Impact of the Physico-Chemical Properties of Water on the Flocculation Performance of Lime, Clay and other Polymers

E. Fosso-Kankeu, F.B. Waanders, R. Swiegers, I.O. Ntwampe, D. Rogers, G. Gericke

Abstract**—** Water is one of the scarce commodities in Africa, mainly due to industrial expansion and climate change. Without water, life and industrial activities are restricted, with adverse consequences more especially in power generation, the most essential industrial activity. Water in the power generation utilities is used for multi-purposes, i.e. drinking, steam processes and cooling. The cooling system is an area which uses an enormous quantity of water due to evaporation at the cooling towers. The cooling water which evaporates has to be replenished with raw water drawn from the dams or rivers, which are the obvious possible supplementary sources. On the other hand, the quality of the processed (cooling blow down) cooling water is not suitable for reuse, hence it requires treatment. In order to avoid unnecessary costs associated with the treatment of cooling water, a study is necessary to investigate a cost effective technique which can be used. Coagulation-flocculation and adsorption methods are the most effective techniques for the removal of salinity, turbidity and heavy metal ions from wastewater because of their relatively low cost, simplicity, rapidness (with regards to the reaction kinetics) and high efficiency. The removal efficiency of the above pollutants using a combination of lime, clay and other polymers was investigated. It was observed that the performance of coagulants varied with the type of water treated; it was therefore possible to achieve more than 70% removal of turbidity and sulphate from raw water and ash water using single or combined flocculants, while RO-reject water responded poorly to the treatment with flocculants. Further investigations are recommended for better understanding of the mechanisms involved.

Index Terms**—**Bentonite clay, coagulation-flocculation, cooling water, hydrated lime, magnesium hydroxide, polyaluminium chloride.

I. Introduction

Due to the strain on the freshwater supply [1], [2] and the risk of significant water shortage [3], [4], industrial activities such as electricity generation, that use large amounts of water, are required to supplement the fresh water intake necessary for the process [2], [5]. Electricity generating plants primarily require water for steam generation and cooling purposes [1], as well as other auxiliary processes. Cooling water evaporates in the cooling towers, which contributes to the deterioration of the cooling water quality due to the concentration of salts and is further impacted upon by the poor quality of the feed raw water [1]. Cooling water of poor quality leads to operating problems such as scaling, corrosion and biological fouling [5], which in turn leads to condenser and pipe leaks and poor heat transfer [6]. It is therefore imperative to operate the cooling system with cooling water of good quality to ensure long term plant health through applying appropriate water management technologies [7]. The wastewater generated from the process can possibly supplement the freshwater intake if it is treated to meet the requirements necessary for successful operation of the plant.

Coagulation-flocculation is a common water treatment technology employed for the treatment of raw and wastewater due to its high turbidity removal efficiency [8]. The poor quality of the wastewater is attributed to suspended and/or dissolved organic and/or inorganic matter, and numerous biological forms such as bacteria, algae, and viruses [9]. This method of water treatment considerably reduces the amount of total suspended solids (TSS) as well as improves the performance of secondary treatment processes [8]. It is recommended to employ such a treatment technique to treat the cooling water which is used in the power utilities to eliminate or reduce the rate of corrosion, scaling, sludge deposition, fouling and microbiological and algal growth. Pollutants in wastewater is classified as hydrophilic (water-loving) or hydrophobic (water-hating) compounds [10], and it is therefore necessary to choose a coagulant/flocculent with high destabilization-hydrolysis potential in order to achieve the optimum pollutant removal. The present study focuses on flocculation-coagulation technique mainly due to its simplicity and cost-effectiveness [8], [11].

Although water treatment is a complex process which is integrated into a variety of physical and chemical reactions, a choice of optimal operating conditions and ideal reagents and techniques are essential. It is therefore vital to choose the reagents with low solubility during wastewater treatment to achieve optimal floc formation during coagulation-flocculation reaction. The parameters which are commonly important in water treatment include pH, turbidity, oxidation-reduction potential (ORP), conductivity, sulphate content, chloride content and total alkalinity, depending on the application of the water after treatment.
Bentonite clay, hydrated lime [$Ca(OH)_2$], magnesium hydroxide [$Mg(OH)_2$], polyaluminium chloride (PACl) as well as a combination of bentonite clay and PACl were applied as flocculants in three different wastewater samples. Studies on the treatment of raw water/wastewater using softening and a combination of lime, clay, $Mg(OH)_2$ and inorganic polymers has shown these polymers could be

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applied to achieve better turbidity removal mostly in acid mine drainage [8], [12], [13], [14], [15], [16], [17], [18].
The wastewater samples which were treated in this study include; ash water return, raw water and RO-reject from Eskom's Komati Power Station. The aim of this study is to determine the impact of the physico-chemical parameters of the wastewater on the flocculation performance of the flocculants.

II. Methodology

A. Materials

1) Flocculants

The flocculants used during the study included bentonite clay, hydrated lime, magnesium hydroxide and polyaluminium chloride (PACl) (synthesised and commercial).

B. Sample Collection

The wastewater studied included ash water return, raw water and RO-reject from Eskom's Komati power station in Middelburg, Mpumalanga. The water samples were transported in 25 L water containers.

C. Characterisation

1) Bentonite Clay

Bentonite clay was ground to a particle size smaller than 65 µm prior to use. Using scanning electron microscopy (SEM) photography (TESCAN, VEGA SEM), the surface morphology of the clay was determined.

2) Water

The water samples were characterized, by measuring the pH, ORP, and conductivity with a Lovibond SensoDirect 150 multi-parameter water quality meter. The turbidity of the water was measured using a 2100Q portable turbidimeter. The sulphate content was measured in a Multiparameter Bench Photometer HI 83099 (Hanna Instruments Inc., USA) while the chloride content and total alkalinity was determined using the Argentometric method and the end point titration method, respectively [19]. The metal species and their concentrations, was determined through inductively coupled plasma optical emission spectrometry (ICP-OES) analysis (Agilent Technologies, USA). The instruments were calibrated using original buffer and standard solutions, prior to use.

D. Synthesis of polyaluminium chloride

PACl was synthesized according to a method by Zouboulis *et al.* [20]. An aluminium solution was prepared using 200 mL of hydrochloric acid (37% HCl) and aluminium foil (9.5 g aluminium foil/100 mL HCl). The HCl was preheated to ≈ 65°C in a 600 mL glass beaker and thereafter the aluminium foil was slowly added while undergoing constant mixing on a magnetic stirrer. Once a reaction was noted, the solution was removed from the heater. A second solution was prepared by slowly adding 11 g aluminium foil to a 10% sodium hydroxide solution (NaOH) (11 g aluminium foil/100 mL NaOH) in a 600 mL glass beaker undergoing rapid mixing using a magnetic stirrer.

It should be noted that small quantities of HCl and NaOH were added to the solutions to replace any anticipated losses due to evaporation.
The reactions occurred as follows:

$$Al_2O_3.3H_2O + 2nHCl \rightarrow 2AlCl_n(OH)_{3-n} + 2nH_2O \text{ (aluminium chloride)} \quad (1)$$

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O \text{ (sodium aluminate)} \quad (2)$$

An aliquot of 30 mL of the sodium aluminate (0.2 mL/min) (2) was added to 100 mL of the aluminium chloride (1) in a 600 mL glass beaker undergoing constant stirring on a magnetic stirrer. This produced a solution of ≈ 97.48 mg Al^+/mL solution when taking under consideration the purity of aluminium foil (99%).
The synthesized PACl was compared to commercial PACl under optimum conditions to determine the efficiency of the synthesized PACl.

E. Jar test

A 6 beaker jar test apparatus with stirring paddles was used to conduct the experiments. Each 600 mL beaker was filled with 200 mL of the respective water samples, where each sample was dosed with bentonite clay, hydrated lime, magnesium hydroxide, PACl and a combination of bentonite clay and PACl respectively. The samples were treated in a jar test employing rapid mixing at 150 rpm for 1 minute, followed by slow mixing at 50 rpm (the slow mixing period was varied). The solution was allowed to settle for 1 hour before characterization. The first step was to determine the optimum concentrations (dosage) of the flocculants in the respective wastewater samples. The optimum concentrations were determined (at constant temperatures and a slow mixing period of 20 minutes) by varying the concentrations of bentonite clay (150 mg/L, 250 mg/L and 400 mg/L), $Ca(OH)_2$ (500 mg/L, 1500 mg/L and 2000 mg/L), $Mg(OH)_2$ (25 mg/L, 50 mg/L and 100 mg/L), PACl (5 mg/L, 10 mg/L and 20 mg/L) and a combination of bentonite clay and PACl (150 mg/L + 5 mg/L, 250 mg/L + 10 mg/L and 400 mg/L + 20 mg/L). Once the optimum concentration was determined, the experiments were repeated to determine the optimum slow mixing period (at constant temperature and at the respective optimum concentrations of the flocculants), which was accomplished by varying it between 5 minutes and 20 minutes. All experiments were duplicated. Once the optimum concentrations and slow mixing periods were determined, the performance of the combinations of hydrated lime and magnesium hydroxide, hydrated lime and PACl, and PACl and magnesium hydroxide were tested in all the wastewater samples.

III. Results and discussion

A. Characterization

1) Bentonite Clay

Bentonite clay was characterised using scanning electron microscopy (SEM) photography to determine the surface

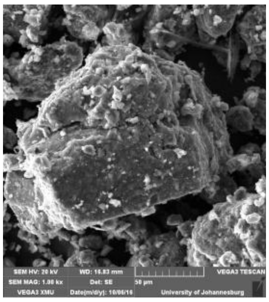
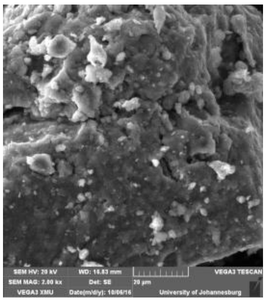
(a)  (b) 

Figure 1: SEM image of bentonite clay magnified by a thousand (a) and magnified by 2000 (b).

TABLE 1
SUMMARY OF THE PHYSICO-CHEMICAL PROPERTIES OF THE WASTEWATER

Property	**Ash Water**	**Raw Water**	**RO-Reject**
pH	12.50	8.40	8.16
ORP (mV)	-285.00	-39.00	-92.00
Conductivity (mS/cm)	3.28	0.23	4.97
Turbidity (NTU)	2.21	1.91	1.24
Alkalinity (mg $CaCO_3$/L)	413.50	51.83	190.17
Chloride (mg Cl^-/L)	1799.44	130.46	1590.01
Sulphate (mg SO_4^{2-}/L)	1757.74	51.40	3520.49

morphology of the clay. From Fig. 1 it can be seen that the morphology of the bentonite clay is porous therefore, indicating a large surface area. This is beneficial to the study, as bentonite clay should act as an adsorbent in the wastewater.

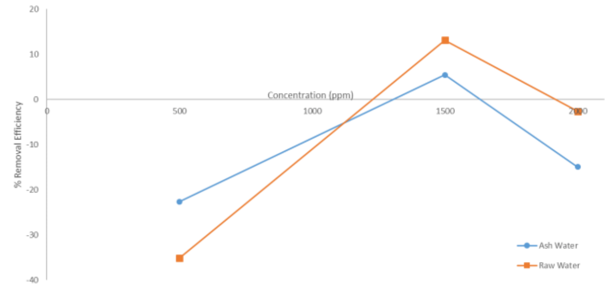
2) Wastewater

From Table 1, the initial physico-chemical parameters of the respective wastewaters can be seen. The pH of the wastewater samples ranges from relatively neutral to alkaline (8.16-12.5). The pH of the ash water is relatively high compared to the raw water and RO-reject, and is therefore more likely to cause scaling in any downstream process. The turbidity of the ash water is also high compared to that of the raw water and RO-reject, this may be due to the presence of a larger amount of particles in the ash water. The sulphate content is the highest in the RO-reject as this water comes from the first stage of the reverse osmosis (RO) process which also concentrates other salts in the retentate.

B. Jar test

1) Effect of concentration of coagulant.

The jar tests were conducted using 5 different coagulants, to determine the removal efficiency of turbidity in each water sample with different characteristics, as shown in Table 1. The first step was to determine the optimum concentration of the various coagulants, without altering any characteristics of the water samples. The addition of bentonite clay to the wastewater samples did not decrease the turbidity in any of the wastewater samples. In Fig. 2 (a) it can be seen that the addition of hydrated lime decreased the turbidity in the ash water and raw water. From Fig. 2 (b) and (c), the magnesium



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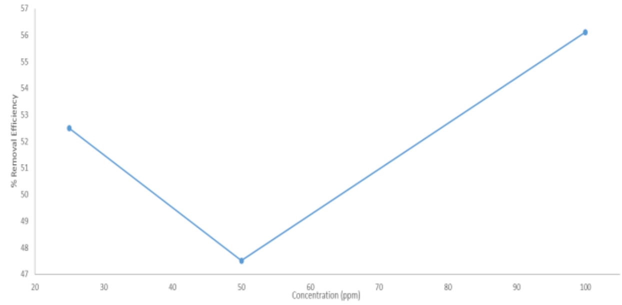

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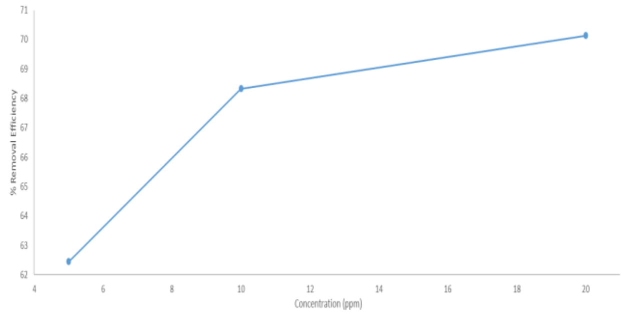


(c)

Figure 2: The effect of the concentration of the coagulants on the % removal efficiency of turbidity of (a) hydrated lime, (b) magnesium hydroxide, and (c) PACl

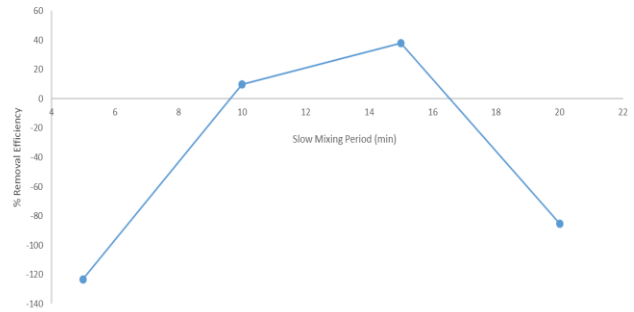
hydroxide and PACl decreased the turbidity in the ash water as the concentration of the respective coagulants increased.

1) Effect of slow mixing period

After determining the optimum concentrations of the respective coagulants, the following step was to determine the optimum slow mixing period. By dosing the respective water samples with the optimum concentration of the different coagulants, the slow mixing period could be varied. From Fig. 3 (a), the optimal slow mixing period for the bentonite clay was 15 minutes, and only lowered the turbidity of the ash water. Fig. 3 (b) shows that the optimal slow mixing period for the hydrated lime, that lowers the turbidity of the ash water and raw water, is 15 minutes. The optimum slow mixing period for magnesium hydroxide can be seen in Fig. 3 (c) as 20 minutes for the ash water. The optimum slow mixing period for PACl is 15 minutes for the ash water.

2) Optimisation of coagulation process

Once the optimum concentrations and slow mixing periods were determined, combinations of the coagulants were tested. These included combinations of PACl with bentonite clay,



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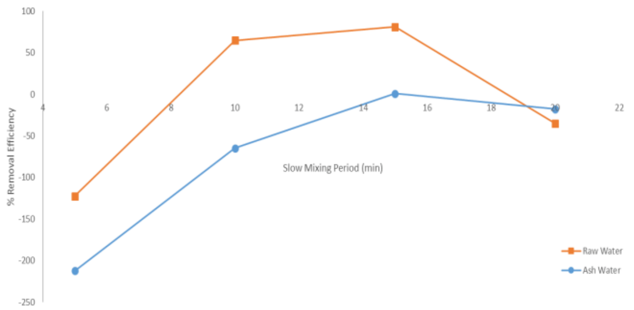

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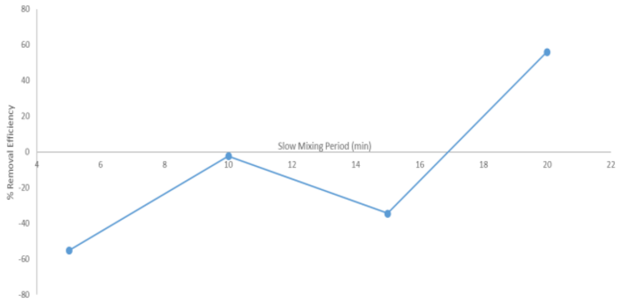

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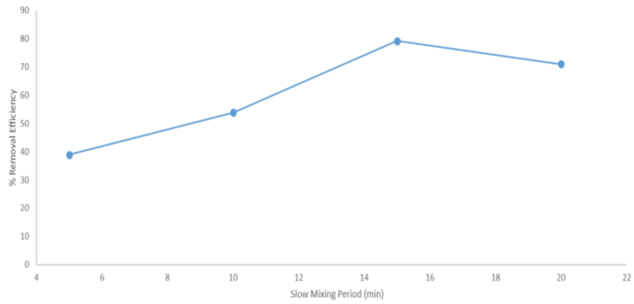


(d)

Figure 3: The effect of the slow mixing period on the % removal efficiency of turbidity of (a) bentonite clay, (b) hydrated lime, (c) magnesium hydroxide, and (d) PACl

hydrated lime, and magnesium hydroxide, as well as hydrated lime with magnesium hydroxide.

From Fig. 4, the bentonite clay, PACl and the combination of hydrated lime with PACl removed the most turbidity from the ash water in comparison to the other coagulants, while Fig. 5 illustrates that only the combinations of hydrated lime and PACl, and PACl and magnesium hydroxide lowered the sulphate content in the ash water. The combination of PACl and magnesium hydroxide lowers the pH of the ash to a higher degree in comparison to the other coagulants, as is illustrated in Fig. 6. Fig. 7 proves that all coagulants performed well in lowering the calcium content in the ash water, while hydrated lime and PACl lowered the magnesium content the most in comparison to the other coagulants.

It is evident from Fig. 4 that the bentonite clay and the combination of PACl and magnesium hydroxide remove the most turbidity in the raw water. Fig. 5 shows that bentonite clay and the combination of hydrated lime and magnesium hydroxide does not lower the sulphate content of the raw water considerably in comparison to the other coagulants and combinations. From Fig. 6 it can be said that bentonite clay has the smallest effect on the pH of the raw water. The magnesium hydroxide alone and in combination with PACl lowers the calcium content of the raw water the most, while the hydrated lime alone and in combination with commercial PACl lowers the magnesium content of the raw water the most.

From Fig. 4, PACl and the combination of (commercial and synthesised) PACl and magnesium hydroxide remove the most turbidity from the RO-reject. The sulphate content is lowered somewhat by all coagulants and combinations thereof, except by the combination of PACl and magnesium hydroxide (Fig. 5). Fig. 6 shows that hydrated lime causes the RO-reject to become relatively alkaline, while the combination of bentonite clay and PACl neutralises the RO-reject. All coagulants and their combinations do not decrease the concentration of calcium in the RO-reject, except for the combination of bentonite clay and commercial PACl. The hydrated lime alone and in combination with the PACl lowers the concentration of the magnesium in the RO-reject (Fig. 7).

3) *Discussion of optimal coagulants*

Considering the results obtained in this study, the combination of hydrated lime and PACl, as well as PACl and magnesium hydroxide are the overall most effective when treating ash water, with the exception of causing a considerable amount of turbidity in the ash water. This may be due to non-dissolved magnesium hydroxide.

None of the coagulants or combinations lowers both the concentrations of calcium and magnesium in the raw water simultaneously. For the purposes of treating the wastewater to be used in the power utilities, the rate of corrosion and scaling must be minimised. Therefore, the coagulants cannot be used to treat the raw water for this purpose. However, bentonite clay and the combination of PACl and magnesium hydroxide, respectively lowers the concentration of calcium and magnesium the most in the raw water. Because calcium and/or magnesium crystals are not formed by bentonite clay and the combination of PACl and magnesium hydroxide, it does not alter the pH and removes less sulphate compared to the other coagulants. PACl in combination with magnesium hydroxide removes a lot of the turbidity in the raw water (from 1.9 NTU to 0.36 NTU).

For the treatment of the RO-reject, bentonite clay, PACl, and a combination of both lowers the sulphate content, and neutralises the water, while the commercial PACl and bentonite clay, in combination, lowers both the concentration of calcium and magnesium in the RO-reject.

The coagulants that performed best in this study, are therefore hydrated lime and PACl, and PACl and magnesium hydroxide for ash water and raw water, respectively.

Bentonite clay, PACl and the combination of bentonite clay and PACl

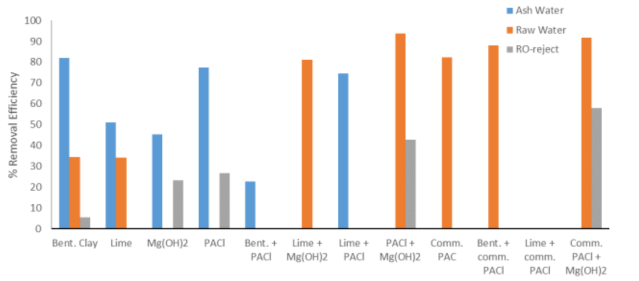


Figure 4: % Removal efficiency of turbidity of all coagulants and their combinations on the respective wastewater samples

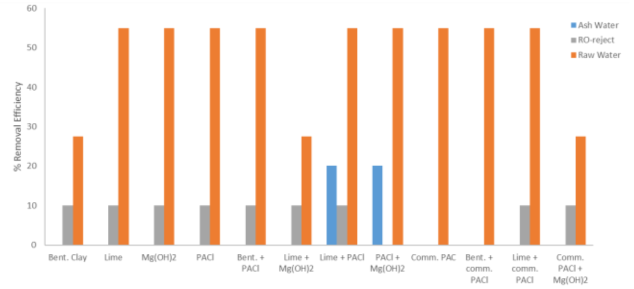


Figure 5: % Removal efficiency of sulphate of all coagulants and their combinations on the respective wastewater samples

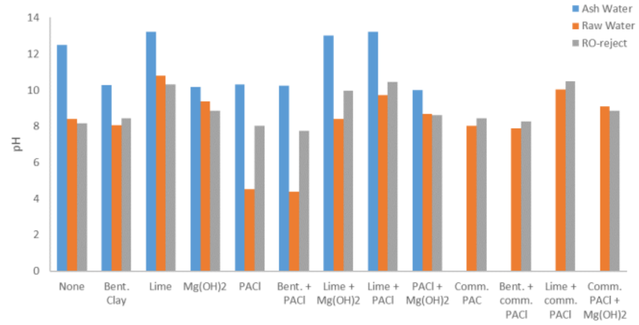
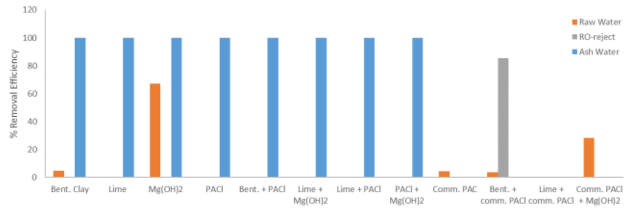
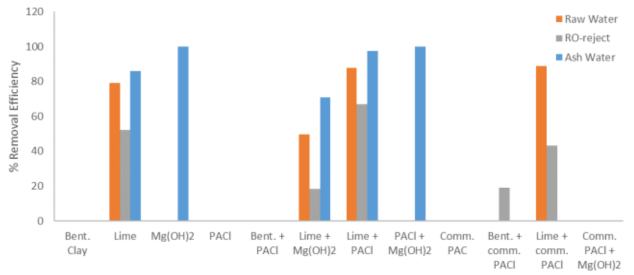


Figure 6: The effect on pH of all coagulants and their combinations on the respective wastewater samples



(a)



(b)

Figure 7: % Removal efficiency for (a) calcium and (b) magnesium of each coagulant and their combinations on the respective wastewater samples

(synthesised and commercial) performed best in the RO-reject.

4) Characterisation of flocs

As previously mentioned, floc formation, growth, and sedimentation is dependent on time, and is greatly affected by coagulant type and dosage, water pH, process conditions, ionic strength, suspended particles, and process conditions [21]. The floc structure is a characteristic of its stability. Large, open flocs are considered more unstable than small and dense flocs [22]. Therefore, SEM photography was used to determine the surface morphology of the sediments/flocs formed by optimal coagulants.

Fig. 8 shows the surface morphology of the sediments formed by hydrated lime and magnesium hydroxide in the ash water. This displays a crystal structure of the sediment, due to the precipitation of metals as metal hydroxides, at the high pH of the treated water sample (13.02).

Fig. 9 shows that the raw water treated with hydrated lime and magnesium hydroxide formed flocs due to the turbidity of the natural clays and colloidal particles. The flocs appear to be small, dense flocs that suggest the flocs are relatively stable.

From Fig. 10 (a) and (b), the SEM photography displays a gel-like structure (a) and a gel-like structure with small, dense flocs (b).

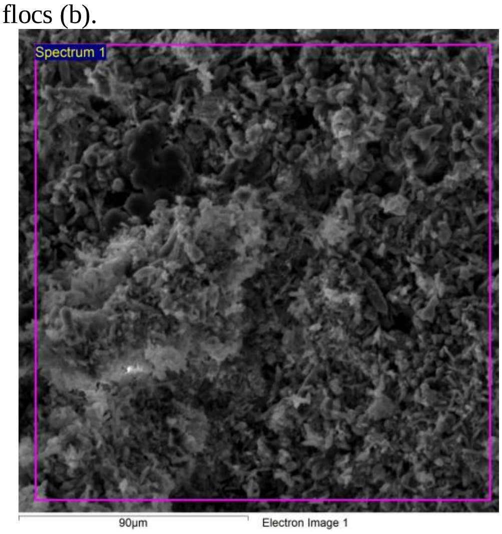


Figure 8: SEM image of ash water dosed with hydrated lime and magnesium hydroxide.

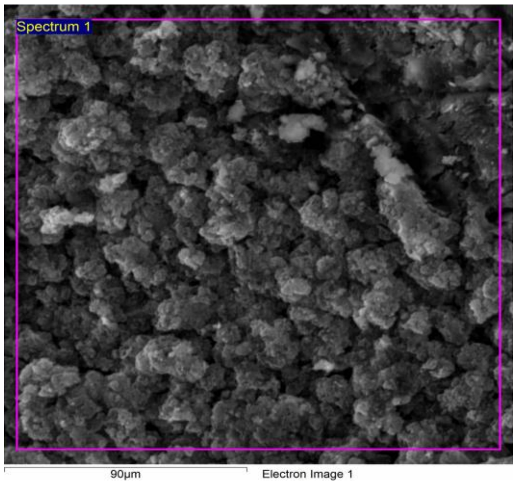


Figure 9: SEM image of raw water dosed with hydrated lime and magnesium hydroxide.

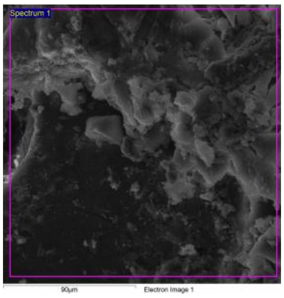
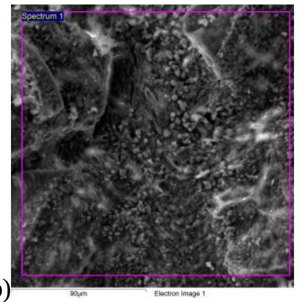
(a)  (b) 

Figure 10: SEM image of RO-reject dosed with (a) bentonite clay and synthesised PACl and (b) bentonite clay and commercial PACl

IV. Conclusion

Table 2 summarises the performance of the flocculants in the different conditions presented by the physico-chemical parameters of the wastewater samples. As predicted, the performance of flocculants was dependent on the properties of the water treated. Bentonite clay and PACl lower the turbidity and calcium content in the alkaline conditions presented by the ash water. Lime and magnesium hydroxide performed best in the ash water and raw water. Both flocculants remove a lot of the scalants in the water, especially from the ash water.

All of the flocculants and the combinations thereof, perform relatively well in the ash water.

The synthesised PACl alone and in combination with bentonite clay, is not suitable for pre-treatment of the raw water in the removal of turbidity and scalants such as calcium and magnesium, while the commercial PACl was efficient in the removal of turbidity. The combination of PACl and bentonite clay (synthesised and commercial) is most effective in the RO-reject. The findings of this study suggest further systematic investigations to better understand the mechanisms of interaction of flocculants with the unwanted substances in the respective water treated.

Table 2: Summary of performance of flocculants in wastewater with different physico-chemical properties

0	Negative to no effect
1	up to 20 % removal
2	up to 60 % removal
3	up to 100 % removal

acd	0-6.5
neut	6.5-9
alk	14-Sep

Property	Bentonite Clay			$Ca(OH)_2$			$Mg(OH)_2$			PACl		
	Ash Water	Raw Water	RO-reject	Ash Water	Raw Water	RO-reject	Ash Water	Raw Water	RO-reject	Ash Water	Raw Water	RO-reject
% Removal Efficiency of Turbidity	3	2	1	2	2	0	2	0	2	3	0	2
% Removal Efficiency of Sulphate	0	2	1	0	2	1	0	2	1	0	2	1
pH	alk	neut	neut	alk	alk	alk	alk	alk	neut	alk	acd	neut
% Removal Efficiency of Calcium	3	1	0	3	0	0	3	3	0	3	0	0
% Removal Efficiency of Magnesium	0	0	0	3	3	2	3	0	0	0	0	0

Property	Bentonite Clay + PACl			$Ca(OH)_2$ + $Mg(OH)_2$			$Ca(OH)_2$ + PACl			PACl + $Mg(OH)_2$		
	Ash Water	Raw Water	RO-reject	Ash Water	Raw Water	RO-reject	Ash Water	Raw Water	RO-reject	Ash Water	Raw Water	RO-reject
% Removal Efficiency of Turbidity	2	0	0	0	3	0	3	0	0	0	3	2
% Removal Efficiency of Sulphate	0	2	1	0	2	1	1	2	1	1	2	0
pH	alk	acd	neut	alk	neut	alk	alk	alk	alk	alk	neut	neut
% Removal Efficiency of Calcium	3	0	0	3	0	0	3	0	0	3	0	0
% Removal Efficiency of Magnesium	0	0	0	3	2	1	3	3	3	3	0	0

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