Regeneration of activated charcoal adsorbent in reducing Fe (III) and Ni (II) concentration by displacement method

E D Siswani, A Fillaeli*, S Kristianingrum, Sulistyani, PC Moneteringtys, IF Sani
Chemistry Study Program, Universitas Negeri Yogyakarta

*Email: annisa_fillaeli@uny.ac.id

Abstract. This research aimed at determining the regeneration ability of activated charcoal adsorbent from sea pandan leaves in lowering the heavy metal ions. The regeneration was needed to extend the adsorbent lifetime. The adsorbent was used to decrease concentration of Fe (III) and Ni (II) ions in electroplating industrial effluent. Regeneration was done by displacement method with doing adsorption and desorption consecutively in five cycles. Adsorption was carried out with metal ionic solution while desorption was carried out with HNO_3. Desorption filtrate were tested using UV-Vis spectrophotometer. The results showed that the activated charcoal from sea pandan leaves used to adsorb Fe ions can be regenerated whereas those used to adsorb Ni metal ions cannot be regenerated. Ni ions have a tendency to continue to be adsorbed but were difficult to be desorbed. The absence of Ni ions in the filtrate after desorption caused a correction factor on the UV-Vis spectrophotometer so that the results obtained were negative. The highest Fe ions in the first cycle reached 26.19% while the desorption efficiency of Ni ions was negative up to -111.84% or considered equal to 0%.

1. Introduction

Adsorption is a process of adsorbate accumulation (adsorbed substances) onto the adsorbent due to the attractive force between adsorbed material and solid molecules by physisorption or chemisorption (Astuti and Kurniawan, 2015). Research on the synthesis of activated charcoal derived from sea pandan leaves (*Pandanus tectorius*) yielded good material as adsorbent mainly for reducing Fe and Ni ions in the electroplating industrial effluent (Arista et al, 2009). It allows for large-scale exploitation of Sea pandan leaves. Additionally, the activated charcoal will become progressively saturated by adsorbed substances and lose their adsorption capacity. Moreover, people viewed the adsorption methods in treating wastewater contamination as leaving the hazardous solid waste (Pei-Jen Lu et al, 2011) therefore after-used adsorbent is considered to be tackled. The adsorbent regeneration is proposed as the solution to this so that the same adsorbent can be used for repetitive adsorption processes. In addition, regeneration of adsorbent also minimizes the generated waste because the adsorbent is used repeatedly and it is not directly disposable.

Regeneration is an attempt to reuse adsorbents. This will provide increased service life so that the potential for adsorbents that have been used for adsorption as waste can be prevented until the adsorbents are saturated. There are several types of methods for regenerating activated carbon such as chemical regeneration, thermal regeneration, microwave regeneration and biological regeneration (Yi

Li et al, 2018). Among this regeneration methods, thermal regeneration of activated carbon become a common practice in most industries. Relatively high operational costs and material losses of around 5-10% are reported as the main cause of disadvantages related to thermal regeneration (Asghar et al, 2019). In such laboratory where the optimization of regeneration method has limited evaluation, using chemical is best due to economical and practical reasons. The method using chemical regeneration called displacement method. Displacement is a way of regeneration with cleaning media that chemical reaction happens. The cleaning media is adsorbed to replace the adsorbed material. Desorption method can be done as a way to regenerate the adsorbent by pouring a solution in the form of a desorption agent with the adsorbent that has been used, so that the metals that have been set aside can be recovered and the adsorbent can be reused. In the displacement method, the acidic, basic, and neutral solutions can be chosen as the desorption agents (Indah and Rohaniah, 2014).

The acidic solutions such as H_2SO_4 was reported good in recovery process after 3 cycles although safe disposal of adsorbent has not been considered (Lata et al, 2015). In some interaction process, H_2SO_4 used leaved problems about raised SO_2 gas, so introducing HNO_3 as the substituent of regeneration agent is prominent. Nitric acid is also known as a good solvent for desorption while at the same time acting as an activator for the adsorbents that have been used because heavy metal ions have high solubility in it. In the desorption process, nitric acid plays a role in open the porosity wider because it eliminates carbonate residues left in pores. Further investigation become the focus in this research on finding the efficiency of using HNO_3 as the regeneration agent.

2. Experimental Sections

2.1 Adsorption

Two grams of activated charcoal, each was added by 100 ml Fe (III) and Ni (II) simulation solutions. The mixture was adsorbed for 24 hours using a shaker at a stirring speed of 90 rpm. The solution was filtered with paper and measured by UV-Vis spectrophotometer for Fe and Ni.

2.2 Desorption

To optimize concentration in desorption, a hundred ml HNO_3 solution was made with a concentration variation of 0.05 M; 0.5 M; 1 M; 2 M. Two grams of activated charcoal from adsorption processes was added to each HNO_3 in a beaker glass. Stir with a shaker for 60 minutes at speed of 90 rpm. The solution was filtered with filter paper and the filtrate was measured.On the other side, time optimization was done by adding 2 grams of activated charcoal that has been used for adsorption to the 1 M 100 mL HNO_3. The mixture were shaken at speed 90 rpm (Syauqiah, Amalia and Kartini, 2011) for 10, 30, 60 and 90 minutes. Then the mixture were filtered by filter paper. The filtrate obtained was tested using UV-Vis spectrophotometer.

2.3 Regeneration

Activated charcoal that has been used for adsorption is desorbed using 100 mL HNO_3 in batch at optimum HNO_3 concentration and contact time. Desorption results were filtered using filter paper. The activated charcoal that has been degraded is reused for the adsorption of 100 mL simulated solution. Adsorption is carried out for 24 hours. The mixture was filtered with filter paper and measured by UV-Vis spectrophotometer. The activated charcoal was desorbed again using 100 mL HNO_3. The adsorption-desorption steps were repeated minimum in 5 cycles.

3. Result and Discussion

Activated charcoal used was made from sea pandan leaves from Trisik beach Kulon Progo. The charcoal was activated by HNO_3 5% and succeed to accordance with some of requirements at INS 06-3730-1995 (Fatimah SD, 2018). Adsorption process in electroplating industrial effluent was studied by simulation solutions using batch system. The mass of adsorbent, contact time and the shaking speed optimum were 2 grams, 24 hours (Kristianingrum, 2014) and 90 rpm respectively in each 100 mL solution. (Isna Syauqiah, 2011).

Determination of concentration optimization of activated charcoal desorption aimed to determine the optimal concentration used for desorption of activated charcoal adsorbents. Based on the relationship curve between the concentration of HNO_3 and percent desorption showed that the optimum concentration of Cu ions desorption occurred at a concentration of 1 M HNO_3.

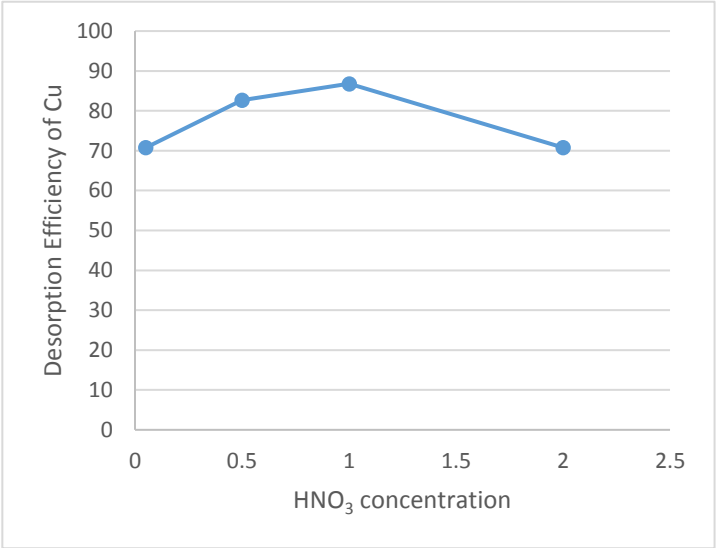

Figure 1. Curve of the optimation concentration in the activated charcoal desorption

On the other hand, the optimization of activated charcoal desorption time was to reach the efficiency of desorption process. The ions were maximally desorbed at a time of stirring 60 minutes and it followed by significant decrease of desorption in the next 30 minutes, 90 minutes. Logically, the longer the stirring time, the greater the ability of activated charcoal to bind the ions, so that more ions is released. However, the ability of desorption of porous material was liked adsorption, therefore table 1 data can be concluded that it had been released in amount adsorbates just like being saturated in adsorption process. The stirring time for 90 minutes has decreased, because in 60 minutes the pores in the activated charcoal become wide again. Widening of the pore on the activated charcoal causes the activated charcoal re-adsorb the removed ions. As a result, desorption process does not take place optimally in the next giving time. The figure indicated that the desorption processes for regenerating activated charcoal in using for reduce Fe(III) in the samples just needed 60 minutes.

Table 1. Data of Fe (III) adsorption-desorption processes in different contact time

Contact time of desorption	Adsorption			Desorption		
	Absorbance	concentration (ppm)	efficiency (%)	Absorbance	concentration (ppm)	Efficiency (%)
10 minutes	0.228	28.9268293	69.4487378	0.121	15.8780488	24.1468843
	0.230	29.1707317	69.1911386	0.117	15.3902439	23.4921817
	0.225	28.5609756	69.8351365	0.117	15.3902439	23.2755441
30 minutes	0.242	30.6341463	67.6455435	0.047	6.85365854	10.7006855
	0.244	30.8780488	67.3879443	0.049	7.09756098	11.1238532
	0.245	28.4390244	69.9639361	0.053	7.58536585	11.4506627
60 minutes	0.237	30.0243902	68.2895415	0.256	32.3424634	50.0188608
	0.245	31.0000000	67.2591448	0.255	32.2195122	50.5936423
	0.245	31.0000000	67.2591448	0.261	32.9512195	51.7426274
90 minutes	0.197	25.1463415	73.4415250	0.046	6.73170732	9.68081375
	0.201	25.6341463	72.9293266	0.046	6.73170732	9.74920523
	0.204	260000000	72.5399279	0.049	7.09756098	10.3338068

Activated charcoal was regenerated by immersing activated carbon in 1 M HNO3 solution for 1 hour. HNO3 was chosen as an activator because it is able to release Fe and Ni ions that have been absorbed by activated charcoal. The greatest desorption of Fe metal ions occurred in the first cycle. The small percentage of metal ions released by activated charcoal indicates that the metal adsorption mechanism that occurred is chemical adsorption. Whereas, the large percentage of ions released by activated charcoal can indicate that the adsorption mechanism through physical adsorption. The release of ions in the Fe (III) was very small, so it can be said that desorption of Fe (III) only occurred chemically.

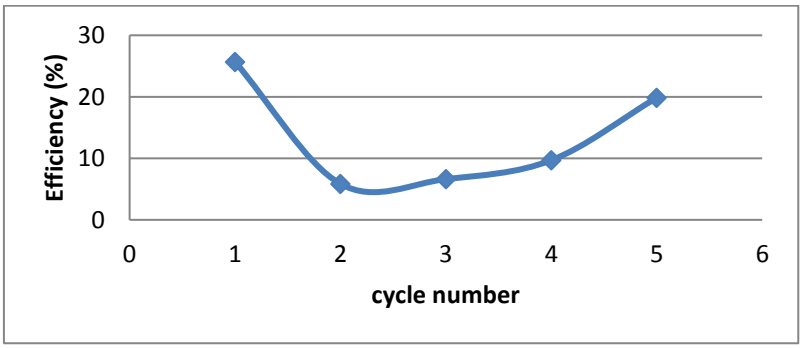

Figure 2. Curve of activated charcoal regeneration profile in several cycles

Fe ion has a tendency to continue to be adsorbed, it was predicted that in the next cycle the adsorption will stop when all pores of activated charcoal have been covered by Fe ions. However, Fe ions are difficult to be desorbed, so the efficiency of regeneration of Fe ion was small. The adsorption efficiency and desorption efficiency were directly proportional, meaning that the more Fe ions were absorbed, the greater of desorption efficiency or the more Fe ions released.

Different with adsorbent regeneration for reducing Fe ions, there was negative result for adsorbent desorption for Ni ions.

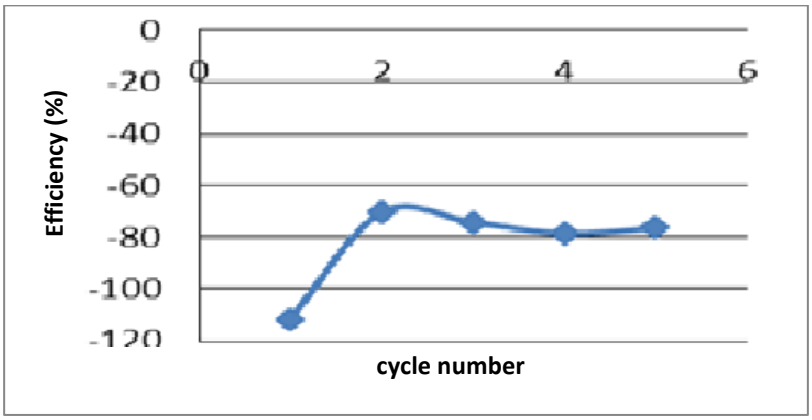

Figure 3. Activated charcoal desorption determination for Ni

Activated charcoal that was interacted to Ni ions cannot be degraded, but it has a tendency to continue to adsorb. This is possible because of the existence of pores that have not yet been closed, so that it can still be absorbed. Negative values generated by the spectrophotometer are caused by several factors, including pH and the color of the solution.

A very low pH causes a yellow ARS complex. At acidic pH, Ni ions would have a greater positive charge. The positive charge on the adsorbent is the basis of adsorption and exchange of metal anions at pH 2, because the negative charge of the metal will be bound to the H + ion in the adsorbent. A small ionic ion will more easily bond with an adsorbent surface because of its lower binding energy compared to a larger ionic valence (Larasati and Notodarmojo, 2014).

The colors that can be detected by a UV-Vis spectrophotometer must be stable and quite old. Long enough stability is needed for the accuracy of absorbance measurements. Instability causes fading or shrinkage of the solution caused by air oxidation, photochemical decomposition, type of solvent, and temperature. The color of the solution must be quite old, or the intensity is high enough to indicate that the solution has a large molar absorptivity. Each complementary color has its own wavelength region, respectively. The data relationship between complementary colors and wavelengths comprise the resulting color of the Ni-ARS adsorption filtrate complex shows purple, with a maximum wavelength of 560 nm, but the Ni-ARS desorption filtrate complex causes a yellow complex. Yellow color shows that the solution works at wavelength of 435-480, so that it becomes a correction factor for the spectrophotometer and causes negative result.

4. Conclusion

Regeneration of activated charcoal from sea pandan leaves for de-concentrating Fe ions has been successfully carried out while Ni ions have failed. Fe ions have a tendency to be easily absorbed by activated charcoal, but are not able to be released maximally by HNO_3 activators. Furthermore, Ni ions has a tendency to continue to be absorbed, but it is difficult to be released again, so desorption is negative. The highest efficiency of Fe ions desorption in the first cycle reached 26.1914804%. The desorption efficiency of the Ni ions is 0% because the Ni metal cannot be desorbed and causes a correction factor on the UV-Vis spectrophotometer.

5. Acknowledgement

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