

# Treatment of Low-Strength Rubber Industry Wastewater Using a Combined Adsorbents and Membrane Technologies

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## Research

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# Abstract

The discharge of liquid waste from rubber industry poses a significant threat to human beings and environment; therefore, it ought to be addressed. Meanwhile, activated sludge technologies are usually used in Indonesia by this industry to handle liquid waste and tackle discharge issues. The combined adsorbents and hybrid membrane UF/RO were proposed in this study to decrease contaminants parameter of rubber industry wastewater (RIW). Furthermore, to achieve this goal three steps of treatments were applied in the current experiment. The first step is filtration using sand filter columns containing silica sand and activated carbon. In addition, the second stage is categorized by adsorption using three types of adsorbents, namely calcium carbide residue (CCR), coal fly ash (CFA) and bentonite. The third stage is separation process using adsorbents and UF/RO. This investigation was conducted using three types of adsorbents arranged in series configuration followed by UF/RO.

Results showed that combined adsorbent (CCR-CFA-bentonite) followed by UF/RO membranes increases the acidity of RIW from 4.70 to 7.28 with removal efficiency of turbidity, chemical oxygen demand (COD), biological oxygen demand (BOD), total suspended solid (TSS), ammonia-nitrogen (AN), and total nitrogen (TN) at 99.0, 88.1, 92.5, 89.5, and 67.5%, respectively.

The currently proposed method is advantageous because it does not require a long processing time or an intensive treatment area. This is applicable in rubber industries wastewater treatment process and is therefore an alternative method to active sludge technologies. In addition, final permeate RO are potentially used as clean water for rubber factory needs.

## 1. Introduction

Rubber trees (*Hevea brasiliensis*) are mainly cultivated in Southeast Asian countries especially Thailand, Indonesia, Vietnam, and Malaysia since the 19th century. These countries supply about 70 to 80% of the global natural rubber production. Furthermore, as second largest natural rubber producer worldwide, Indonesia supplied about 26% of natural rubber to the global market in 2013. Meanwhile, due to the rapid industrial and economic development, some changes in land usage occurred in middle 1980's and therefore large plantation were converted for industrial, commercial, and residential uses. In addition, large quantities of wastewater are presently produced by rubber processing factories in Asia and Africa, this discharge to soil and water bodies poses a lot of environmental danger [1–5].

Moreover, processing of natural rubber consumes a large quantity of water, in addition to some chemicals. The considerable amount of wastewater generated along with effluents are toxic and equally have strong colors, low pH, high suspended solids, temperature, chemical oxygen demand (COD), and biological oxygen demand (BOD) [5]. These characteristics have increased the importance of treating raw rubber processing wastewater before being disposed into water bodies. The liquid waste from this activity do not only contain high organic substances, but high nitrogen pollutants as well [6]. These, liquid

waste contains other components including organic matter especially sugar, protein, lipids, nitrogenous, and additional compounds specifically sulfates and heavy metals.

The conventional rubber industry wastewater (RIW) treatment facility needs a large processing area, due to time involved and odor factor. Furthermore, most factories have an open-type wastewater treatment systems due to the low operating costs and ease of maintenance [7]. Therefore, the environment ought to be protected through recycling and therefore a combination of two or more advanced treatment wastewater processes has been proposed [8–10]. The processing of RIW is currently done using conventional methods especially coagulation and ozonation [9], aerobic and anaerobic bacteria [11], adsorption and membrane technology [12–15]. This method has been replaced by membrane-based processes especially ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) which is known to be highly effective for water reclamation without consuming much chemicals.

A few studies to reduce the contaminant parameters of the RIW have notably been performed by researchers. The integration of NF membrane and evaporation technologies to treat rubber wastewater show that the use of retentate from NF has improved feed water and evaporators capacity with 55% reduced energy cost [8]. Meanwhile, application of aerobic granular sludge for RIW treatment was reported to have removal efficiencies of about 96.5% COD, 94.7% ammonia-nitrogen (AN) and 89.4% total nitrogen (TN) at the end of the granulation period [12]. Previous study have examined the treatment of RIW using pilot-scale up flow anaerobic sludge blanket (UASB) and downflow hanging sponge system combined with a baffled reactor in addition to settling tanks [14]. The results therefore indicated UASB reactors achieved a total removal efficiency of 39.0 to 72.2% for COD and 67.5 to 88.1% for BOD. In addition, the system proposed about 92% and 80% reduction of greenhouse gas emissions and hydraulic retention times respectively.

The application of direct contact membrane distillation in the RIW treated decreases total organic carbon (TOC), sulfate, color, turbidity, conductivity and TDS by almost 96% [16]. Previous study on the use of palm oil mill effluent (POME) for water reuse when combined with UF and RO membranes showed turbidity and BOD<sub>5</sub> were reduced by about 99% and 98.9%, respectively [17]. The final permeates of RO were noticed to comply with standards for water reuse. In addition, the combination of UF and RO method was concluded to be a viable alternative with great potential for use in palm oil industries.

A recent study shown when the RIW treated by sand filtration, cartridge filtration, UF, NF and then RO membranes successively produce the permeate was much better than biological treatment. The removal efficiencies of BOD and COD in this process exceeded 99%, while TN and AN were leveled at 93% [10].

The adsorption method is equally a prevailing technique for removal of contaminants from liquid waste due to the simplicity and effectiveness in treatment of industrial effluents. The increased number of publications on adsorption of toxic compounds by adsorbents, is a sign of enhanced interest in synthesis of new low-cost adsorbents for water treatment [18–26].

CCR is a solid waste product from acetylene production and popularly used as a raw material for polyvinyl chloride (PVC) synthesis where 1.5–1.9 tons of CCR was obtained while manufacturing 1.0 ton of PVC. This by product is also released by welding processes and mainly comprises calcium hydroxide, a highly alkaline ( $\text{pH} > 12$ ) substance [20],[27].

Meanwhile, CFA is a particulate by-product generated from coal combustion in power plants and often used as a construction raw material [28] due to the residue's chemical and mineralogical composition. The compound is a cheap and abundant aluminosilicate source for producing valuable pollutant adsorbents including zeolites, catalysts, photo-catalysts, and geo-polymers. Many studies have also identified these substances as efficient and cost-effective alternatives to remove aqueous and gaseous pollutants, as well as for mercury adsorption [24], radioactive-isotope and rare element separation [27], geo-polymer synthesis [29], acid mine drainage treatment [30], coking wastewater treatment [31], and crude oil purification (32). Furthermore, related research disclosed these CFA based materials were potential wastewater remediation adsorbents and membrane filters [27].

Bentonite is a volcanic ash clay comprising mainly montmorillonite (a smectite crystal with two tetrahedral silica sheets and a central alumina octahedral layer structure). The mineral may be used as a sorbent in waste water treatment with or without prior modification [19]. These chemical alterations are possible due to the surface water molecules plus exchangeable cation interlayer configuration [33] and are applicable in heavy metal cationic exchange including copper, tin, cadmium, zinc, and iron removal [21].

Therefore, this study's purpose is to combine these adsorbents with sand filter and a hybrid membrane UF/RO to decrease effluent COD, BOD, TSS, AN, TN, and turbidity levels as well as to increase pH and RIW quality.

## 2. Materials And Method

### 2.1. Materials

The main equipment for rubber industry wastewater treatment are sand filter (SF) and adsorbent columns with UF and RO membranes. A type 1054 fiber Reinforced Plastic (FRP) (fiber cylindrical tube with diameter 10 in and height 54 in) was used for SF and served as the adsorbents column. The SF column was filled by 45 kg of sand in the bottom and 10 kg active carbon on the top of column. Meanwhile, the UF module was a HM 90 commercial hollow fiber membrane (Molecular Weight Cut Off 50,000–150,000 DA and a 1 m<sup>2</sup> active membrane area) and the RO module was a spiral wound membrane CSM (Korea) type RF 4021–TE (active membrane area of 3.3 m<sup>2</sup>) [30].

The RIW sample ( $\pm 6000$  L) was obtained from a South Sumatra rubber factory, Indonesia, then placed into five 1200 L polyethylene tanks and subsequently pumped into the sand filter and adsorbent columns at a constant flowrate (5 L/min).

## 2.2. Method

The RIW samples were pumped at a constant 5 L/min feed rate into the SF, CCR, CFA and bentonite columns arranged in a serial configuration. These filtrates were then placed in separate 200 L polyethylene tanks. Subsequently, aliquots were collected with a beaker every fifteen minutes and analyzed. Furthermore, each adsorbent column output was fed to the UF and permeate was temporarily collected in the UF tank then pumped using RO high pressure pump to the RO membrane. The permeate from this process was collected at the reservoir tank, while the retentate was channeled into a 200 L plastic drum.

Figure 1 shows the columns' arrangement (CCR (4), CFA (5), and bentonite column (6), respectively). The results from this experiment were also compared with the wastewater treatment implemented in rubber factories including the active sludge, aerobic granular sludge, and anaerobic processes.

## 3. Results And Discussion

Table 1 shows the RIW sample characteristic, where the initial pH, COD, BOD, AN, and TN exceed the South Sumatra Governor Regulation No. 8/2012 permissible limits. However, these guidelines do not apply to turbidity, therefore the effluent was directly discharged into the river after all standard requirements were attained. The final COD content was observed to be lower than 10,000 mg/L) [8], hence, the RIW was categorized as low strength rubber wastewater.

Table 1  
Rubber industry wastewater characteristics

Parameter	Units	Results	Standard
pH	-	4.7	6–9
Turbidity	NTU	268	n.a
COD	mg/L	350	200
BOD	mg/L	280	60
TSS	mg/L	125	100
NH <sub>3</sub> -N	mg/L	9.5	5
TN	mg/L	18.0	10

### 3.1. Effect of sand filter and adsorbents on performance

#### 3.1.1. Acidity (pH) of filtrates

Figure 2 showed the effect of pretreatment time on the process, following the employment of SF, CCR, CFA, and bentonite in RIW pH alteration. The wastewater had an initial pH of 4.7 and increased to 6.5 after 90 minutes of operation due to the presence of active carbon in the SF column. The acidity was observed to increase slightly when CFA was used as the adsorbent, and the resultant pH of the column filtrate was within the range of 6.5–6.8. In addition, several results were obtained with the employment of CCR as the adsorbent and basicity was noted to vary from 8.5 to 9.8. The result revealed the greater pH-increasing power of CCR in comparison with bentonite and CFA. However, the values obtained exceeded the standard, and the rise in acidity was detected to be induced by the alkaline (pH > 12) property of CCR attributable to a predominant composition with calcium hydroxide [34]. The existence of activated carbon in the sand filter column also promoted the adsorption of acidic anions from the feed and further synergized this reaction.

Figure 3 illustrated the pH of the UF and RO residues and filtrates following the use of combined adsorbents. The combination of CCR, CFA and bentonite were able to elevate the acidity of the deposits and filtrates as observed from the membranes and adsorbents. This occurred as the supply device was relatively free of contaminants comprising heavy metal ions, as well as anions including nitrates, nitrites, and sulfides.

The filtrates from the adsorptive mixture had a pH between 7.1 to 7.3 revealing the combination of CCR, CFA and bentonite performed suitably in the RIW acidity neutralization, and also influenced the compliance of the final permeate.

### **3.1.2. Turbidity**

Turbidity refers to water or wastewater clarity evaluation prompted by the presence of suspended solids [35]. During membrane filtration, the dispersed particles initiate a flux decline in the membrane system [36], hence, pretreatment processes are necessary for cloudy liquids to prevent pollution and scaling on the membrane surface. The exclusion efficiency of pretreatment techniques and hybrid UF/RO on the RIW are displayed in Fig. 4, and the results demonstrated the capability of the SF to reduce the turbidity by 93-94.5% after a period of 90 minutes. The CCR, CFA, and bentonite columns therefore produced turbidity of 97%, 94.2% and 97.8%, respectively, while approximately 99% was eliminated by UF and RO.

The procedures showing the adsorbent employment are displayed in a series configuration in Fig. 5 and Fig. 6. In these experiments, the filtrates were withdrawn from the column (6) (Fig. 1), and the removal efficiency of AN during the study was observed to be higher compared to each adsorbent.

### **3.1.3. Chemical Oxygen Demand (COD)**

The COD was the major parameter considered in the wastewater treatment, and also represented the organic substances in the RIW. In addition, higher values were implicated in the production of odors, resulting from the low dissolved oxygen concentrations present in decomposing organic liquid waste matter. Figure 6 demonstrated the average COD removal efficiency to be 88.6% during CCR-UF/RO system use. This value was 89.3% while using the CFA-UF/RO method, and > 96% with the Bentonite-UF/RO

system. The simultaneous use of the combined adsorbents and UF/RO effectively diminished this parameter from 350.2 mg/L to 22.8 mg/L (93.4%).

### **3.1.4. Biological Oxygen Demand (BOD<sub>5</sub>)**

The BOD<sub>5</sub> signifies the amount of dissolved oxygen required by microbes, especially bacteria, to decompose organic matter under aerobic conditions. This phenomenon is an extensively applied factor for water quality assessment as information regarding the readily biodegradable organic fractions in water and wastewater are provided accordingly [37]. Figure 6 also showed the average BOD removal efficiency of CCR- UF/RO system to be 97.8%. However, the BOD was lower when CFA was used, and the CFA-UF/RO and bentonite-UF/RO systems were detected to decrease the average BOD by 94.8% and 93.8% respectively. The application of both adsorbent mixtures with UF/RO therefore, effectively diminished this parameter from 280.2 mg/L to 6.8 mg/L (97.57%).

### **3.1.5. Total suspended solids (TSS)**

The liquid waste from rubber industries contains high levels of TSS, and the effect of pretreatment using the sand filter and bentonite adsorbent columns on decreasing this component in RIW was shown in Fig. 6. The CCR, CFA, and bentonite modified the TSS values by 89.2, 93.1, and 97.6% consecutively, while the adsorbent blend followed by UF/RO depleted this parameter from 124.5 mg/L to 9.3 mg/L (92.5%). Meanwhile, the fairly diminished TSS efficiency was chiefly as a result of the adsorbent shielding by the suspended colloids in the sample.

### **3.1.6. Ammonia-nitrogen (NH<sub>3</sub>-N)**

Ammonia is implicated in several roles, including as a water pollutant, toxic substance, as well as a dangerous organic material. Therefore, high concentrations of AN in liquid waste triggers poisoning in the biota. The average quantity normally varies from 5 to 1000 mg/L in industrial wastewater and 10 to 200 mg/L in municipal liquid waste [38]. The initial strength of AN in the sample was 9.5 mg/L, and this value exceeded the standard established by the Governor of South Sumatra regulation No. 8/2012. The removal efficiencies of CCR-UF/RO technique were 67, 57.2, and 55.8%, respectively, and dissimilar results were obtained with CFA use. The removal efficiencies for CFA-UF/RO system were 87.4%, 98.4%, and 99.6%, while the bentonite-UF/RO system produced figures of 79.9%, 83.7%, and 89.5%, consecutively.

Figure 6 demonstrated the AN removal efficiency of 49.5%, 56.7%, 58.7% and 59.2%, respectively following an increase in contact time. However, the removal efficiencies were observed to decline after 90 minutes. It is similar to study of Seruga et al (2019) that the highest adsorption capacity of ammonium ions with the maximum removal efficiency (52.3%) was obtained for bentonite with a 0-0.05 mm particle size in 3 h of contact time [39]. Figure 6 also showed a decline in the average ammonia-nitrogen concentration from 9.5 mg/L to 3.4 mg/L (64.2%) produced by the application of the adsorbent combination and UF/RO.

### **3.1.7. Total Nitrogen**

TN concentration is one of the parameters known to affect water quality. Therefore, the removal is referred to as nitrification and denitrification in the wastewater treatment plant, including RIW where the activated sludge process is applied. The method termed eutrophication is known to reduce the effect of nitrogen compound in the water bodies. Figure 6. shows the outcome of pretreatment using sand filter and bentonite adsorbent column to decrease the TN. Furthermore, the efficiency for CCR-UF-RO systems were 72.1, 94.4, and 94.4%, respectively. These figures increase with the use of CFA as an adsorbent. The corresponding efficiency values were 88.9, 91.1, and 97.8%. However, bentonite-UF/RO system decreased the value to 76.1, 80.6, 94.4% respectively, while the TN reduced from 18 mg/L to 5.9 mg/L (67.5%) for the combined adsorbent.

### 3.1.8. Comparison with other processes

The RIW sample in the current experiment was provided by a rubber factory where the active sludge process was employed during liquid waste treatment. Table 2 illustrated a comparison between the present method and other treatment processes.

Table 2.

Removal efficiencies comparison of the combined adsorbents-UF/RO and another rubber wastewater treatment processes

Parameter	pH	Turbidity	COD	BOD	TSS	AN	TN
Processes		(%)	(%)	(%)	(%)	(%)	(%)
Adsorbents/ UF/RO	7.28	99.0	93.5	97.6	92.5	64.2	67.5
Active Sludge <sup>a)</sup>							
· January	6.70	n.a	91.5	95.9	91.8	84.6	86.4
· July	6.63	n.a	87.9	94.4	79.1	83.7	80.8
· August	6.60	n.a	87.7	97.5	92.2	57.8	82.4
· September	6.03	n.a	92.0	93.8	95.7	86.2	87.1
· October	6.53	n.a	82.3	82.7	70.0	83.1	94.7
· November	6.01	n.a	94.5	96.6	86.3	90.4	88.9
Average	6.41	n.a	89.3	93.5	85.8	80.9	86.7
Microphyte pond <sup>b)</sup>	n.a	n.a	85.5	90.6	n.a	n.a	n.a
UASB upflow anaerobic sludge blanket <sup>c)</sup>	n.a	n.a	72	90.1	98	n.a	82
Aerobic granular sludge <sup>d)</sup>	n.a	n.a	96.5	n.a	n.a	94.7	89.4
Bioremediation with <i>Athrobacter. sp</i> <sup>e)</sup>	n.a	n.a	79.4	72.1	75.7	71.3	n.a



a) average after six months of monitoring (January, July-November 2018). b) Owamah et al. (2015), c) Watari et.al (2016), d) Rosman et. al., (2013) e) Smitha et.al., (2012).

Furthermore, the conclusions derived from Table 2 showed the ability for adsorbents combined with UF and RO membranes to increase pH and reduce various RIW parameters. This proposed method has an advantage compared to the active sludge technology applied by most rubber industries in Indonesia, to ensure high removal of COD, BOD, TSS concentration. Consequently, filtrates are produced more clearly for utility in the internal needs of rubber factories, despite the lower removal efficiency of AN and TN.

## **3.2. Scanning electron microscope of adsorbents**

### **3.2.1. Calcium carbide residue**

The pores structure needs to be examined with SEM in attempts to explore the morphology of adsorbent surface.

Figure 7a illustrates CCR images at 10100x of magnification and Fig. 7b shows the SEM images of raw CCR with pore diameter between 0.39–0.86  $\mu\text{m}$ . The residue contains aluminum, silicon, calcium, magnesium, and some metal oxide impurities, consisting of copper, potassium, titanium and barium. In addition, calcium is possibly identified in the form of  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$ , known to be the main chemical component of CCR, while silicon, aluminum, and magnesium always appeared together. These existed in the form of silicates, including  $\text{Al}_2\text{SiO}_5$  and  $\text{MgSiO}_3$  [20]. Also, EDS spectrum showed the existence of sulfur compounds on the adsorbent surface after adsorption. This suggested the presence of sulfur compounds in the rubber wastewater is the result from a highly organic compound or protein retained in the latex processing, characterized by the rotten-egg smell. Therefore, CCR has the potential to remove odor caused by these chemicals in the wastewater. The EDS spectra in Fig. 8a and Fig. 8b, show raw CCR contain 82%  $\text{CaO}$  and 18%  $\text{Sb}_2\text{S}_3$ . Also, the presence of  $\text{Sb}_2\text{S}_3$  probably results from the welding process and other mechanical activities in the CCR sample location.

Figure 9a and 9b show the SEM images of bentonite at 10100x magnification reflect the morphological solid and dark-shape with a particle surface area between 5251.8  $\mu\text{m}$  and 6503.9  $\mu\text{m}$ . Figure 10a and Fig. 10b also illustrate the highest average content of EDS before and after use, comprising elements of silicon, aluminum, carbon and iron.

Table 3  
Bentonite compounds before and after adsorbing the cation from the RIW

Compound	Raw bentonite (% mass)	Adsorbed bentonite (%mass)
SiO <sub>2</sub>	55.60	62.57
Al <sub>2</sub> O <sub>3</sub>	28.92	25.56
MgO	2.06	2.40
CaO	3.07	1.52
Fe <sub>2</sub> O <sub>3</sub>	1.98	5.39
Na <sub>2</sub> O	0.32	-
O <sub>2</sub> F	5.64	-
ClO <sub>3</sub> <sup>-</sup>	0.06	-
K <sub>2</sub> O	1.89	1.10
TiO <sub>2</sub>	0.03	1.46
CoO	1.42	-

Table 3 shows the bentonite compound characteristics before and after cation adsorption from RIW. This indicates the raw form is dominated by silica, alumina, and iron with other impurities, encompassing magnesium, calcium, sodium, titanium, cobalt and potassium. Also, the substance is a nonmetallic clay mineral based on montmorillonite, while the lamellar structure of the crystal cell contains some cations, including Cu<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, etc. However, bentonite properly performs cationic contaminant adsorption by an exchange mechanism, because the particles are very unstable and easily replaced [21]. The EDS chromatogram of the compound demonstrates the cationic substitution of silicon, aluminum, and magnesium with those of the RIW.

### 3.2.1. Coal fly- ash

CFA is applied either directly or indirectly to adsorb heavy metals, along with organic and inorganic pollutants from wastewater. These contaminants include phosphorus, fluorides, boron, phenolic compounds, pesticide, dyes etc. CFA is usually categorized into high ( $\geq 10\%$  CaO) and low calcium fly ash ( $\leq 10\%$  CaO) according to the CaO content [23]. Increased adsorption capacity of this substance is related to a large surface area, pore volume, porosity and an elevated unburnt carbon content. The

morphology of CFA in Fig. 11a showed the presence of adhered superficial fragments indicating the competency as an adsorbent.

Fig,11b showed the SEM images of cenospheres, an important coal fly ash fraction. These CFA components are a mixture of aluminosilicate glasses with mullite and quartz crystalline phases [40]. The coal particles were noted to have experienced an acidic attack from compounds with pH of 4.7 in the RIW, capable of reacting with silicon and aluminum linkages contained in the CFA as the bond ratios are close to 1. Cenospheres are majorly composed of silica, alumina and iron oxides, and are extensively used due to the possession of unique properties including sphericity, inertness, lower densities than water, alongside water-resistance. Intensifications in the CFA surface aluminum concentration indicated the continuous use of alum instead of formic acid by numerous rubber farmers in South Sumatra, for the latex freezing process prior to factory transfer.

Table 4.

Energy Dispersive X-Ray of CFA

Element	Raw CFA (%)	Adsorbed CFA (%)
SiO <sub>2</sub>	54.41	3.06
Al <sub>2</sub> O <sub>3</sub>	39.57	67.36
NaO <sub>2</sub>	3.32	11.64
MgO	0.41	4.84
BaO	0.32	-
F <sub>2</sub> O	0.93	-
SeO <sub>2</sub>	0.01	-
In <sub>2</sub> O <sub>3</sub>	0.53	-
TiO <sub>2</sub>	0.50	-
Fe <sub>2</sub> O <sub>3</sub>	-	10.20
K <sub>2</sub> O	-	3.07

Table 4 showed the predominance of CFA contents by aluminum and silica and the presence of these elements were detected to increase the sensitivity of the residues to decreasing sample COD, BOD, TSS, AN, as well as TN by cationic exchange. The adsorbed CFA illustrated surges in oxygen and carbon percentages owing to organic substance absorption from the waste. According to [41], the solute binds to silanol (Si-O) groups from silica and OH groups from Al and Fe. Conversely, this value decreases for Al as

a result of the amphoteric nature, hence, the element functions as a base under acidic condition and increases the pH of the solution. CFA was therefore presumed to be useful as an adsorbent for wastewater treatment [42].

## 4. Conclusions

The decontamination of rubber industry wastewater through the use of sand filters in combination with three forms of adsorbents namely calcium carbide residue, bentonite, and coal fly ash followed by UF/RO membrane revealed the ability of these components to reduce the significant impurities present in the fluids to be processed.

1. Calcium carbide residue had a removal efficiency comprising 41.1% COD, 41.3% BOD, 22.9% TSS, 47.4% AN, and 94.4% TN, respectively. The filtrates from the residue produced pH values ranging from 8.5 to 9.5.
2. Bentonite column generated the removal efficiencies of 97% COD, 98.5% BOD, 97.3% TSS, 98.5% AN, 94.4% TN, and 88.7% turbidity, respectively and increased the acidity of the rubber industry wastewater from 4.7 to 6.9.
3. Coal fly ash had a removal efficiency of 99.2% COD, 98.9% BOD and 97.4% TSS, 99.8% AN, 97.7% TN, and 99% turbidity, respectively. The filtrate from the coal fly ash column had an approximate pH of 7.
4. The adsorbent combination together with UF/RO were able to cause reductions of 93.5% COD, 97.6% BOD, 92.5% TSS, 64.2% AN, 67.5% TN, along with 99% turbidity, and a consecutive increase in the acidity from 4.7 to 7.2 of the liquid waste.

Overall, the pilot scale designed for the treatment of RIW with the use of sand filters, adsorbent mixtures, and UF/RO employment is applicable in the acidity enhancement and contaminant depletion of rubber industry wastewater. All the adsorbents used were able to increase RIW acidity and the final RO filtrates accomplished water reuse standards.

## Declarations

### AVAILABILITY OF DATA

The data used to support the findings of this study are available from the corresponding author upon request.

### COMPETING INTEREST

The authors declare that they have no competing interests

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## **AUTHORS CONTRIBUTION**

Conceptualization and design of experimental, S.N., E.R.L.G., S.S., A.M., Collected the sample and data S.N., E.R.L.S., S.S., M.M., SN writing-original draft preparation, S.N., A.M. writing-review and editing, funding acquisition S.N.,

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## Figures

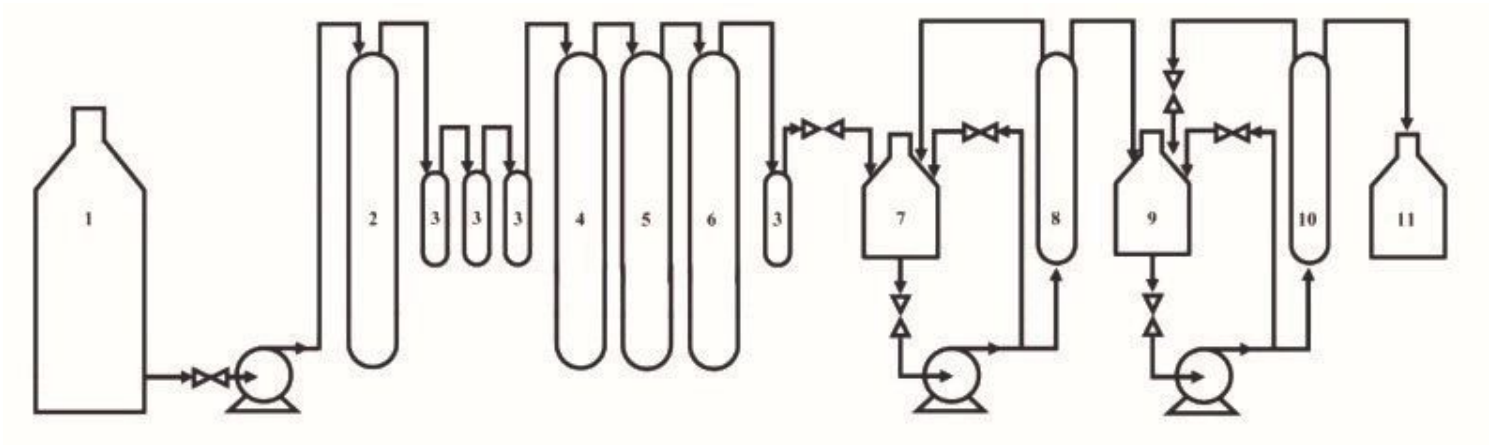


Figure 1

Wastewater treatment of rubber industry experimental set-up (1. The RIW tank 2. Sand filter column 3. Filter spoon 4. CCR column 5. CFA column 6. Bentonite column; 7. Storage tank 8. Ultrafiltration membrane module 9. Ultrafiltration storage tank; 10. Reverse osmosis module 11. RO permeate tank).

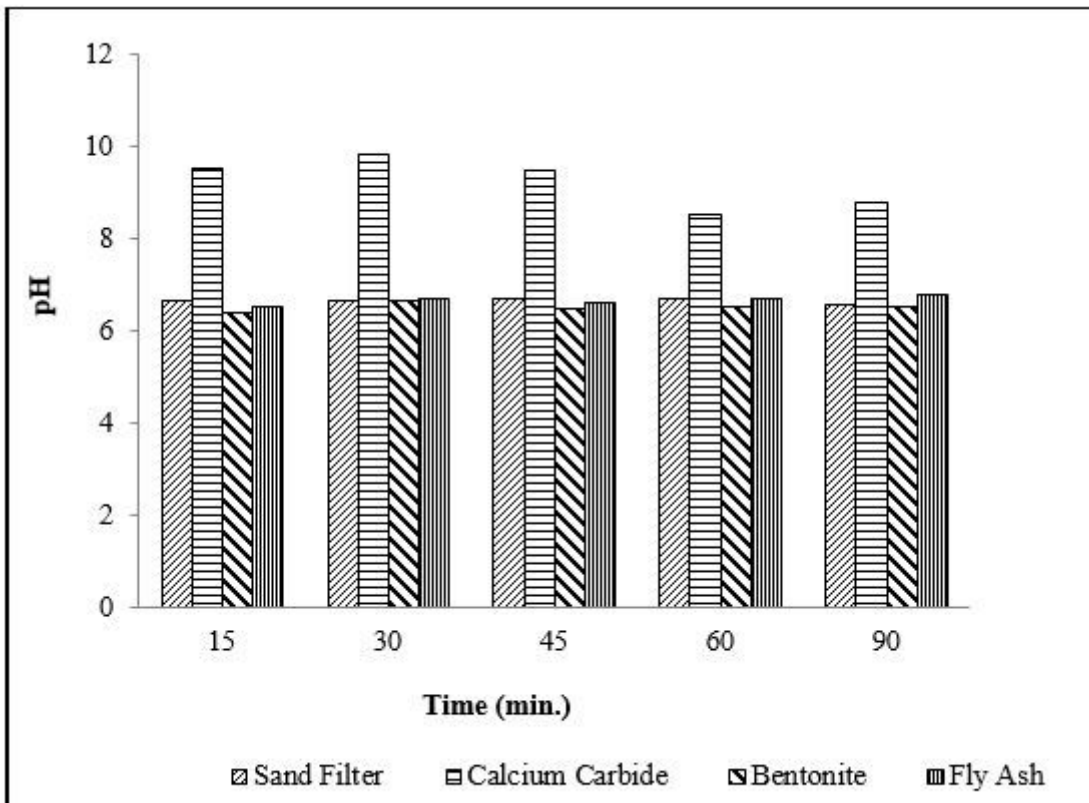


Figure 2



Change in pH for sand filter and different adsorbent

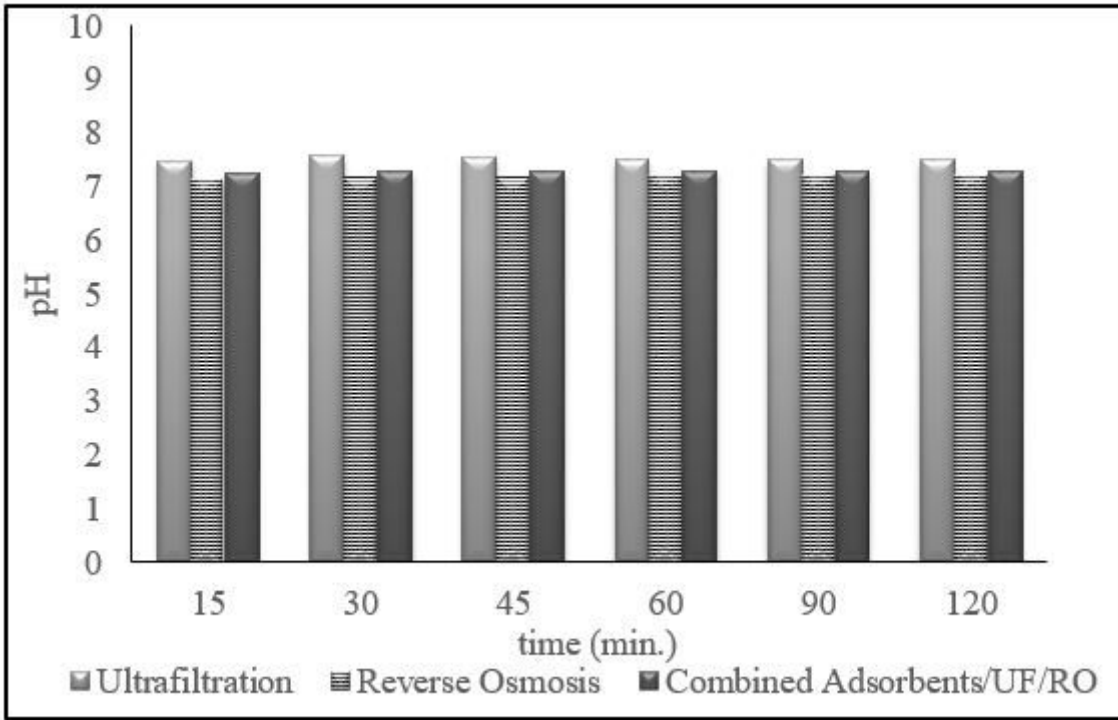
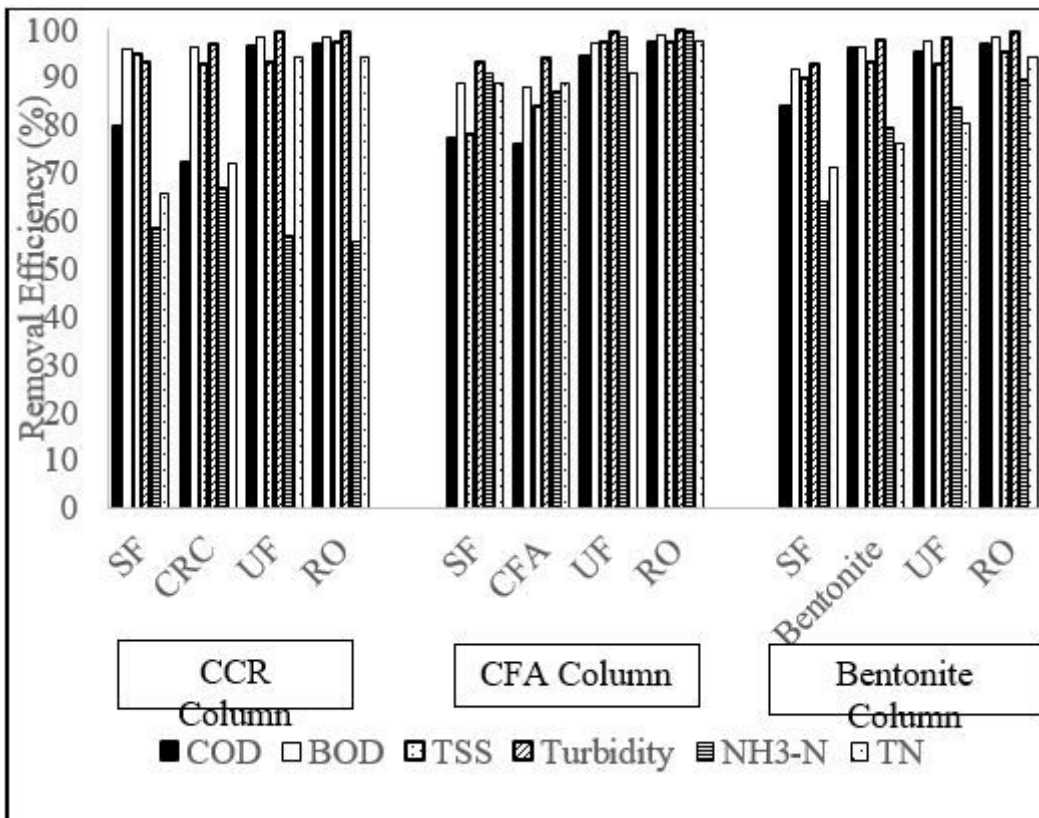


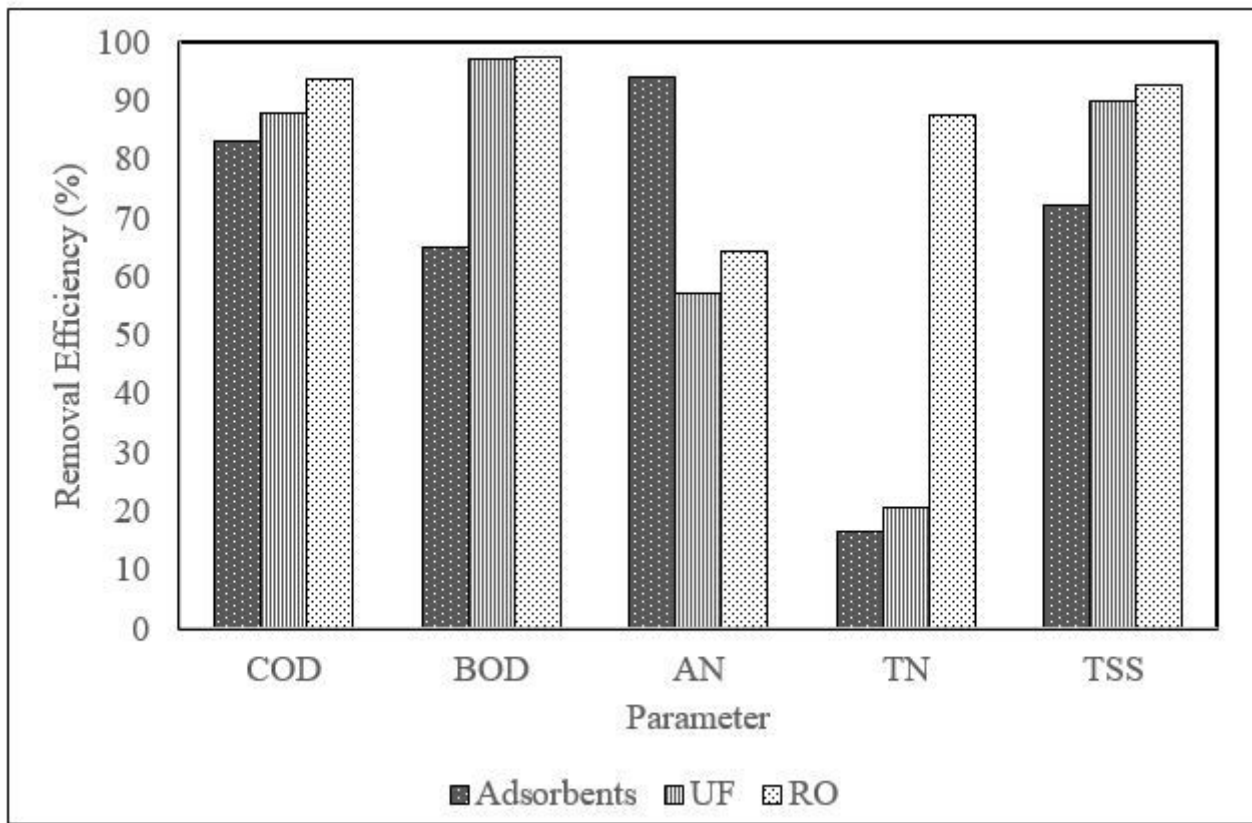
Figure 3

Change in pH for membranes and combined adsorbent



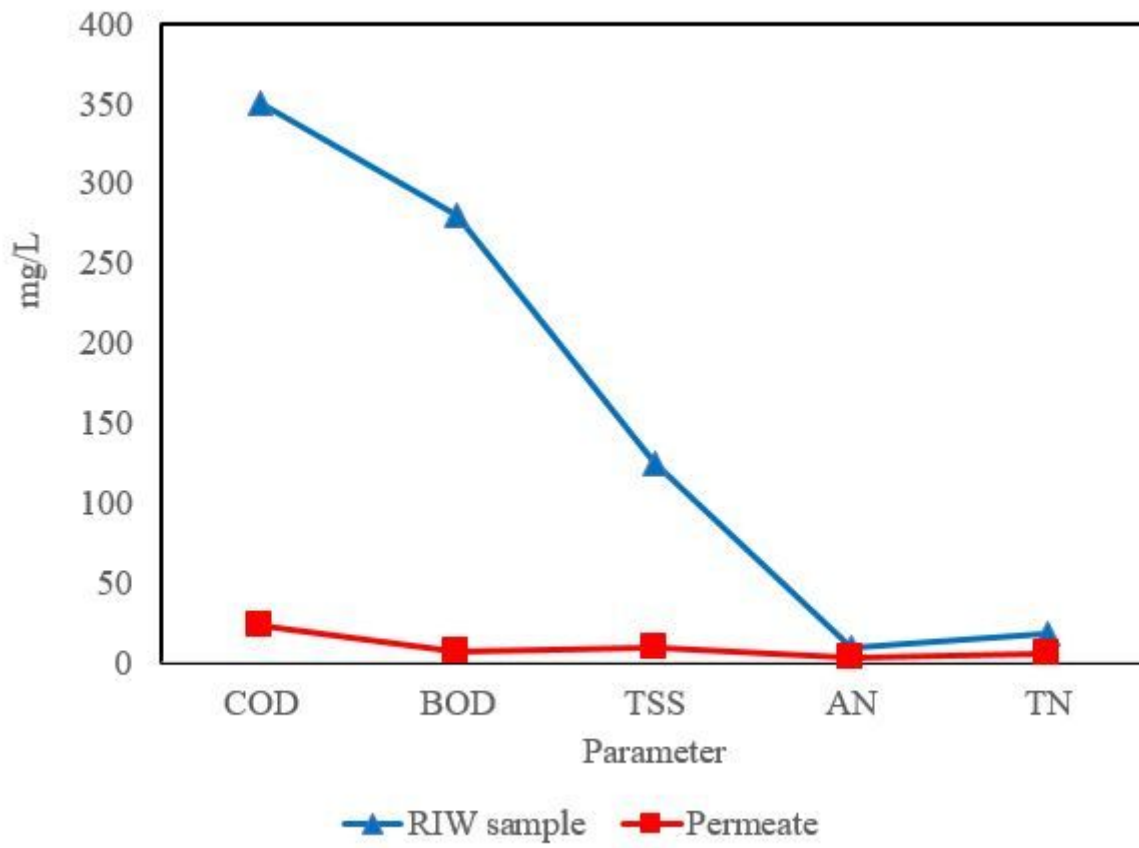
**Figure 4**

Removal efficiency of processes



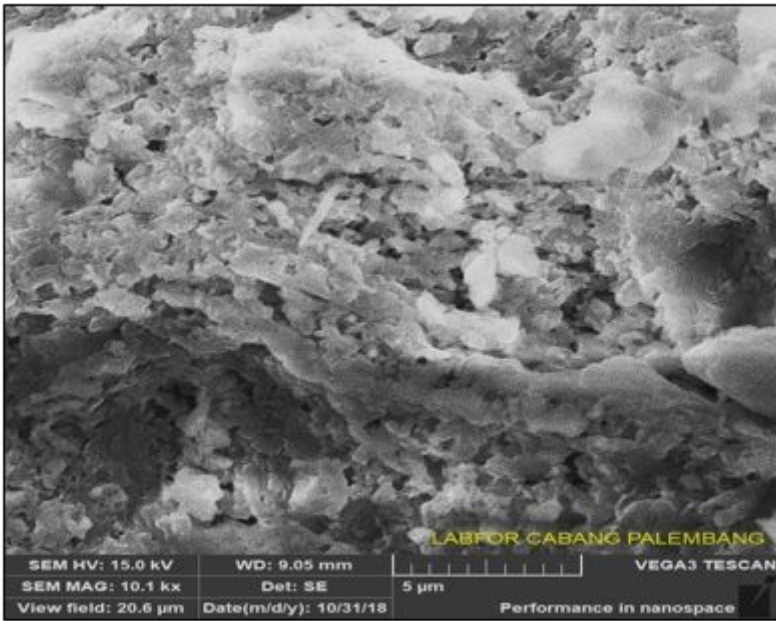
**Figure 5**

Removal efficiency of combined adsorbents, ultrafiltration, and reverse osmosis

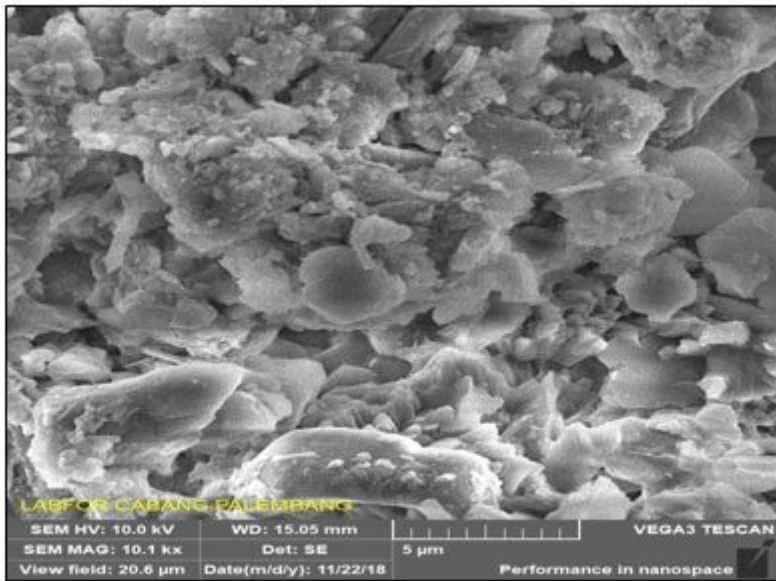


**Figure 6**

Change of the RIW parameter of combined adsorbents-UF and RO



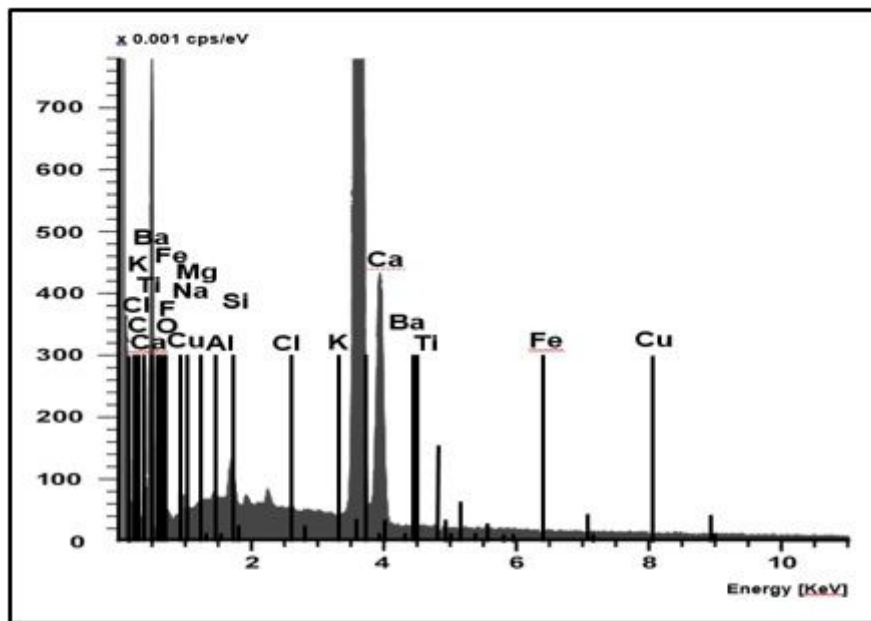
7a



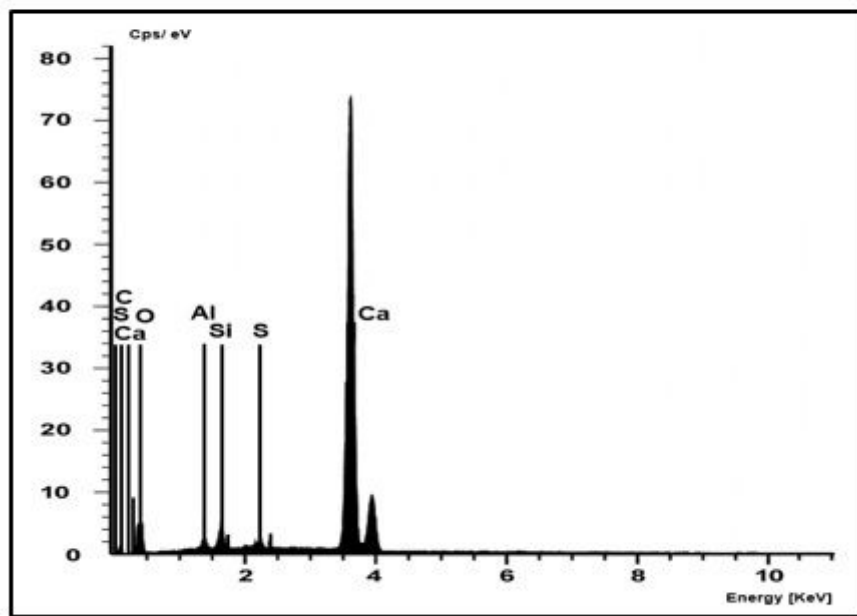
7b

Figure 7

7a. Scanning electron microscope image of CCR before pretreatment at magnification of 10.1kx 7b. Scanning electron microscope image of CCR after pretreatment at magnification of 10.1kx



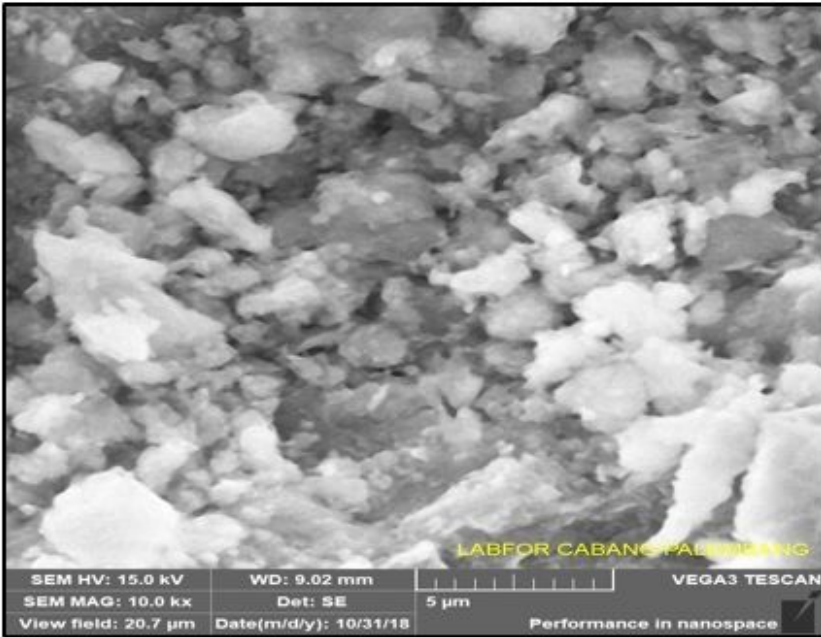
8a.



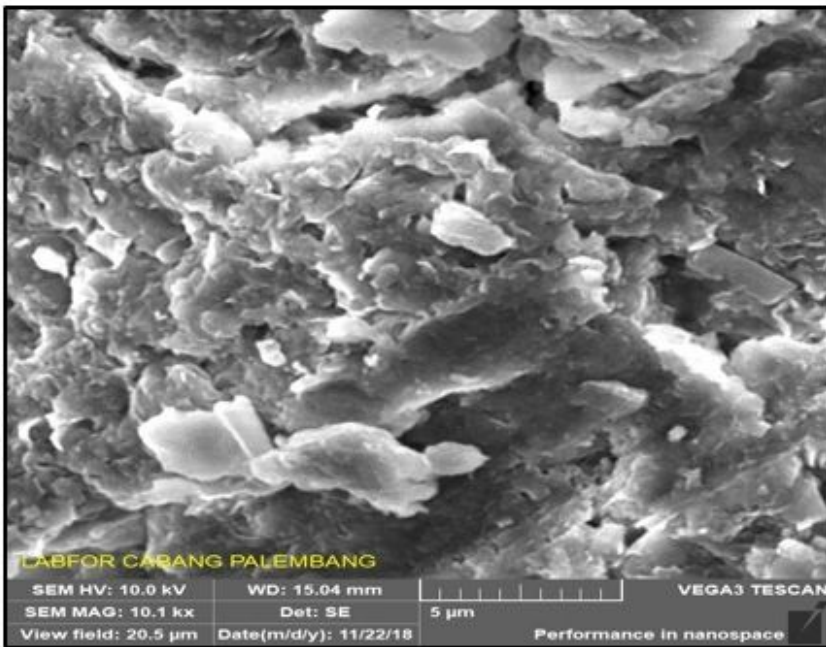
8b.

Figure 8

8a. CCR spectra EDS before pretreatment 8b. CCR spectra EDS after pretreatment



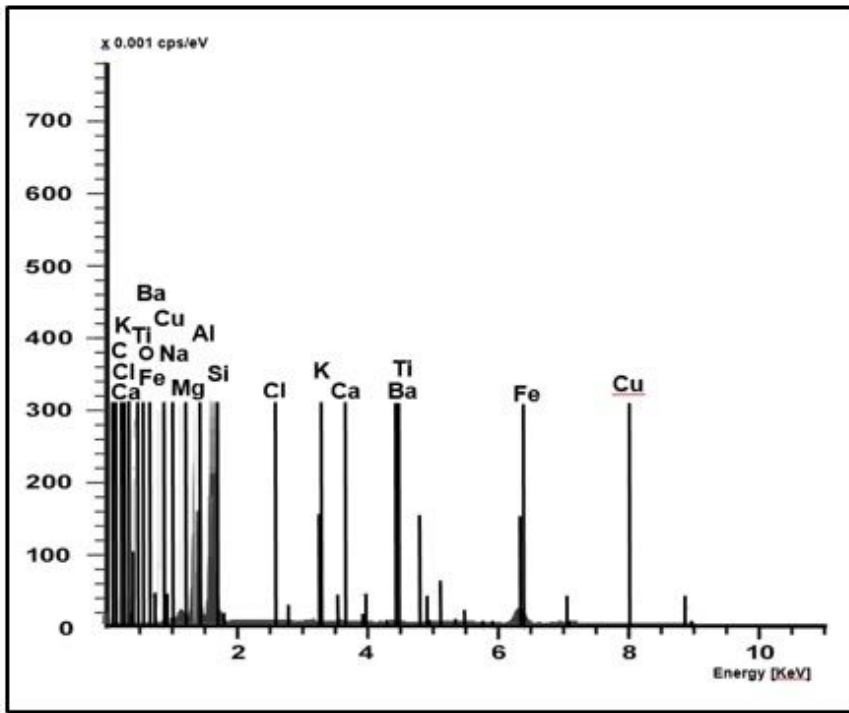
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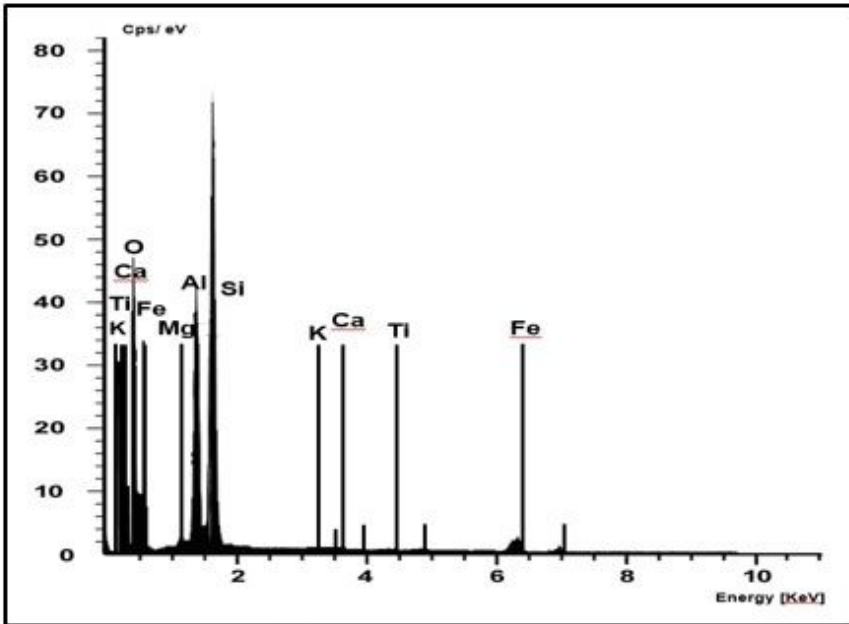
9b

Figure 9

9 a. Scanning electron microscope image of Bentonite before pretreatment at magnification of 10.0kx 9b. Scanning electron microscope image of Bentonite after pretreatment at magnification of 10.1kx



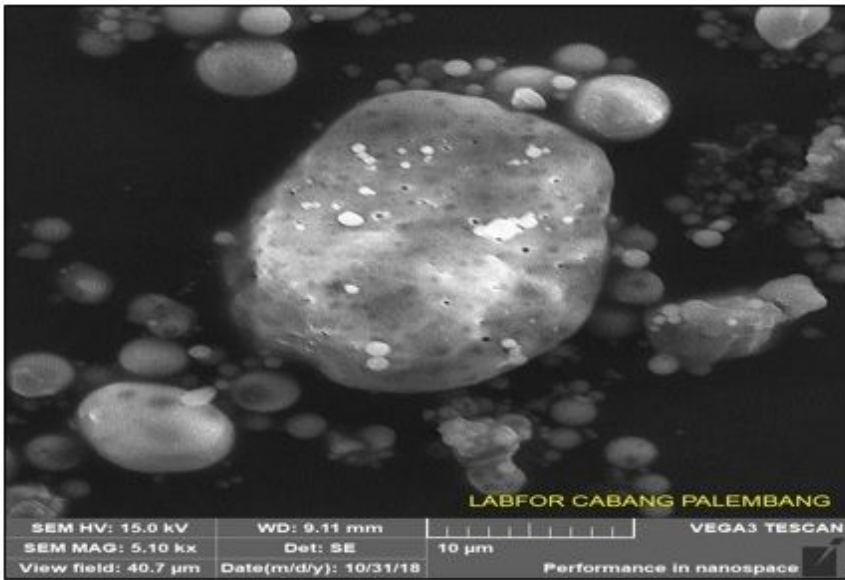
10a



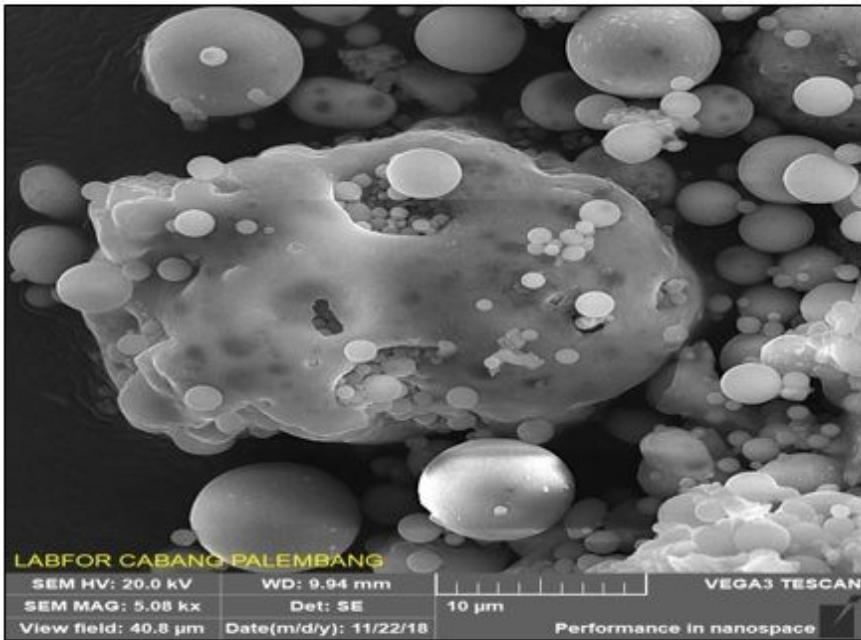
10b

Figure 10

10a. Bentonite spectra EDS before pretreatment 10b. Bentonite spectra EDS after pretreatment



11a

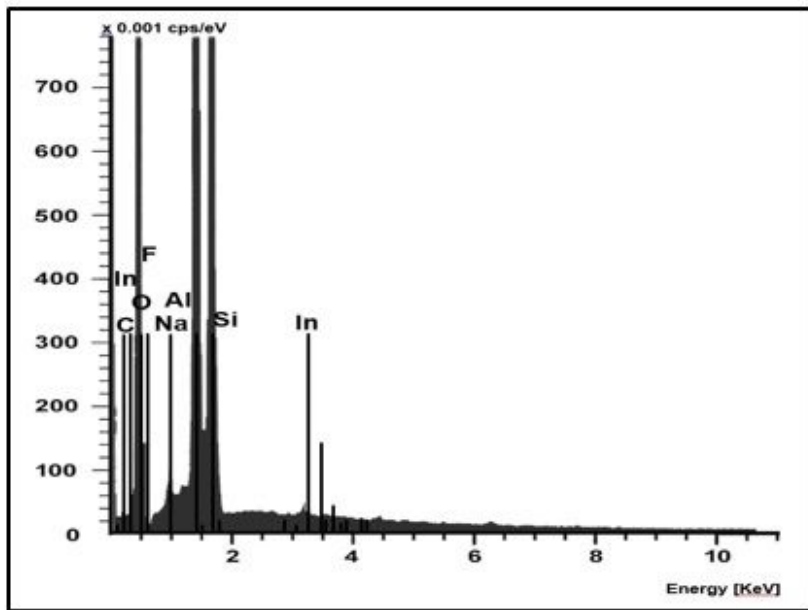


11b

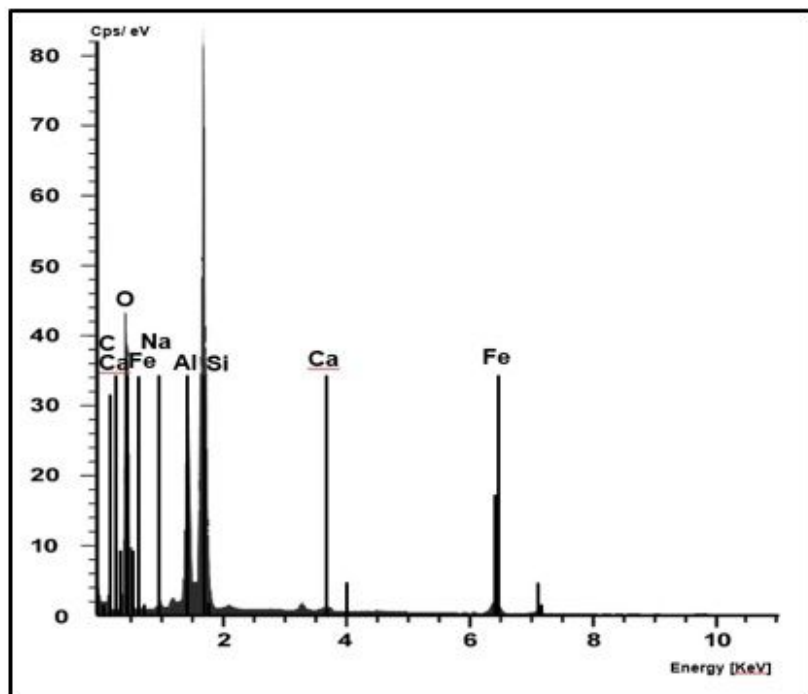
Figure 11

11a. Scanning electron microscope image of Fly Ash before pretreatment at magnification of 5.10kx 11b. Scanning electron microscope image of Fly Ash after pretreatment at magnification of 5.08kx





12a



12b

Figure 12

12a. Fly Ash Spectra EDS before pretreatment 12 b. Fly Ash Spectra EDS after pretreatment