeolite ZSM-5 powder for 30 minutes at a variety of pH 4 with initial levels of Mn (II) 49.91 ± 0.24 ppm to 0.53 ± 0.02 ppm, has resulted in a percentage reduction of $98.95 \pm 0.05\%$.

Coconut shell charcoal acts as an adsorbent to absorb heavy metals by absorbing free ions in the water including manganese, thus, the charcoal shell is often used as charcoal or activated carbon. Activated carbon is a material in the form of amorphous carbon which mostly consists of free carbon and has good adsorption capacity. Activated carbon is used as a bleaching agent (dyest remover), gas absorber, and metal absorber (Kurniawan & Risiana, 2009). Activated charcoal contains cellulose. According to Li et al. (2016), the presence of an OH group in cellulose [$C_6H_{10}O_5$] results in polar properties of the adsorbent, thus cellulose is stronger in adsorption of polar substances than those that are less polar. The Cellulose contained in activated carbon determines the adsorption ability, cellulose is composed of carboxyl (-COO-) and hydroxyl (-OH) groups.

Activation on zeolite and activated carbon as adsorbent media was carried out to obtain a large surface area in order to maximally absorb pollutants in wastewater. The activation process carried out in this study was done using chemical activation with a NaOH activator. According to Suryani (2018), chemical activation has advantages over physical activation because the temperature required during the process is is lower than on physical activation, besides, the chemical activation time runs faster because the carbonization and activation processes can run simultaneously, and a wider surface area of activated carbon is obtained. The use of NaOH activator is based on the research conducted by Fitriani (2015) which states that the use of NaOH activated bagasse at a bed depth variation of 20 cm with a flow rate of 5 ml/minute can set asidedecrease the manganese levels in water by 95.7%.

The reduction in manganese level was also caused by the adsorption process. Adsorption is a process that occurs when a fluid, liquid or gas, is bound to a solid or liquid which will eventually form a thin layer or film on its surface. According to Susilawati et al. (2019), the adsorption mechanism that occurs between the positively charged -OH group bound to the metal ions exchange is an ion-exchange mechanism. The interaction that occurs between the –OH group and metal ions is possible through the mechanism of a complex coordination formation of an ion, because the oxygen atom in the –OH group has a lone pair of electrons. Mn^{2+} ions will interact strongly with anions that are strong bases, such as –OH. The bond between Mn^{2+} ions with –OH in polysaccharides is formed through the coordination bonds. Where The lone pair of electrons from O on OH will bind to Mn^{2+} metal ions forming complex bonds through covalent bonds.

Among the three variations of the media thickness, the highest percentage reduction was obtained in the 80 cm variation thickness with 80% of reduction. This can be caused by one of the factors that affect adsorption, which is the surface area. The larger the surface area of the adsorbent, the more substances are adsorbed. The surface area of the adsorbent can also be determined by the particle size and the amount of adsorbent. Usyauqiah, 2011). This is in line with the research conducted by Ratna (2019), the most optimum reduction in the manganese levels is found in the 70 cm thickness of natural zeolite adsorbent media and 20 cm thickness of activated carbon with a debit of 0.5 liter/minute, resulting in 63% reduction. In addition, a study by Purwonugroho (2013) has stated that the manganese levels in community wells can be reduced by using 60 cm thickness of zeolite and activated carbon media, which resulted in an efficiency reduction of 77%.

Based On the basis of theon bivariate data analysis using the Kruskal-Wallis test, it showed that there was no significant difference between media thickness variations of 40 cm, 60 cm, and 80 cm in reducing the manganese levels in the NDT wastewater because the asymptotic significance value is greater than alpha (0.644 > 0.05). This is also due to the small number of samples used in this studstudy, causing the data distribution to be uneven and abnormal. However, based on the amount of reduction, the combination of

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zeolite and activated carbon as absorbent media are was shown to be effective in reducing the manganese level in NDT wastewater.

CONCLUSIONS

Based On the basis of on the research, the average phenol levels after the given treatment at a thickness of 40 cm, 60 cm, and 80 cm were 0.98 mg/L with a percentage reduction of 63%, 0.59 mg/L with a percentage reduction of 77%, and 0.27 mg/L with a percentage reduction of 89% respectively. Meanwhile, the average manganese level after the given thickness treatment of 40 cm, 60 cm, and 80 cm was 0.10 mg/L with a percentage reduction of 61%, 0.06 mg/L with a percentage reduction of 76%, and 0.05 mg/L with a percentage reduction of 80% respectively. The most effective adsorbent media thickness of zeolite and activated carbon in reducing phenol and manganese levels in the NDT wastewater of Industry Y is at an 80 cm thickness.

The suggestions for further research can be done by conducting the research studies on the saturation conditions of the zeolite and activated carbon media in phenol and manganese levels adsorption with a continuous flow system, thus, the research can be applied in the field.

Acknowledgements

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Effect of Zeolite and Activated Carbon Thickness Variation as Adsorbent Media in Reducing Phenol and Manganese Levels in Wastewater of Non-Destructive Testing Unit

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ABSTRACT

The production wastewater contains phenol from the Non-Destructive Testing (NDT) unit because it uses solvents; meanwhile, the manganese originates from the metal material washing process. On the basis of laboratory test results, the wastewater originating from the NDT unit of Y Industry, resulted in a phenol level of 2.33 mg/L, exceeding the quality standard of 0.5 mg/L and manganese level of 14.13 mg/L that exceeded the quality standard of 2 mg/L, based on the Regulation of the Minister of the Environment Number 5 of 2014 concerning Wastewater Quality Standards. This research used the pretest-posttest experimental research design without control. The sample in this study was wastewater from the NDT unit of the Y Industry. The average phenol level after passing through the adsorbent media at a thickness of 40 cm, 60 cm, and 80 cm resulted in 0.99 mg/L with 63% reduction, 0.60 mg/L with 77% reduction, and 0,28 mg/L with 89% reduction, respectively. The average manganese level after passing through the adsorbent media at a thickness of 40 cm, 60 cm, and 80 cm resulted in 0.10 mg/L with 61% reduction, 0.06 mg/L with 76% reduction, and 0,05 mg/L with 80% reduction, respectively. The most effective thickness variation in reducing the phenol and manganese levels of NDT wastewater is 80 cm thickness.

Keywords: NDT wastewater, adsorption, zeolite, activated carbon, phenol, manganese.

INTRODUCTION

Industrial wastewater is all types of wastewater originating from the by-products of an industrial process. Depending to the source, the liquid waste produced by the industry is an outcome of various industrial activities processes, such as materials processing, sanitation activities from the bathroom, cooling water waste from the engine cooling system, waste from boilers (boiler), and waste originating from the material cleaning process (Siagian, 2016).

On the basis of the laboratory examinations results, the quality outcome of the wastewater generated from the NDT Waste Water Treatment Plant (WWTP), there are still several quality standard parameters that have not met the requirements. Several parameters in the NDT wastewater that did not meet the requirement were phenol with an initial level of 2.33 mg/L, while the quality standard was 0.5 mg/L and manganese with an initial concentration of 14.13 mg/L, while the quality standard was 2 mg/L.

The source of phenol in the NDT wastewater comes from the solvent used. This is according to the the fact that ethanol is a polar solvent; thus, this solvent is oftenly used to identify flavonoid compounds. Flavonoid compounds are one of the phenol derivative compounds, hence, there is a linkage between the use of solvents and phenol levels in wastewater (Suhendra et al., 2019). Meanwhile, the source of manganese in NDT wastewater comes from the washing process of materials made of metal. This is because manganese is widely used in the iron-steel smelting and metal processing industries. Generally, manganese is used as an alloy for the manufacturing of stainless steel and alloys, In this case, the use of manganese aims to increase its strength, hardness, and resistance (Safitri, 2016).

Phenols are organic compounds found in the wastewater discharged from various industries such as petrochemical refineries, pharmaceuticals, coal processing, resins, polymers, pesticide industries and so on (Sun et al., 2019). Phenol in low concentrations can cause high toxicity and is considered as one of the most dangerous compounds. Phenol exposure can have serious effects on humans, be it through inhalation, ingestion, or absorption of the skin, it's exposure can cause coma, convulsions, cyanosis, and can also cause liver, kidneys, lungs, and vascular system failures. Ingestion of 1 gram of phenol can be very lethal to humans (Zhang et al., 2016). Meanwhile, the presence of a small amount of manganese in the human body will not cause health problems, but in large quantities, it can accumulate in the liver and kidneys. It can also be toxic to the respiratory system. Exposure to high doses in a short time shows symptoms of obesity, skin disorders, skeletal disorders, changes in hair color, nervous system disorders, and digestive tract irritation. Water containing manganese will form deposits; hence, it can cause stains on white objects, odor and taste in drinking water, low or high water turbidity, and a brownish color on clothes (Sinambela, 2020). Hence, wastewater treatment is compulsory before discharging the wastewater to waterways or the sea.

Adsorption is one of the methods that can be applied to control the phenol and manganese pollution in wastewater. The adsorbent media used in the adsorption process are natural adsorbents, namely zeolite

and activated carbon. On the basis of the research conducted by Khalid (in Ramirez et al. (2017)) regarding the removal of phenol using four types of zeolites as adsorbents and the comparison of its adsorption properties with activated carbon. In this study, diluted phenol solution was used as a contaminant and adsorption was carried out in batch and continuous streams. The BEA zeolite contains silica with slightly higher adsorption capacity at low phenol concentration (1.6 g/L) compared to activated carbon. BEA zeolites containing silica are proved to be efficient as adsorbents that can be easily regenerated (Ramirez et al., 2018). Another study conducted by Abustan et al. (2017) reported that the use of activated carbon in granular form was more effective than the use of zeolite in eliminating manganese in water with a removal efficiency of 99.39 %. The highest manganese removal was achieved when the adsorbent dose was increased to 10 grams with a stirring speed of 200 rpm.

On the basis of the above, the researchers are interested in conducting the research on the thickness variations effect of zeolite and activated carbon media adsorbent in reducing phenol and manganese levels of NDT wastewater.

MATERIALS AND METHODS

This study used experimental research with a pretest-posttest design without control. The sample in this study was the effluent of wastewater produced at Y Industry. This study aimed to observe the process of eliminating phenol and manganese levels in production wastewater using zeolite and activated carbon as adsorbent media. The research tool design is as seen in Figure 1.

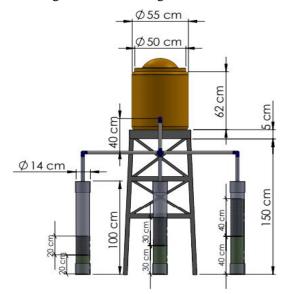


Figure 1. Filter Reactor

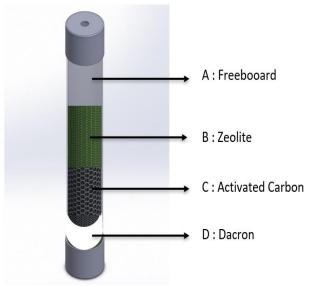




Figure 2. Filter Materials in Detail (this study)

Figure 3. Experiment Tool (this study)

The filter reactor contains zeolite and activated carbon media which are made in various media thicknesses, namely 40 cm, 60 cm, and 80 cm. The size of the zeolite used is 14-20 mesh and the activated carbon is 80 mesh.

In this study, 6 repetitions were carried out with 3 treatments. The pre-test was carried out by taking samples before the wastewater was contacted with the adsorbent media, while the post-test was carried out by taking samples that had been contacted with the adsorbent media. The test was carried out for 3 days with 2 repetitions each day. The number of samples in this study was 36.

RESULTS AND DISCUSSION

pH Measurement Results of NDT Wastewater

Table 1. The pH measurement results of NDT wastewater before and after treatment using zeolite and activated carbon as adsorbent media at Y industry in June 2021

	pH Measurement Results						
Repetition	40 cm Thickness		60 cm T	60 cm Thickness		80 cm Thickness	
F	Pre-test	Post-test	Pre-test	Post-test	Pre-test	Post-test	
1	7.18	7.18	6.99	7.57	6.71	7.95	
2	7.40	7.30	6.80	7.88	6.64	7.30	
3	7.12	7.76	6.39	7.85	6.71	7.92	
4	6.74	7.34	6.83	7.41	6.77	7.71	
5	6.54	7.91	6.67	7.91	6.79	7.95	
6	7.50	7.33	6.76	7.58	6.63	7.58	
Average	7.08	7.47	6.74	7.70	6.70	7.70	

]	pH Measuren	nent Results		
Repetition	40 cm Thickness		60 cm Thickness		80 cm Thickness	
533 F 13333	Pre-test	Post-test	Pre-test	Post-test	Pre-test	Post-test
Minimum	6.54	7.18	6.39	7.41	6.63	7.30
Maximum	7.50	7.91	6.99	7.91	6.79	7.95

On the basis of table 1, the media thickness variation of 40 cm, 60 cm, and 80 cm resulted in an average pH of 7.47 after the given treatment from 7.08 before treatment, average pH of 7.70 after the given treatment from 6.74 before treatment, and average pH of 7.70 after the given treatment from 6.70 before treatment, respectively.

The pH is a measure to determine the nature of acid or base. The pH is one of the factors that affect the adsorption process. On the basis on this research, there is a change in the pH of the wastewater after passing through the adsorbent medium of zeolite and activated carbon. The wastewater pH after passing through the media tends to rise compared to the wastewater that has not been passed through zeolite and activated carbon as the absorbent media. This is because activated carbon is an effective absorbent material and binds metal ions in solution. In the adsorption process, the metal elements in wastewater will be broken down into metal ions and hydroxide ions (OH-). The metal ions will be attracted to the activated carbon by the Van der Waals force, thus leaving the (OH-) ion behind.

The interaction between metal ions and activated carbon is that metal ions exchanged for the acidic functional group on the surface of activated carbon cause the (H+) ions to reduce. In addition to the activated carbon effect, zeolite as a filtration media also affects the increasing pH of the adsorption results. The wastewater that passes through the zeolite will be bound to the cations because of negatively charged properties of the zeolite to balance the ions, leaving the negative ions behind. The reduction of ions (H+) and the remaining ions left (OH-) in the adsorption results is the cause of the increase in pH level (Heriyani and Dan, 2016).

The Temperature Measurement Results of NDT Wastewater

Table 2. The temperature measurement results of NDT wastewater before and after treatment using zeolite and activated carbon as adsorbent media at Y industry in June 2021

	Temperature Measurement Results							
Danatitian	40 cm T	40 cm Thickness		60 cm Thickness		80 cm Thickness		
Repetition	Pre-test	Post-test	Pre-test	Post-test	Pre-test	Post-test		
	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)		
1	29	28	27	28	27	28		
2	28	29	28	29	28	29		
3	24	23	23	23	23	23		
4	23	24	23	24	23	24		

	Temperature Measurement Results							
Donatition	40 cm Thickness		60 cm Thickness		80 cm Thickness			
Repetition	Pre-test	Post-test	Pre-test	Post-test	Pre-test	Post-test		
	(°C)	(°C)	(°C)	(°C)	(°C)	(°C)		
5	23	24	23	24	23	24		
6	24	25	24	25	24	25		
Average	25	25	24	25	24	25		
Minimum	23	23	23	23	23	23		
Maximum	29	29	28	29	28	29		

On the basis of table 2, the media thickness variation of 40 cm, 60 cm, and 80 cm, resulted in an average temperature of 25°C after the given treatment from 25°C before treatment, an average temperature of 25°C after the given treatment from 24°C before treatment, and an average temperature of 25°C after the given treatment from 24°C before treatment, respectively.

On the basis of the research, the researchers measured the temperature of the wastewater before and after passing through the zeolite and activated carbon adsorbent media as supporting data. Temperature is one of the factors affecting the adsorption energy. When adsorbate molecules are attached to the surface of the adsorbent, there is a certain amount of energy released, classified as exothermic adsorption. When the temperature is low, the adsorption ability increases, as does the adsorbate (Putri, 2019). The results of this study indicate that the wastewater temperature before and after passing through the adsorbent media of zeolite and activated carbon varies according to the surrounding environmental conditions.

The Phenol Level Examinations Results of NDT Wastewater

Table 3. The results of phenol level examinations of NDT wastewater before and after treatment using zeolite and activated carbon as adsorbent media at Y Industry in June 2021

		Phenol	Level Exan	ninations Resu	ılts	
Repetition	Thickness 40 cm		Thickness 60 cm		Thickness 80 cm	
Repetition	Pre-test	Post-test	Pre-test	Post-test	Pre-test	Post-test
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
1	2.39	1.05	2.15	0.15	2.51	0.39
2	2.51	0.36	2.17	0.55	2.48	0.15
3	2.93	1.23	2.71	1.12	2.85	0.26
4	2.76	1.45	2.81	0.41	2.75	0.31
5	2.53	1.32	2.41	0.15	2.36	0.37
6	2.65	0.51	2.72	1.20	2.15	0.18
Average	2.63	0.98	2.50	0.59	2.52	0.27
Minimum	2.39	0.36	2.15	0.15	2.15	0.15
Maximum	2.93	1.45	2.81	1.20	2.85	0.39

According to table 3, the media thickness variation of 40 cm, 60 cm, and 80 cm resulted in the average phenol level of 0.98 mg/L after the given treatment from 2.63 mg/L before treatment, phenol level average of 0.59 mg/L after the given treatment from 2.50 mg/L before treatment, and phenol level average of 0.27 mg/L after the given treatment from 2.52 mg/L before treatment, respectively.

Table 4. The Phenol level reduction results of NDT wastewater before and after treatment using zeolite and activated carbon as adsorbent media at Y industry in June 2021

	The Phenol Level Reduction Results in Zeolites Thickness Variations						
Repetition	40 cm (mg/L)	60 cm (mg/L)	80 cm (mg/L)				
1	1.34	2.00	2.12				
2	2.15	1.62	2.33				
3	1.70	1.59	2.59				
4	1.31	2.40	2.44				
5	1.21	2.26	1.99				
6	2.14	1.52	1.97				
Average	1.64	1.90	2.24				
Minimum	1.21	1.52	1.97				
Maximum	2.15	2.40	2.59				

According to table 4, the reduction difference of phenol levels in Industry Y's NDT wastewater for media thickness variation of 40 cm, 60 cm, and 80 cm resulted in the average phenol levels reduction difference of 1,64 mg/L, 1,90 mg/L and, 2,24 mg/L, respectively.

The reduction of phenol levels happened due to the zeolite and activated carbon as the adsorbent media. According to Trisunaryanti, zeolites contain amorphous silica-alumina and crystalline mordenite that will have a good capability in absorbing wastewater pollutants when activated and modified. In addition, zeolite has a porous crystal structure with a large surface area (Atikah, 2016).

Activated carbon has a very large surface area of $1.95 \times 106 \,\mathrm{m}^2/\mathrm{kg}$, with a total pore volume of $10.28 \times 10^{-4} \,\mathrm{m}^3/\mathrm{kg}$ and an average of $21.6 \,\mathrm{\mathring{A}}$ pore diameter, enabling the activated carbon to absorb large amounts of the adsorbate (Achmad, 2018). On the basis of the research conducted by Lorenc-Grabowska et al.(2016) has stated that the main mechanism that determines the phenol adsorption process is the activated carbon particle size ranging from $0.8 \,\mathrm{to} \, 1.4 \,\mathrm{nm}$.

Activation on zeolite and activated carbon adsorbent media was carried out to obtain a large surface area in order to maximally absorb pollutants in wastewater. The activation was done using chemical activation with NaOH activator, the use of NaOH is based on the research conducted by Bakalar Thomas et al (2018) which has stated that natural zeolites originating from the Manisa-Demirat area (Turkey) and their modifications using NaOH were also used for manganese removal, the maximum adsorption capacity was obtained within the zeolite treated with 1.5 mol L-1 NaOH (Grabowska et al., 2016). The functional NaOH concentration not only caused a reduction in absorption capacity but also caused a significant deformation in the zeolite structure.

Researchers activated zeolite and activated carbon chemically, because based on the research by Suryani (2018), chemical activation has advantages over physical activation because the temperature used is lower than physical activation; besides, the chemical activation time runs faster because the

carbonization and activation processes can run simultaneously, and a wider activated carbon surface area is obtained. The activation process on activated carbon can increase the absorption capacity of phenol. This is due to the surface of the active group on the activated carbon, the active groups include the oxide group, the oxide group is formed due to chemical adsorption between the surface of the activated carbon and oxygen in the air; thus, it can bind phenol, within the existing hydroxyl group structure in the phenol that can be bound by the carbon surface (Mubarokah, 2010).

The reduction of phenol levels was also caused by the adsorption process. Adsorption is a physical process and/or chemical process in which a substance accumulates on a surface. The substance that is transferred from the liquid phase to the surface is called the adsorbate and the solid phase in this process is known as the adsorbent. Physical adsorption is relatively non-specific and is caused by weak intermolecular forces. Chemical adsorption is also based on electrostatic forces, but with stronger forces in the process. In chemical adsorption, the attraction forces between the adsorbent and the adsorbate are caused by covalent bonds or electrostatic forces between atoms (Ramirez et al, 2018).

Among the three variations of the media thickness, the highest percentage reduction was obtained in the 80 cm variation thickness of zeolite adsorbent media and activated carbon activated by NaOH, with a contact time of 60 minutes, with an 89% of reduction. This is in accordance with research conducted by Mubarokah (2010), the most optimum reduction in phenol levels were found in the adsorbent media zeolite and activated carbon thickness of 80 cm with a percentage reduction of 75.69%, which resulted in 2.03 mg/L of phenol level after treatment from 8.37 mg/L. Besides, research conducted by Arief (2014) using activated carbon from Kluwak shell with a mass of 1 gram and potassium oxide activator (KOH) is proven to reduce phenol levels in wastewater with an efficiency of 91.97%. Similar to the research conducted by Siregar (2021), natural zeolite that has been activated by CTABr (Centhyl Trimethyl Ammonium Bromide) compound were able to adsorb phenol in wastewater with an initial concentration of 80 ppm and a contact time of 120 minutes, that resulted in adsorption capacity of 3.424 g/mg. Dalang (2016) has also proven that zeolite can be used as an adsorbent, because it can adsorb phenol with an initial concentration of 282-658 ppm using 25 grams as the most optimum dose of zeolite, resulting in a percentage reduction of 68% in phenol level.

The Manganese Level Examinations Results of the NDT Wastewater

Table 5. The manganese level examinations results of NDT wastewater before and after treatment using zeolite and activated carbon as adsorbent media at Y industry in June 2021

		The Manganese Level Examinations Results						
Danling	Thickne	ess 40 cm	Thickness 60 cm		Thickness 80 cm			
Replica	Pre-test	Post-test	Pre-test	Post-test	Pre-test	Post-test		
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)		
1	0.27	0.12	0.27	0.02	0.27	0.01		
2	0.27	0.16	0.27	0.00	0.27	0.01		

	The Manganese Level Examinations Results						
D1:	Thickness 40 cm		Thickne	Thickness 60 cm		Thickness 80 cm	
Replica	Pre-test	Post-test	Pre-test	Post-test	Pre-test	Post-test	
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	
3	0.26	0.03	0.26	0.18	0.26	0.16	
Average	0.26	0.10	0.26	0.06	0.26	0.05	
Minimum	0.26	0.03	0.26	0.00	0.26	0.01	
Maximum	0.27	0.16	0.27	0.18	0.27	0.16	

According to table 5, the media thickness variation of 40 cm, 60 cm, and 80 cm, resulted in the average manganese level of 0.10 mg/L after the given treatment from 0.26 mg/L before treatment, average manganese level of 0.06 mg/L after the given treatment from 0.26 mg/L before treatment, and average manganese level of 0.05 mg/L from 0,26 mg/L before treatment, respectively.

Table 6. The manganese level reduction difference results of the NDT wastewater before and after treatment using zeolite and activated carbon as adsorbent media at Y industry in June 2021

Replica	The Manganese Level Reduction Difference Results in Zeolites Thickness Variations					
Керпси	40 cm (mg/L)	60 cm (mg/L)	80 cm (mg/L)			
1	0.15	0.25	0.26			
2	0.11	0.27	0.26			
3	0.23	0.08	0.10			
Average	0.16	0.20	0.21			
Minimum	0.11	0.08	0.10			
Maximum	0.23	0.27	0.26			

According to table 6, the reduction difference of the manganese levels in Industry Y's NDT wastewater for media thickness variation of 40 cm, 60 cm, and 80 cm resulted in the average manganese level reduction difference of 0.16 mg/L, 0.20 mg/L, and, 0.21 mg/L, respectively.

The reduction in manganese levels can be caused by the use of adsorbent media in the form of zeolite and activated carbon. Zeolite has a high capacity as an absorbent. This is because zeolites can separate molecules based on the size and configuration of the molecule. The adsorption mechanisms that may occur are physical adsorption (involving Van der Waals forces), chemical adsorption (involving electrostatic forces), hydrogen bonding, and the formation of coordination complexes (Tarigan, 2020).

This is in line with the research conducted by Tarigan (2020) which has proven that phosphoric acid-activated zeolite can adsorb manganese in water with an adsorbent dose of 0.3 grams and a contact time of 30 minutes, which resulted in an adsorption capacity of 29.737 g/mg thus, it has the reduction efficiency of 88,68%. Similarly to the research conducted by Fuad et al. (2018) which has proven that the effective reduction in the level of Mn(II) ion with the addition of 1% zeolite powder, for 30 minutes at a variety of

pH 4, with initial levels of Mn (II) 49.91 ± 0.24 ppm to 0.53 ± 0.02 ppm, has resulted in a percentage reduction of 98.95%.

Coconut shell charcoal acts as an adsorbent to absorb heavy metals by absorbing free ions in the water including manganese; thus, the charcoal shell is often used as charcoal or activated carbon. Activated carbon is a material in the form of amorphous carbon which mostly consists of free carbon and has good adsorption capacity. Activated carbon is used as a bleaching agent (dye remover), gas absorber, and metal absorber (Kurniawan & Risiana, 2009). Activated charcoal contains cellulose. According to Li et al (2016), the presence of an OH group in cellulose [$C_6H_{10}O_5$] results in polar properties of the adsorbent, thus cellulose is stronger in adsorption of polar substances than those that are less polar. The cellulose contained in activated carbon determines the adsorption ability, cellulose is composed of carboxyl (-COO-) and hydroxyl (-OH) groups.

Activation on zeolite and activated carbon as adsorbent media was carried out to obtain a large surface area in order to maximally absorb pollutants in wastewater. The activation process carried out in this study was done using chemical activation with a NaOH activator. According to Suryani (2018), chemical activation has advantages over physical activation because the temperature required during the process is is lower than on physical activation, besides, the chemical activation time runs faster because the carbonization and activation processes can run simultaneously, and a wider surface area of activated carbon is obtained. The use of NaOH activator is based on the research conducted by Fitriani (2015) which states that the use of NaOH activated bagasse at a bed depth variation of 20 cm with a flow rate of 5 ml/minute can set decrease the manganese levels in water by 95.7%.

The reduction in manganese level was also caused by the adsorption process. Adsorption is a process that occurs when a fluid, liquid or gas, is bound to a solid or liquid which will eventually form a thin layer or film on its surface. According to Susilawati et al. (2019), the adsorption mechanism that occurs between the positively charged -OH group bound to the metal ions exchange is an ion-exchange mechanism. The interaction that occurs between the -OH group and metal ions is possible through the mechanism of a complex coordination formation of an ion, because the oxygen atom in the -OH group has a lone pair of electrons. Mn²⁺ ions will interact strongly with anions that are strong bases, such as -OH. The bond between Mn²⁺ ions with -OH in polysaccharides is formed through the coordination bonds. The lone pair of electrons from O on OH will bind to Mn²⁺ metal ions forming complex bonds through covalent bonds.

Among the three variations of the media thickness, the highest percentage reduction was obtained in the 80 cm variation thickness with 80% of reduction. This can be caused by one of the factors that affect adsorption, which is the surface area. The larger the surface area of the adsorbent; the more substances are adsorbed. The surface area of the adsorbent can also be determined by the particle size and the amount of adsorbent; thus, when the number of adsorbents increases, more adsorbate will be absorbed by the adsorbent

(Syauqiah, 2011). This is in line with the research conducted by Ratna (2019), the most optimum reduction in manganese levels is found in the 70 cm thickness of natural zeolite adsorbent media and 20 cm thickness of activated carbon with a debit of 0.5 liter/minute, resulting in 63% reduction. In addition, a study by Purwonugroho (2013) has stated that the manganese levels in community wells can be reduced by using 60 cm thickness of zeolite and activated carbon media, which resulted in an efficiency reduction of 77%.

On the basis of the bivariate data analysis using the Kruskal-Wallis test, it showed that there was no significant difference between media thickness variations of 40 cm, 60 cm, and 80 cm in reducing the manganese levels in the NDT wastewater because the asymptotic significance value is greater than alpha (0.644 > 0.05). This is also due to the small number of samples used in this study, causing the data distribution to be uneven and abnormal. However, based on the amount of reduction, the combination of zeolite and activated carbon as absorbent media was shown to be effective in reducing the manganese level in NDT wastewater.

CONCLUSIONS

On the basis of the research, the average phenol levels after the given treatment at a thickness of 40 cm, 60 cm, and 80 cm were 0.98 mg/L with a percentage reduction of 63%, 0.59 mg/L with a percentage reduction of 77%, and 0.27 mg/L with a percentage reduction of 89%, respectively. Meanwhile, the average manganese level after the given thickness treatment of 40 cm, 60 cm, and 80 cm was 0.10 mg/L with a percentage reduction of 61%, 0.06 mg/L with a percentage reduction of 76%, and 0.05 mg/L with a percentage reduction of 80%, respectively. The most effective adsorbent media thickness of zeolite and activated carbon in reducing phenol and manganese levels in the NDT wastewater of Industry Y is at an 80 cm thickness.

The suggestions for further research can be done by conducting the studies on the saturation conditions of the zeolite and activated carbon media in phenol and manganese levels adsorption with a continuous flow system; thus, the research can be applied in the field.

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Conflict of interest

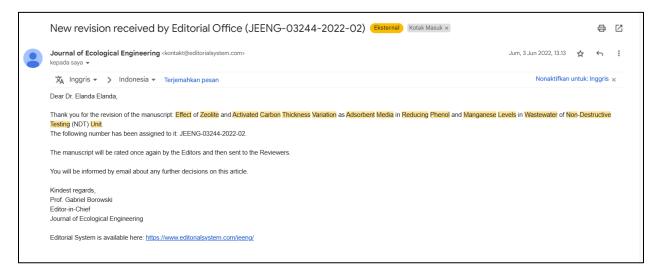
The Authors do not declare conflict of interest

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MENDAPATKAN NOTIFIKASI PENERIMAAN HASIL REVISI PAPER (3 JUNI 2022)



ACCEPTED (3 JUNI 2022)



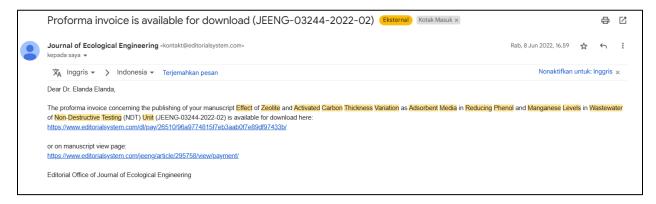
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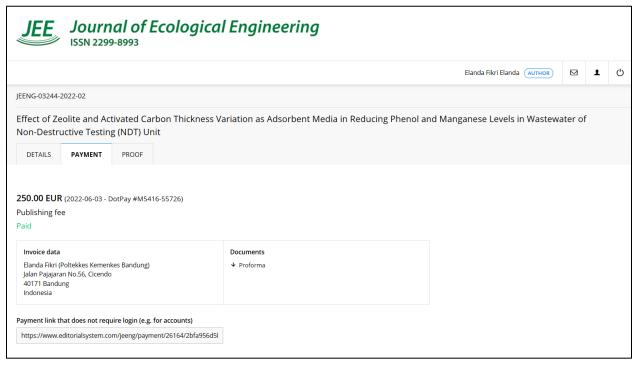


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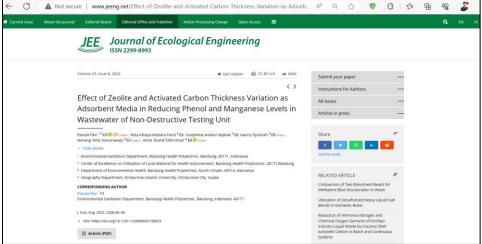


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vents; meanwhile, the manganese originates from the metal material washing process. On the basis of laboratory test results, the wastewater originating from the NDT unit of Y Industry, resulted in a phenol level of 2.33 mg/L, exceeding the quality standard of 0.5 mg/L and manganese level of 14.13 mg/L that exceeded the quality standard of 2 mg/L, based on the Regulation of the Minister of the Environment Number 5 of 2014 concerning Wastewater Quality Standards. This research used the pretest-postets experimental research design without control. The sample in this study was wastewater from the NDT unit of the Y Industry. The average phenol level after passing through the adsorbent media at a thickness of 40 cm, and 80 cm resulted in 0.99 mg/L with 63% reduction, a0.60 mg/S were fully with 77% reduction, a0.60 mg/L with 78% reduction, a0.60 mg/S were duction, a0.60 mg/S were duction, a0.60 mg/L with 78% respectively. The average manganese level after passing through the adsorbent media at a thickness of 40 cm, 60 cm, and 80 cm resulted in 0.10 mg/L with 61% reduction, a0.60 mg/L with 76% reduction, a0.60 mg/S reduction, a0.60 mg/S reduction, a0.60 mg/S reduction, a0.60 mg/S with 61% reduction, a0.60 mg/L with 76% reduction, a0.60 mg/S respectively. The most effective thickness variation in reducing the phenol and manganese levels of NDT wastewater is 80 cm thickness.

Keywords: NDT wastewater, adsorption, zeolite, activated carbon, phenol, manganese

INTRODUCTION

Industrial wastewater is all types of wastewater in grainsting from the by-products of an industrial process. Depending to the source, the liquid waste produced by the industry is an outcome of various industrial activities processes, such as materials processing, sanitation activities from the bathroom, cooling water waste from the engine cooling system, waste from boilers (boiler), and waste originating from the material cleaning process (Siagain, 2016).

On the basis of the laboratory examinations results, the quality outcome of the wastewater generated from the NDT Waste Water Treatment

Plant (WWTP), there are still several quality standard parameters that have not met the requirements. Several parameters in the NDT wastewater that did not meet the requirement were phenol with an initial level of 2.33 mg/L, while the quality standard was 0.5 mg/L and manganese with an initial concentration of 14.13 mg/L, while the quality standard was 2 mg/L.

The source of phenol in the NDT wastewater comes from the solvent used. This is according to the the fact that ethanol is a polar solvent; thus, this solvent is oftenly used to identify flavonoid compounds. Flavonoid compounds are one of the phenol derivative compounds, hence, there is a linkage