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The Use of Immobilised Iron/Copper Bimetallic Nanoparticles for Rubber Wastewater Treatment

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The highly contaminated rubber wastewater (RWW) was the main obstacle for the rubber industry in Malaysia. Bimetallic nanoparticles have demonstrated outstanding performance in wastewater treatment attributed to the synergistic effect among the different metals. In this study, immobilised iron/copper bimetallic nanoparticles (nanoFeCu) were used to remove ammonia, organic matter, and total suspended solids (TSS) from RWW. The effect of the RWW flow rate on the treatment was studied using nanoFeCu packed column, and its long-term performance was validated under the optimum flow rate. The results showed that a lower flow rate (36 x 10^{-3} mLs^{-1}) favours the removal of ammonia (37 %), suggesting longer contact time is required. Meanwhile, a higher is desired for COD removal of RWW, where 115 x 10^{-3} mLs^{-1} was identified as the optimum flow rate. This suggested that the higher flow rate increased the mass transfer coefficient, which flavours the organic matter removal. Under the optimised flow rate, the nanoFeCu successfully removed 95.83 % of ammonia from RWW after 520 min. The final ammonia concentration in the treated RWW reached 25 mgL^{-1} in 9 h, which is close to the desired discharge value. Further research on the hybrid nanoFeCu-membrane separation treatment process is needed to deliver high-quality water that meets stringent standards.

1. Introduction

Malaysia is the seventh-largest producer and eighth-largest consumer of natural rubber in the world due to the high demand for rubber, particularly in the automotive industries. However, the rapid development in the rubber industry has generated a large amount of wastewater. It is estimated that 18 m^3 of rubber wastewater (RWW) is produced by 1 ton of natural rubber concentrated latex (Nguyen and Luong, 2012). It is estimated that 10.5 m^3 of latex-concentrated wastewater (LCWW) is generated from 1 ton of natural rubber latex concentrated (dry basis) processing (Nguyen and Luong, 2012). As the RWW is heavily polluted by various contaminants, proper waste treatment is necessary to mitigate the adverse effect on the environment. Most rubber factories have adopted conventional open pond wastewater treatment systems due to their simplicity and low cost. Nevertheless, the conventional system requires a large land area, has odour problems, and has a long treatment duration. Besides, the conventional treatment is unable to meet the increasingly stringent discharge standard, particularly total nitrogen and ammonia (Watari et al., 2017). For instance, the Department of Environment in Malaysia has imposed a more stringent effluent discharge requirement for plants processing raw rubber in the selected states as part of sustainability initiatives.

There are few advanced treatment methods for RWW. Biological treatment is simple and suitable for the treatment of nitrogen compounds in rubber industry wastewater however it requires a large installation area and a long retention time (Jasni et al., 2020). On the other hand, membrane treatment requires a small footprint, produces high-quality water, and low energy consumption, but membrane fouling is a major problem that hinders their widespread and large-scale applications. Whereas, chemical treatment, such as coagulation/flocculation and advanced oxidation processes, is less cost-effective and could lead to secondary pollution of water bodies (Mohammadi et al., 2010). Recently, many studies have proven that nanotechnology has significant potential as a nano-remediation strategy to remove nitrogen compounds from wastewater (Adam et al., 2019). The

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nanoparticles could be used as nano adsorbents to bind pollutants from rubber industry wastewater due to the abundant active sites (Teow et al., 2020). Ali et al. (2020) have produced nano zero-valent iron-supported acid-activated rice straw and successfully removed nitrate by 91.62%. However, adsorption has several disadvantages, including environmental impact due to the disposal of adsorbent, regeneration cost, and stability of the performance.

The use of iron/copper bimetallic nanoparticles (nanoFeCu) for ammonia removal was first studied by Chan et al. (2021), and the finding concluded that ammonia was removed via oxidation in the presence of nanoFeCu. The release of nitrogen gas, low concentration of nitrate and nitrite, and the raised pH of the solution confirmed the findings. An attempt was made to investigate the performance of nanoFeCu in sewage, which consists of a high concentration of ammonia. The ammonia concentration of sewage was treated to 4.8 mgL^{-1} from 22 mgL^{-1} in 6 h, while the BOD of the solution was reduced from 205 to 55 ppm (Chan et al., 2022). The COD of sewage was also reduced by 50 % after the sewage was treated with nanoFeCu. The quality of nanoFeCu-treated discharge complied with Malaysia sewage discharge standards. Besides, nanotechnology also demonstrated the benefits of a small carbon footprint and efficiency due to high reactive surface area. Hence, it was reasonable to conclude that nanoFeCu is a novel solution to the traditional nitrification and denitrification treatment. However, the use of nanoFeCu has not been studied for RWW treatment, which is also highly concentrated with ammoniacal nitrogen in the range of 300 to 600 mgL^{-1} (Isa, 2006) and total nitrogen in the range of 500 to 800 mgL^{-1} (Subhramaniyun et al., 2019).

The objective of this study was to evaluate the performance of immobilised nanoFeCu in treating RWW, in terms of ammonia, organic matter, and total suspended solid (TSS). The iFeCu was used to treat the RWW at varied flow rate conditions to identify the optimum flow rate. Once the optimum flow rate was identified, the experiment was repeated for a long period to determine the effect of contact time on the performance of iFeCu. The colour changes of iFeCu were observed using an optical microscope, which served as evidence of the oxidation reaction during the pollutant removal process.

2. Methodology

2.1 Materials

Iron (II) sulfate heptahydrate, $FeSO_4.7H_2O$ (Merck, Grade ACS) and ethylenediaminetetraacetic acid, EDTA (Fisher Scientific) were used as received. Sodium borohydride, $NaBH_4$ (Fisher Scientific, ≥ 98.5 %), ethanol (Fisher Scientific), copper (II) chloride dihydrate, $CuCl_2.2H_2O$ (Friendemann Schmidt, Grade AR), were supplied by Fisher Scientific (M) Sdn. Bhd. Commercial available Original Sculpey oven-bake clay was used as received. The rubber wastewater was collected at Mardec Industrial Latex Sdn. Bhd., Tapah, which produces latex concentrate and is kept at 4 °C (US EPA, 2006).

2.2 Experiment

2.2.1 Pollutants removal experiment

NanoFeCu was synthesised according to the method reported in the previous work (Chan et al., 2021), immobilised on polymer clay and moulded into a hollow cylindrical shape to enhance the effective surface area for reaction, labelled as iFeCu. iFeCu was regenerated in 1 M of Na_2CO_3 at 60 °C for 15 h before use.

The iFeCu with 4 g of nanoFeCu was packed into a column with a 50 cm length and flushed with nitrogen gas to remove excessive Na_2CO_3 on the surface of iFeCu. The pH of the RWW was adjusted from pH 4.24 to 7.05 by using 1 M of NaOH as nanoFeCu perform better in neutral pH compared to acidic condition (Chan et al., 2018). The RWW was filtered using the filter paper (filtraTECH 5 – 13 µm) to remove coarse particles and delivered to the column at varied flowrate in the range of 30 x 10^{-3} to 200 mLs^{-1} at a dosage of 12.5 mL RWW/g iFeCu. The quality of the RWW is presented in Table 1. The treated sample was collected at the exit point of the column and measured in terms of ammonia, pH, COD and TSS.

Table 1: The quality of RWW after pH adjustment and filtration

Parameters	Value
pH	7.00
Ammonia (mgL^{-1})	750
TSS (mgL^{-1})	62
COD (mgL^{-1})	8850

The ammonia concentration of the sample was measured using Ammonia Salicylate reagent and Ammonia Cyanurate reagent (Hach Method 10031). DR 3900 UV spectrophotometer was used to read the ammonia concentration and TSS of the samples. The pH of the testing solution was measured using a pH meter (Eutech

Instruments pH 2700). The COD of the samples were measured by using the Reactor Digestion Method via calorimetric determination (Hach Method 8000).
The image of the pure polymer clay, iFeCu and oxidised iFeCu was imaged using an optical microscope to record the colour changes of the materials.

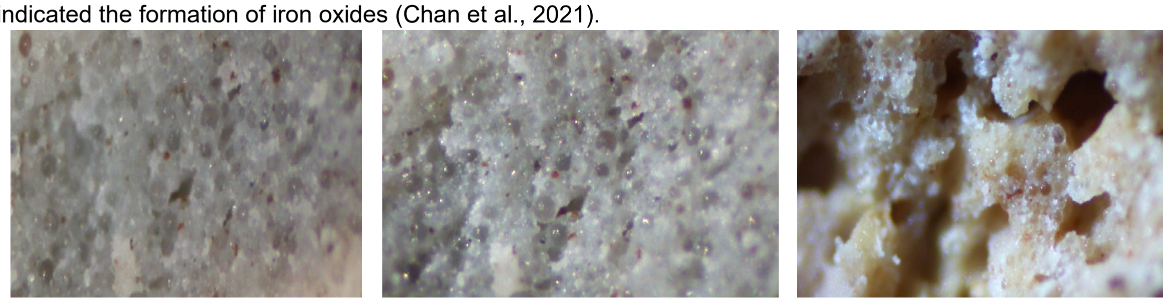
2.2.2 Long-term performance test

The column was equipped with a peristaltic pump to recycle the treated RWW at the optimum flow rate identified from Section 2.2.1 to the column until it is closed to the newly introduced discharge limit (Kamarulzaman and Mohamed, 2018). The pH and concentration of the ammonia were measured by using a multi-parameter water quality monitor (Model HY-T9050s). The nitrate and nitrite concentrations were measured using Nitrate NitraVer@5 Nitrate and NitriVer@3 Nitrite reagent powder pillows, respectively. A dosage of 37.5 mL RWW/g iFeCu was adopted in this study.

3. Result and discussion

3.1 The color changes of iFeCu

Figure 1 depicts the colour of pure polymer clay, iFeCu and oxidised iFeCu. The polymer clay, as shown in Figure 1 (a), was grey in colour, with numerous spherical shapes on the surface. No change of colour was observed after the nanoFeCu was immobilised to the polymer clay (Figure 1 (b)), as the nano-size of FeCu could not be observed by an optical microscope. Additionally, the nanoFeCu was well blended with the polymer clay, which made its natural blackish colour difficult to be observed at the magnification of 4x. However, a change of colour from grey to brown was seen in the oxidised iFeCu, as illustrated in Figure 1 (c), which indicated that the occurrence of ammonia oxidation process after the iFeCu was exposed to RWW, and the brown colour indicated the formation of iron oxides (Chan et al., 2021).



(a) (b) (c)

Figure 1: The image of (a) polymer clay (b) iFeCu (c) oxidised iFeCu, magnified at 4x using optical microscope

3.2 Effect of flowrate on the performance of iFeCu in pollutants removal

The effect of flow rate on the performance of iFeCu in removing ammonia and COD is illustrated in Figure 2. When the flow rate was increased from 36 x 10^{-3} to 200 x 10^{-3} mLs^{-1}, the ammonia concentration in the RWW increased. This indicated that the ammonia was oxidised (Chan et al., 2021) slower at the higher flow rate of RWW. The highest ammonia removal rate of 37 % was achieved at a flow rate of 36 x 10^{-3} mLs^{-1}. This suggested that a longer contact time between the iFeCu and ammonia was required to achieve a better removal rate. The ammonia removal rate of 37 % is comparable with the performance of an anaerobic digester, which was used to treat the wastewater from swine, rubber, seafood and palm oil factories (Nookwam et al., 2022). For instance, ~ 38 % of Total Kjeldahl Nitrogen (TKN) was reduced from the palm oil wastewater with a concentration of ~ 504 mgL^{-1} TKN. Similarly, ~ 4.6 % of TKN was removed from seafood industry wastewater which consisted of ~ 610 mgL^{-1} TKN.
On the other hand, the flow rate affects the organic matter in a different way, where the higher flowrate enhances the COD removal of RWW, as shown in Figure 2.115 x 10^{-3} mLs^{-1} was identified as the optimum flow rate to remove organic matter using iFeCu as it exhibited the lowest COD value of ~ 8,400 mgL^{-1}. This suggested that the higher flow rate increased the mass transfer coefficient (Hijjaji et al., 2021), which favours organic matter removal. The removal of COD could be due to the combined effect of adsorption and reductive reaction (Amen et al., 2018). Chan et al. (2022) also reported a similar finding where the immobilised FeCu nanoparticles reduced the COD of sewage from ~ 71 to ~ 40 mgL^{-1}.
The effect of flow rate on the TSS and pH of iFeCu-treated RWW is presented in Table 2. The TSS was within the range of 51 to 55 mgL^{-1}, slightly lower than the raw RWW, as iFeCu behaves as a flocculant (Dlamini et al., 2021). However, the flow rate did not contribute a great impact on TSS removal. Similarly, the pH of the treated

RWW was ~ 10, regardless of the adopted flow rate. The alkalinity of the treated RWW was due to the oxidation of ammonia. Ammonia was oxidised to nitrate and nitrite in the presence of oxygen, followed by the production of nitrogen gas in the presence of Fe^0. This reaction produces -OH, as reported in the previous study (Chan et al. 2021).

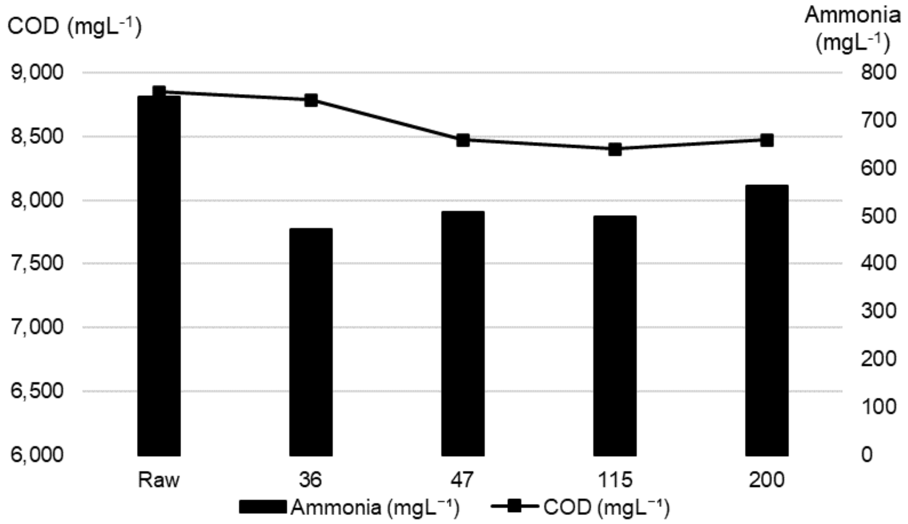


Figure 2: Effect of flowrate on the performance of iFeCu in terms of ammonia and COD

Table 2: TSS and pH data of iFeCu treated RWW at a varied flow rate

Q (x 10^{-3} mLs^{-1})	TSS (mgL^{-1})	pH
Raw	62	7.00
36	51	10.19
47	49	10.19
115	52	10.15
200	55	9.95

3.3 Effect of contact time on the performance of iFeCu in terms of ammonia

This section focuses on the effect of contact time on ammonia removal as the finding in Section 3.2 indicated that the selectivity of iFeCu is more towards ammonia, compared to COD and TSS. Figure 3 shows that the continuous removal of ammonia was observed as the contact time increased. 95.83 % of ammonia was removed at the end of the experiment. The final concentration of ammonia at the 9^{th} h was ~ 25 mgL^{-1}, which is very close to the desired discharge limit of 20 mgL^{-1}. The pH of the RWW was increased from 6.04 to 9.14 due to the release of -OH during the ammonia oxidation reaction. This finding is comparable with the anaerobic-aerobic method studied by Tanikawa et al. (2019) in treating synthetic natural rubber wastewater. The final discharge of the sample consisted of ~ 34 mgL^{-1} of ammonia for a hydraulic retention time of 11.8 h. Similarly, the ammonia removal rate of iFeCu was also comparable with the membrane-treated RWW (Kusworo et al., 2021), which was within 78 to 92 % (Kusworo et al., 2020). Besides, iFeCu also reduced the nitrate and nitrite content of raw RWW from 54 to 23 mgL^{-1} and 0.175 to 0.086 mgL^{-1}; as tabulated in Table 3. The TSS was reduced from 436 to 87 mgL^{-1}.

Table 3: Quality of RWW before and after treated with iFeCu

Parameter/Sample	Raw RWW	Final Discharge
Contact time (min)	0	540
pH	6.04	9.14
TSS (mgL^{-1})	436	87
NO_3 (mgL^{-1})	54	23
NO_2 (mgL^{-1})	0.175	0.086

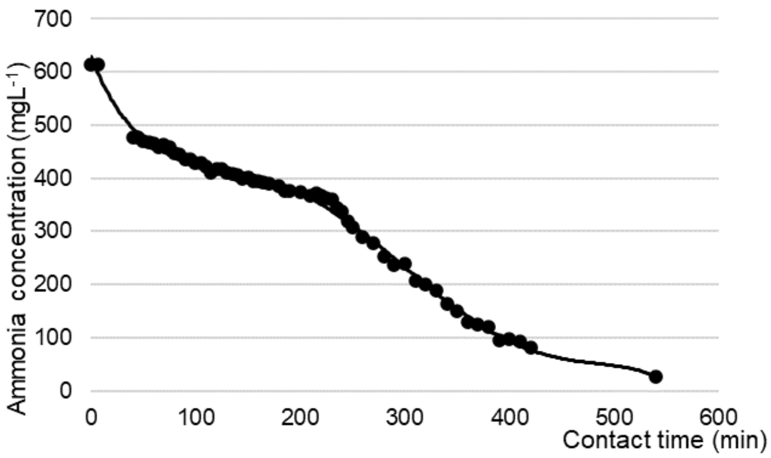


Figure 3: Effect of contact time on iFeCu treated RWW, in terms of ammonia

3.4 Limitations and recommendation

This study proved that iFeCu is a good alternative to treated rubber wastewater, especially in eliminating ammonia. The ammonia concentration of raw RWW was treated to ~ 25 mgL^{-1}, which was very close to the desired discharge limit in 520 min. However, the performance of iFeCu in removing COD needs to be enhanced due to the low selectivity of iFeCu to organic matter. Alternatively, a hybrid of the iFeCu-membrane separation treatment process could be considered as the membrane is a proven technology for COD removal (Yu et al., 2018).

4. Conclusions

This study investigated the performance of iFeCu in treating RWW by considering the effect of flow rate and contact time. The results showed that a low flow rate favours the ammonia removal and 36 x 10^{-3} mLs^{-1} waidentifiedfy as the optimum flow rate, which suggested that a long contact time was desired to reveal the actual performance of iFeCu. Under the optimised flow rate, the iFeCu treated the RWW to a final ammonia concentration of ~ 25 mgL^{-1} in 9 h, which is very close to the desired discharge value, and it is also comparable with findings reported in the literature. COD removal is relatively low in the iFeCu-treated RWW, thus research work has to be done to enhance the selectivity of iFeCu to organic matter.

Nomenclature

BOD – biochemical oxygen demand, -
COD – chemical oxygen demand, -
$CuCl_2.2H_2O$ – copper (II) chloride dihydrate, -
EDTA – ethylenediaminetetraacetic acid, -
$FeSO_4.7H_2O$ – iron (II) sulfate heptahydrate, -
iFeCu – immobilised iron/copper bimetallic nanoparticles, -
LCWW – latex concentrated wastewater, -
Na_2CO_3 – sodium carbonate, -
$NaBH_4$ – sodium borohydride, -
nanoFeCu – iron/copper bimetallic nanoparticles, -
NaOH – sodium hydroxide, -
NO_2 – nitrite, -
NO_3 – nitrate, -
Q - flowrate, m^3
RO – reverse osmosis, -
RWW – rubber wastewater, -
TKN – total kjeldahl nitrogen, -
TSS total suspended solid,

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