TREATMENT OF DISTILLERY WASTEWATER BY USING THERMALLY AND CHEMICALLY ACTIVATED KAOLIN

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Abstract

Large volumes of dark brown molasses spent wash is generated from the distillation step in Distilleries and consequently, detrimental to the sustainability of the environment. In this study, kaolin from Wallan village, Mon State was activated to prepare low cost adsorbent for removal of colour and specific organic pollutants from the wastewaters. The removal efficiencies of kaolin were firstly investigated by treating the effluentwith natural kaolin using various dosages of kaolin (3 to 9% wt/v) and different contact time (30 min to 150 min). Then the effects of combined mechanical and thermal activation (from 100 to 600ºC),and chemical activation (2.5 to 5.5 M sulphuric acid) on the contaminant removal efficiencies of kaolin were examined. The physico-chemical characteristics of wastewater such as colour, turbidity, chemical oxygen demand (COD) and UV/Vis absorbance at 436 nm before and after treatment were systematically analysed. The collected wastewater is characterized by extremely high chemical oxygen demand, turbidity and solid contents, apart from low pH, unpleasant odor and dark brown color. The experiments showed that natural kaolin (NK) largely removed colour imparting contaminants than turbidity and COD from wastewater. Activating the NK by methods such as grinding, grinding and heating, acid activation decreased its colour removal efficiencies while its turbidity and COD removal efficiencies dramatically increased upon activation.Among the natural and activated kaolin samples, acid activation of kaolin enhanced its turbidity and colour removal efficiencies. The maximum turbidity and COD removalefficiencies of ~80% and ~60%, respectively were achieved with acid activated kaolin (4.5 M sulphuric acid) for 30 min contact time whereas those of ~17% and ~36%, respectively with natural kaolin for 150 min.

Keywords: distillery wastewater, kaolin, mechanical and thermal activation, chemical activation, contaminant removal efficiencies

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Introduction

The molasses spent wash (MSW)released from distilleries contains colouring compound called melanoidin, high chemical oxygen demand, biochemical oxygen demand, suspended solids, inorganic solids and low pH (Saha *et al.,* 2005). It is conventionally treated by anaerobic digestion for generation of methane and then aerobically using trickling filter or by activated sludge system prior to disposal. Although biological treatment can significantly remove COD, the effluent still has the dark color due to the presence of melanoidin. Furthermore, multistage biological treatment not only reduces the organic contaminants but also intensifies the color due to re-polymerization of colored compounds (Pena *et al.,* 2003).Adsorption is the most popular physicochemical treatment for the removal of dissolved organics from water (Meroufel *et al.,* 2013).Activated carbon is widely used due to its large surface area, microporus structure, high adsorption capacity and high degree of surface reactivity. Since large volume of water is used in distillery industries, activated carbon is not cost effective for treating the large volumes of distillery spent wash. Thus, there exist a potential to reach for low cost adsorbents.

Kaolin, one of the low-cost adsorbents that is commonly used in wastewater treatments (Nandi, *et al.,* 2009; Shirsath, *et al.,* 2013),is abundantly found in Myanmar. Kaolin consists of clay minerals such as kaolinite, illite, halloysite, and montmorillonite, and of non-clay minerals as quartz and feldspar, anastase, and gibbsite (Panda *et al.,* 2010). Kaolinite, 1:1 type aluminosilicate clay mineral, $(Si_4)_{IV}(Al_4)_{VI}O_{10}(OH)_8$, has variable charge that depends on the pH, on alumina face and on the edges arising from the protonation and deprotonation of exposed hydroxyl groups (James, 1995). Since the terminal OH groups have either a partial positive or partial negative charge groups, they also possibly chemisorb certain types of ions, regardless of the pH value. The industrial applications depend on the surface modifications of kaolin. Many researchers have reported that the mineralogical and textural properties of kaolin can be altered by activating it mechanically or chemically, in particular using sulfuric acid (Nguetnkam *et al.,* 2008; Didi *et al.,* 2009). However, there are limitations in the existing

methods and it is necessary to evaluate the treatment processes that provide a better solution for distillery spent wash.

The objectives of this study are (i) to prepare kaolin which is abundantly found in Myanmar as an adsorbent for wastewater treatment and (ii) to evaluate the effect of mechanical, thermal and chemical activation on their contaminant removal efficiencies.

Materials and Methodology

Materials

Kaolin from Wallan village, Chaunghsone Township, Mon State was supplied by Mupon Ceramic Factory.The distillery wastewater was collected from the effluent storage tank at the Shwe Myanmar Factory, Industrial Zone 2, Mandalay.

Figure 1: Raw Materials. (a) Kaolin; (b) Distillery Wastewater

Methodology

Preparation of Kaolin

The pale yellow-colored kaolinwas washed with distilled water until the pH of kaolin suspension reached about 7to remove the soluble mineralogical impurities. The sample was dried in an oven (Pelion 0°C-300°C) at 100°C for 24 hr and then sieved to 200 mesh kaolin powder, referred to as NK (Natural Kaolin). Less than 2 μm fraction is also better size for studying coarser-grained clay minerals such as kaolinite and chlorite (Srodon, 2006).

Combined Mechanical and Thermal Activation of Kaolin

Natural kaolin was ground using the iron pot pulverizer (Labtechnics). NK was ground with the three centrifugal rings rotatingat 300 rpm for 15 min to test the effect of small particles on the kaolin's contaminant removal efficiency. The ground kaolin (GK) was heated for 1 hr in a muffle furnace (O Lab) at 600°C and then, screened with 200 mesh sieve. The resulting sample is regarded as GHK (Ground and Heated Kaolin).The same procedure was repeated at different temperatures such as 100°C, 200°C and 400°C.

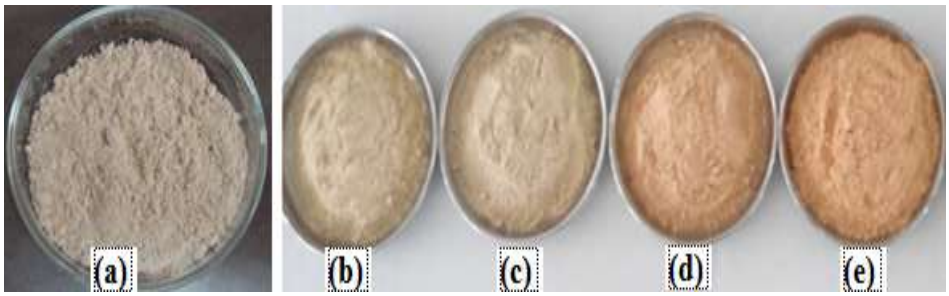


Figure 2: Ground Kaolin (a); Ground and Heated Kaolin Prepared at Different Temperatures (b) 100°C (c) 200°C (d) 400°C and (e) 600°C

Chemical Activation of Kaolin

The kaolin powder was refluxed with 2.5M sulphuric acid solution in the solid-liquid ratio of 1:50 (10 g of kaolin to 500 mL of H_2SO_4) at 80°C for 4 hr under mechanical stirring. The acid-refluxed kaolin samples were washed with distilled water until reaching pH of 3. It was dried at 100°C for 24 hr and then, screened with 200 mesh sieve. The sample produced is referred to as AAK (Acid Activated Kaolin).The same procedure was repeated using various sulphuric acid concentrations of 3.5M, 4.5 M and 5.5 M.

Figure 3: Natural Kaolin (a); Acid Activated Kaolin Prepared using Various Sulphuric Acid Concentrations(b) 2.5 M (c) 3.5 M (d) 4.5 M and (e) 5.5 M

Preparation of Distillery Wastewater

Collected distillery wastewater was filtered using filter cloth to remove sand and other undissolved impurities.

Adsorption Studies

Treatment of Distillery Wastewater

Natural kaolin (3% (w/v)) was mixed with the distillery wastewater under agitation at 150 rpm for 30 min. The mixture was then centrifuged at 2,000 rpm for 15 min and filtered through a filter paper.

To study the effect of kaolin dosage on the removal of contaminants from wastewater, the same procedure was repeated using different NK dosages such as 5%, 7% and 9% (w/v). Wastewater was treated with NK 7% (w/v) (the most suitable dosage in this study) for different contact time (30-150 min) to evaluate the optimum treatment time. The effects of physical and chemical activation on kaolin were also studied. The same experiments were done using activated kaolins such as ground and heated kaolin (GHK) and acid activated kaolin (AAK) samples in the kaolin dose of 7% (w/v) for 30 min. All the adsorption experiments were done at room temperature. Values reported in tables and figures are the means of duplications.

Analysis of Raw and Treated Distillery Wastewater

The true colour (TCU- True Colour Units) of filtrate was determined at 565 nm and 635 nm absorbance for green and red colour, respectively after scanning the wavelength at 430 nm, 470 nm, 565 nm and 635 nm using colourimeter (labquest). Turbidity (NTU-Nephelometric Turbidity Units) was determined with Vernier turbidity sensor using Absorptometric method. The pH of the distillery wastewaters before and after treatments with optimized kaolin samples was tested with VernierpH meter. Chemical Oxygen Demand (COD) was determined by titration method. The filtrate was tested to measure the yellow colour representing organic compounds in wastewater using the UV/Vis spectrophotometer (LABOMED UV-2550). In the Photometric method, the filtered distilled water was calibrated at zero and the spectrophotometer was set at visible range 436 nm.

Results and Discussion

In this research, the contaminant removal efficiencies of natural and activated kaolin on distillery wastewater were studied. The physical and chemical characteristics of distillery wastewater were compared with literature values as shown in Table (1). It had extremely high COD (256000 mg/L), Turbidity (~52 mg/L), but pH was low, unpleasant odor and dark brown color. The characteristics of the spent wash depend on the raw material used (Mall and Kumar, 1997). The contaminants removal efficiencies of kaolin were firstly investigated by treating the wastewaters with natural kaolin using various dosages of kaolin (3 to 9% wt/v) and the results are shown in Table (2). Some contaminants imparting green and red colour, turbidity and COD were increasingly decreased with increasing kaolin doses. The removal efficiencies on green color is from ~31% to ~72%, red color is from ~44% to ~46% and turbidity is from ~16% to ~80% (Figure 4). This is due to the increase in surface area and active sites on kaolin and consequently, causing the kaolin to be adsorbed with organic matter from the effluent. However, COD removal was slightly increased from ~5% to ~16% when kaolin dosage was increased from 3% to 7% (wt/v). Further increased to 9% (wt/v) of kaolin, the COD removal efficiency was decreased to ~11% (Figure 4-b). This

means increasing natural kaolin (NK) doses had slightly affected COD and also yellow-colored organic materials removal efficiencies of NK.

The characteristics of distillery wastewater before and after treatment with NK for 30 min, 90 min and 150 min are shown in Tables (3).True colour measured at 565 nm and 635 nm and visible absorbance at 436 nm of treated wastewater were also decreased except the contact time 90 min was applied for wastewater treatment. This means the materials imparting green, red and yellow colour representing organic compounds in wastewater were removed by adsorption. The color removal efficiencies were high whereas turbidity and COD removal efficiencies of NK were low when wastewater was treated with 7% (wt/v) of kaolin for 30 min. Further increasing of treatment time to 150min, the green colour, yellow colour and turbidity removal efficiencies decreased from ~70% to ~28%, ~13% to ~5% and ~13% to ~5% (Figure 5). However, COD reduced from 196300 mg/L to 164800 mg/L when wastewater treatment time was increased from 30 min to 150 min. The slight increase in COD removal efficiency (from ~24% to ~36%) with increasing time also indicates that treatment time did not significantly affect on the NK. Therefore, the suitable conditions are selected as kaolin dosages (7% wt/v) and treatment time (30 min) for distillery wastewater treatment.

Ground Kaolin was activated with different temperatures ranging from 100°C to 600°C and the results are shown in Table (4) and Figure (6). All the pollution parameters of treated wastewater decreased upon treating with GK. When ground kaolin was heated to 100°C, the yellow colour removal efficiencies were decreased from ~22% to ~2% while removal for COD and turbidity were increased from ~23% to ~46% and ~33% to ~58% (Figure 6). However, heating GK above 100°Cduring activation slightly decreased the colours (@ 565 nm and 635 nm) of distillery wastewater at 600°C from 1.087 to1.017 and from 0.484 to 0.365 (Table 4).Among of the ground and heated kaolin (GHK samples), the ground kaolin heated at 100°C gave the most suitable conditions for distillery wastewater treatment. At this temperature, COD and turbidity of treated wastewater were at the least value (137600 mg/L and 22 NTU units)as shown in Table (4). The analyzed parameters (COD and turbidity) were increased with increasing heating temperatures from 100°C to 600°C: COD and turbidity values increased to 174400 mg/L and to 35.1 NTU

units, respectively and removal efficiencies for COD was decreased to ~32% and turbidity to ~32%. Mechanical activation breaks down kaolinite structure and OH bonds which lead to changes in fineness of solid particles, surface area and number of active sites of the materials (Pacheco-Torgal et al., 2011). In the course of a thermal activation, kaolinite loses the most part of its structural water and passes into a metastable state (Dudkin et al., 2005) resulting in collapsed and disarranged clay structure (Sabir et al., 2001) and hence a decrease in the specific surface area which leads to decrease in color removal (James et al., 2008).

Effect of different sulphuric acid concentrations (2.5 M to 5.5 M) on the contaminant removal efficiencies of kaolin were shown in Table (5) and Figure (7). When the natural kaolin was activated using 2.5 M sulphuric acid, the turbidity values was dramatically decreased from ~43 to ~15 NTU units whereas other parameters such as colour and COD values were increased. The turbidity removal efficiency of AAK (2.5 M sulphuric acid) was increased from ~16% to ~71% upon acid activation (Figure 7-b). However, further increasing the acid concentration to 4.5 M increased the contaminant removal efficiencies of AAK samples. The colour at 565 nm, colour at 635 m, turbidity and COD values were decreased to~0.99, 0.47, 10.4 NTU units and 104000 mg/L, respectively. Acid activated kaolin (4.5 M sulphuric acid) gave the maximum COD and turbidity removal of ~60% and ~80%, respectively. The colour and COD removal efficiencies of AAK decreased when the acid concentration was increased to 5.5 M. Acid activation leaves a large number of highly active silanol and aluminol groups on the adsorbent sites (Dudkin et al., 2005). Upon acid activation, specific surface area, porosity and number of acid centers are also changed in the activated clay due to the leaching of alumina and other mineral impurities (Rhodes and Brown, 1992). However, sorption properties decreased at high acid concentrations along with the extensive leaching of alumina from the clay corresponding to the collapse of clay structure.

The contaminants removal efficiencies of natural kaolin, ground kaolin, ground and heated kaolin (at 100°C), and acid activated kaolin (4.5 M) was shown in Table (6) and illustrated in Figure (8). NK gave the lowest colour value and the highest turbidity and COD values. This indicates that NK

largely removed colour imparting contaminants than turbidity and COD from wastewater. Activating the kaolin (NK) such as grinding, grinding and heating, acid activation decreased its colour removal efficiencies while its turbidity and COD removal efficiencies largely increased. Among these activated kaolin samples, acid activated kaolin (AAK) gave the maximum turbidity and COD removal efficiencies of ~80% and ~60%, respectively (Figure 8). The pH value of treated wastewater was increased from 4.76 to 8.08 after treatment with natural kaolin and to 7.42 with ground kaolin. However, pH value was changed to ~4.4 when the wastewater was treated with activated kaolin (such as GHK and AAK).Though kaolinite is the least reactive clay, its high pH dependency enhances or inhibits the adsorption of metals according to the pH of the environment (Bhattacharyya and Gupta, 2008). Based on the COD and turbidity removal efficiencies, the acid activated kaolin (4.5 M sulphuric acid) gave the most suitable conditions for distillery wastewater treatment.

Table 1: Physical and Chemical Characteristics of Distillery Wastewater

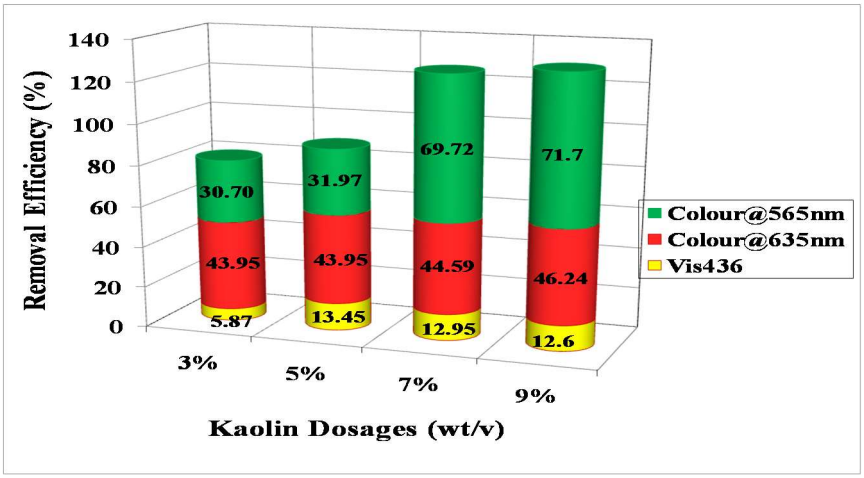
Sr. No	Parameters	Distillery Wastewater	Literature[a] Values
	Physical Characteristics		
1	Colour TCU (at 565 nm) TCU (at 635 nm)	 1.417 0.785	 - -
2	Turbidity (NTU unit)	51.5	-
	Chemical Characteristics		
3	pH	4.76	3-5.4
4	COD (mg/L)	256000	104000-134400
	Absorbance @ 436nm		
5	Vis_{436}	2.826	-

[a] Pathate (1999)

Table 2: Characteristics of Distillery Wastewater Before and After Treatment with Various Dosages of Natural Kaolin (NK)

Sr. No	Parameters	Before Treatment	After Treatment (Treated with Various NK Doses (wt/v))			
			3%	5%	*7%	9%
1	Colour TCU (at 565 nm) TCU (at 635 nm)	 1.417 0.785	 0.982 0.44	 0.964 0.44	 0.429 0.435	 0.401 0.422
2	Turbidity (NTU unit)	51.5	46.2	45.1	43.3	42.1
3	COD(mg/L)	256000	243558	234675	215111	227558
4	Vis_{436}	2.826	2.66	2.446	2.46	2.47

* Most Suitable Condition



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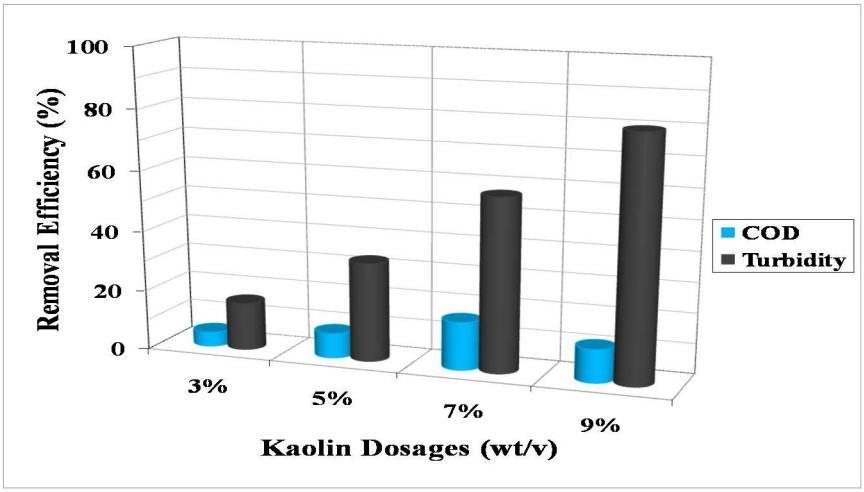

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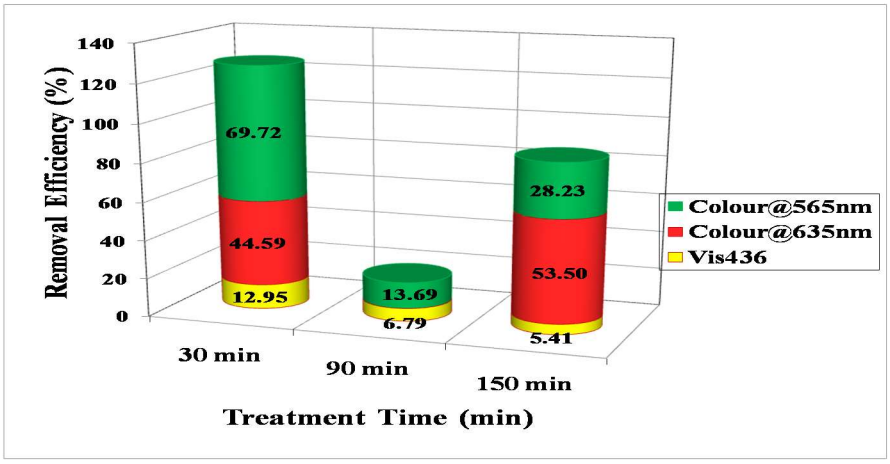
Figure 4: Effect of Different Dosages on NK for Removal of Contaminants from Wastewater. (a) Color Removal; (b) COD and Turbidity Removal

Table 3: Characteristics of Distillery Wastewater Before and After Treatment with Natural Kaolin (NK) for Different Treatment Time

Sr. No	Parameters	Before Treatment	After Treatment with NK (Treated for Different Time)		
			*30min	90 min	150 min
1	Colour TCU (at 565 nm) TCU (at 635 nm)	 1.417 0.785	 0.429 0.435	 1.223 0.924	 1.017 0.365
2	Turbidity(NTU unit)	51.5	43.3	38.5	42.6
3	COD (mg/L)	256000	193600	172800	164800
4	Vis_{436}	2.826	2.46	2.634	2.673

* Most Suitable Condition

(a)



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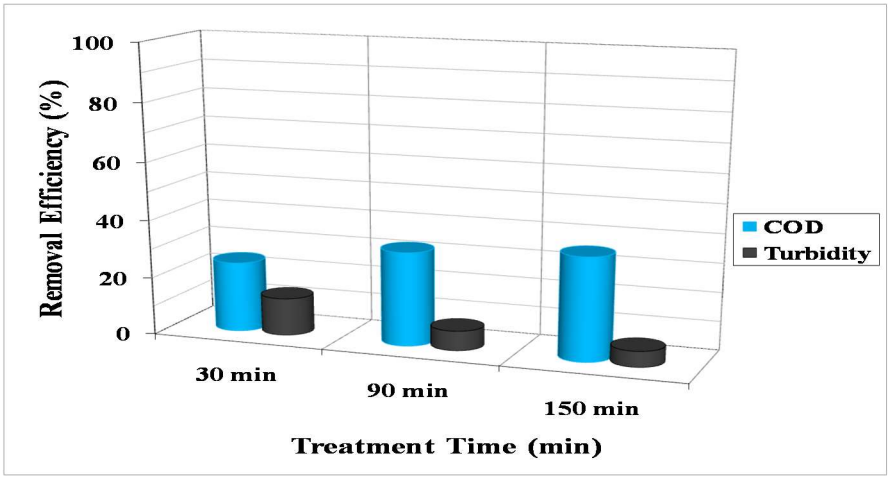
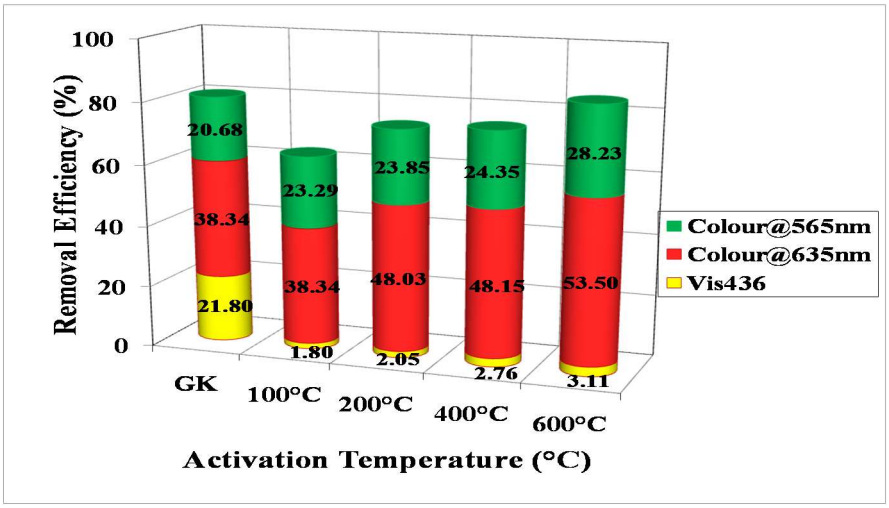


Figure 5: Effect of Wastewater Treatment Time on NK for Removal of Contaminants from Wastewater. (a) Color Removal; (b) COD and Turbidity Removal

Table 4: Characteristics of Distillery Wastewater Before and After Treatment with Ground Kaolin (GK) and Ground and Heated Kaolin (GHK)

Sr. No	Parameters	Before Treatment	After Treatment with GK and GHK				
			GK	GHK: Activated at Different Temperatures			
				*100°C	200°C	400°C	600°C
1	Colour TCU (at 565 nm) TCU (at 635 nm)	 1.417 0.785	 1.124 0.484	 1.087 0.484	 1.079 0.408	 1.072 0.407	 1.017 0.365
2	Turbidity (NTU unit)	51.5	34.6	22	30.1	34.1	35.1
3	COD (mg/L)	256000	196800	137600	148800	176000	174400
4	Vis_{436}	2.826	2.21	2.775	2.768	2.748	2.738

* Most Suitable Condition
Treatment Conditions: Time = 30 mins, Kaolin Dosage = 7 % (wt/v)



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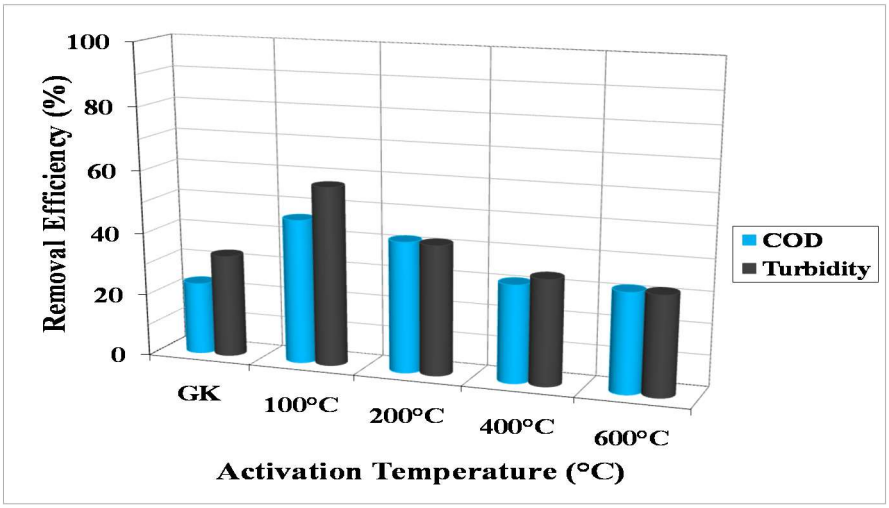


(b)

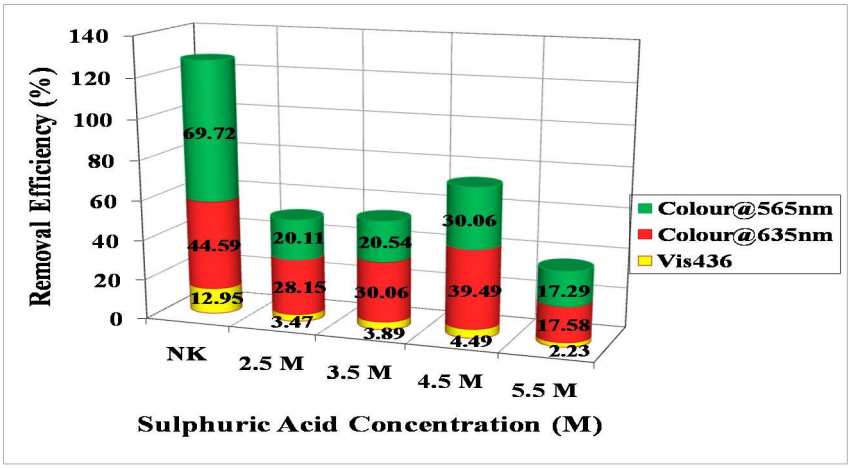
Figure 6: Effect of Activation Temperature on GK for Removal of Contaminants from Wastewater. (a) Color Removal; (b) COD and Turbidity Removal

Table 5: Characteristics of Distillery Wastewater Before and After Treatment with Acid Activated Kaolin (AAK)

Sr. No	Parameters	Before Treatment	After Treatment with NK and AAK				
			NK	AAK: Activated using Various Sulphuric Acid Concentrations			
				2.5 M	3.5 M	*4.5 M	5.5 M
1	Colour TCU (at 565 nm) TCU (at 635 nm)	 1.417 0.785	 0.429 0.435	 1.132 0.564	 1.126 0.549	 0.991 0.475	 1.172 0.647
2	Turbidity (NTU unit)	51.5	43.3	14.8	12.6	10.4	9.9
3	COD (mg/L)	256000	215111	217600	187200	104000	213600
4	Vis_{436}	2.826	2.46	2.728	2.716	2.699	2.763

* Most Suitable Condition

Treatment Conditions: Time = 30 mins, Kaolin Dosage = 7 % (wt/v)



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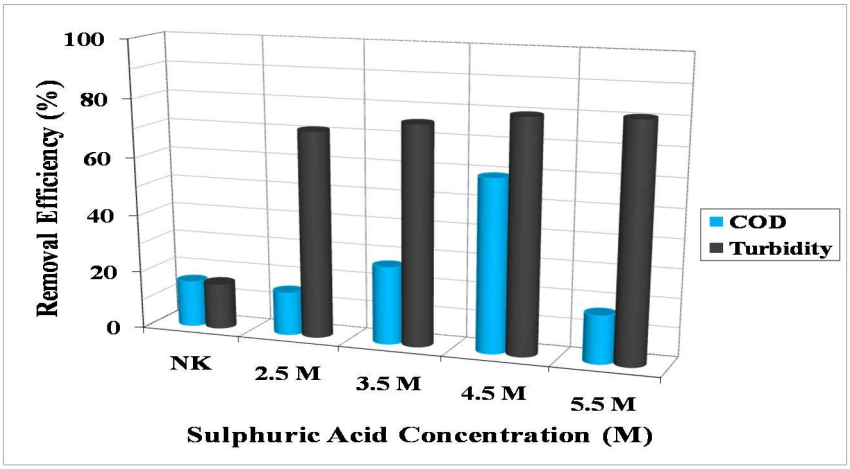


(b)

Figure 7: Effect of Sulphuric Acid Concentration on NK for Removal of Contaminants from Wastewater. (a) Colour Removal; (b) COD and Turbidity Removal

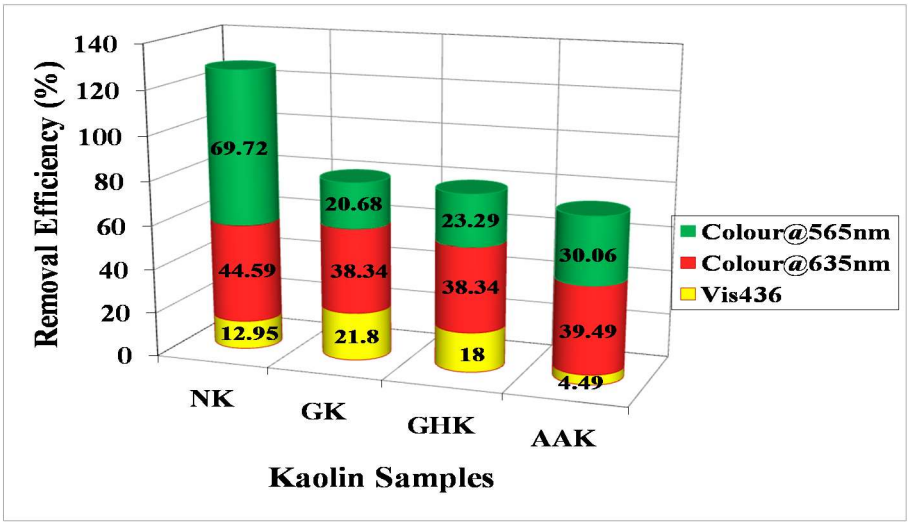
Table 6: Comparison of Distillery Wastewater's Characteristics Before and After Treatment with Optimized Natural and Activated Kaolin

Sr. No	Parameters	Before Treatment	After Treatment (Treated with Different Kaolin Samples)			
			NK	GK	GHK	*AAK
1	Colour TCU (at 565 nm) TCU (at 635 nm)	 1.417 0.785	 0.429 0.435	 1.124 0.484	 1.087 0.484	 0.991 0.475
2	Turbidity (NTU unit)	51.5	43.3	34.6	22	10.4
3	pH	4.76	8.08	7.42	4.46	4.41
4	COD (mg/L)	256000	215111	196800	137600	104000
5	Vis_{436}	2.826	2.46	2.21	2.775	2.699

* Most Suitable Condition;

NK=Natural Kaolin, GK=Ground Kaolin, GHK= Ground Kaolin heated at 100°C, AAK= Kaolin Activated using 4.5 M Sulphuric Acid;

Treatment Conditions; Time = 30 mins, Kaolin Dosage= 7 % (wt/v)



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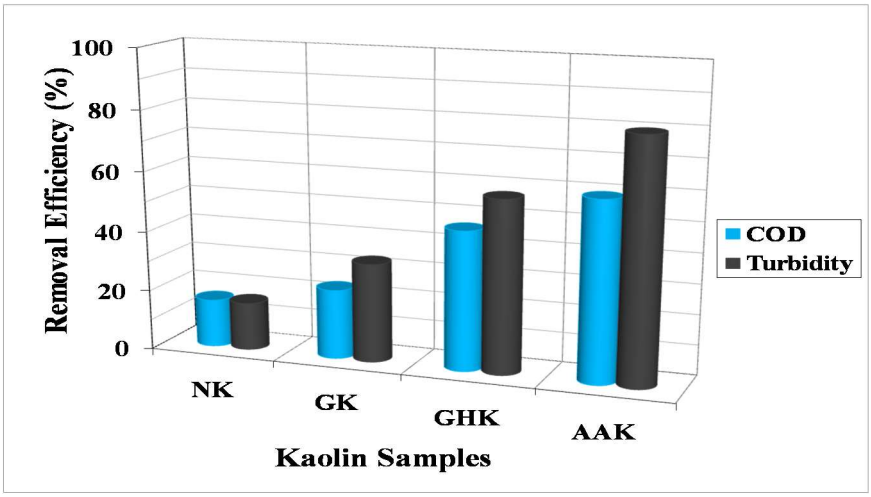

(b)

Figure 8: Comparison of the Contaminant Removal Efficiencies of Natural and Activated Kaolin. (a) Color Removal; (b) COD and Turbidity Removal

(NK=Natural Kaolin, GK=Ground Kaolin, GHK= Ground and Heated Kaolin at 100°C, AAK= Activated Kaolin using 4.5 M Sulphuric Acid; Treatment Conditions: Time = 30 mins, Kaolin Dosage= 7 % (wt/v))

Conclusion

It was noted that the wastewater should be pretreated by an appropriate method before discharging into the receiving watercourses. Upon treatment, COD, turbidity, colour and the absorbance measured at 436 nm were reduced as compared with those of raw wastewater. Among GHK samples. preheating the ground kaolin at 100°C gave better results for removal of turbidity and COD. These removal capacities decreased with increasing heating temperatures. The colour removal capacities of acid activated kaolins were decreased while those of COD and turbidity increased with increasing sulphuric acid concentrations from 2.5M to4.5M during activation. Beyond this optimum acid concentration (5.5 M H_2SO_4), the contaminants removal efficiency was decreased.This study finds that the acid activation of kaolin (using 4.5 M H_2SO_4)is a suitable method for preparing kaolin as an adsorbent for distillery wastewater treatments.

Acknowledgements

The authors are extremely grateful to Professor Dr Cho Cho Oo, Head of the Department of Industrial Chemistry, University of Yangon, for her encouragement and valuable suggestions for writing this research paper. We wish to express our sincere gratitude to Dr Yi Yi Myint, Professor and Head (Retd.) of the Department of Industrial Chemistry, Yadanabon University, for giving us permission to do research and support research facilities throughout this research work. We also would like to deeply appreciate Dr Khin Hnin Aye, Professor and Head of the Department of Industrial Chemistry, and Professor Dr Nwe Nwe Aung, Yadanabon University for giving permission us to use the necessary facilities of the laboratory at the Industrial Chemistry Department, Yadanabon University.

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