Treatment of Raw and Processed Waters from Coal Power Plant using PACl Supplemented with Cationic Organic Polymer and Bentonite

Elvis Fosso-Kankeu, Frans Waanders, Divan van Niekerk, David Rogers, Gerhard Gericke

Abstract—This study investigates the potential of polyaluminium chloride (PACl) supplemented with bentonite clay and polyethylenimine (PEI) in the desalination of the Komati power plant reject water from the reverse osmosis raw water feed. The 6-beaker jar test was applied to initiate rapid mixing and slow mixing for different time intervals and different concentrations of PACl, bentonite and PEI. XRD and XRF analyses were performed on the bentonite clay to determine its mineralogical and elemental composition respectively. The PACl was prepared from different solutions of HCl and NaOH combined with aluminium. PACl showed great removal effectiveness with regard to sulphate, but in turn lowered the pH significantly with little to no change in the conductivity for both the RO reject and raw water samples. Combinations of PACl, bentonite and PEI was investigated and it was found that PACl and bentonite combinations delivered the best results lowering the sulphate concentrations by 85% for the RO reject sample and 81% for the raw water samples. The value of parameters such as the conductivity did not vary considerably. The PACl combined with the bentonite and PEI delivered good results overall. Influences on the turbidity and pH must be noted for future references.

Keywords — Bentonite, cationic, coagulation, flocculation, PACl, PEI, polymer

I. INTRODUCTION

Water scarcity is a major problem in the world today. The mean precipitation average of South Africa is 497mm per year, which is far below that of the global average of 860mm per year. The shortage of this natural resource therefor constitute a fundamental constraint to the country`s development, especially when the country has already depleted its excess water and dilution capacity [18]. The pressure is even high on the southern Africa`s water resources which is expected to decrease as a result of the ever increasing threat of climate change.

The use of reverse osmosis systems in South Africa has shown great potential for desalination and water recovery for re-use due to limited supply of fresh water in many regions. The emergence of more stringent water quality regulations have accelerated the development of membrane technologies. Reverse osmosis (RO) and nanofiltration (NF) are now widely recognized as the most promising water treatment technologies for water treatment and for production of potable water [11]. However, membrane fouling is still a major obstacle for effective operation of RO and NF systems. This fouling is a matter of increased salt concentration in the recycled feed to the RO system, increasing fouling and scaling risks. Thus, the justification for pre-treatment of the recycled feed to the RO system is required.

The energy sector of South Africa is dominated by coal-fired power stations. Due to the coal-fired power stations` immense water usage, there is pressing need for improved water management. The strategy is to decrease fresh water intake to the Komati power plant to decrease usage as this water is the main source of cooling of the coal-fired plant. Wet cooled power plants normally operate their cooling water at a number of cycles of concentration. The number of cycles depends on raw water quality and chemical specifications to maintain material integrity. The recycling of this water throughout the plant leads to an increase in concentrated salt in the water, leading to major scaling and fouling problems, most notably seen on the reverse osmosis (RO) system used to recover cooling water blow down for re-use. As stated by [11], studies on the consequences of colloidal fouling of RO on salt rejection are rather limited. The proper pre-treatment technology of the recycled RO feed is therefore very important in reducing scaling and fouling problems that have risen most notably in the last few years at the Komati power plant. The RO blowdown stream was thus used as this stream is recycled, alongside this, the raw water feed to the plant was also considered and treated by coagulants such as PACl, PEI and bentonite, individually and in combination.

PACl is an affordable coagulant with a very good success rate in the treatment of wastewater. Bentonite clay is also a very affordable coagulant readily available in South Africa, which has also proven to be very effective in the treatment of wastewater. The coagulation/flocculation process is the process of choice because of its basic principle that is easily understood

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http://doi.org/10.15242/IAE.IAE1116412

and applied. Many of the contaminants in water and wastewater contain matter in colloidal form. These colloids result in a stable suspension. In general this suspension is stable enough so that gravity forces will not cause precipitation of the particles. Thus they need a special treatment to remove them from the solution. This destabilization of colloids is called coagulation. In the treatment of water, colour, turbidity, bacteria, algae and other organic matter are either in the colloidal form or behave as colloids.

The potential of polyaluminium chloride (PACl), supplemented by bentonite clay and a cationic polymer, polyethylenimine (PEI) was investigated. The coagulation/flocculation performance of these three reagents was investigated with special emphasis on the removal of sulphate content as well as the pH, conductivity and turbidity. This process was aided by the 6-beaker jar test to enhance contact probability between the coagulants and the water sample for optimal flocculation.

II. MATERIALS AND METHODS

A. *Preparation of PACl*

The synthesis of polyaluminium chloride was adapted from the procedure described by Zouboulis et al (2010) [25]. Aluminium solution, consisting of about 9.5 g Al/100 mL was prepared by dissolving aluminium foil, with a purity of between 92% - 99%, in Hydrochloric acid (40%). The aluminium foil, teared into fine strips, was introduced slowly and in small portions into the HCl solution. The addition of the aluminium was done whilst the HCl solution, placed in a 600 mL beaker, was under continuous stirring by means of a magnetic stirrer. Caution was taken with addition of aluminium as it creates an exothermic reaction.

In a similar way, sodium aluminate solution was prepared. The sodium hydroxide solution (40 %) was placed in a 600 mL beaker with a magnetic stirrer. Aluminium foil (11 g), teared into small strips, was then added to the sodium hydroxide solution (100 mL) with continuous stirring. Caution was once again taking as the addition of aluminium to the sodium hydroxide solution caused an exothermic reaction.

Following this, 30 mL of the sodium aluminate solution was added at a rate of 0.2 mL/min under vigorous stirring to the HCl and aluminium solution until completely mixed.

The following equation, Eq.1, was used to determine the basicity of the PACl created in the laboratory:

$$Basicity = {}^{OH}/_{Al} \times 100\% \tag{1}$$

The basicity of the prepared PACl was calculated to be 46% and the aluminium content was calculated as 11 % w/w aluminium approximately. Characterization of bentonite

The bentonite clay was ground by using a ring-mill, and then sieved through a 64 µm sieve to obtain an optimum particle size [5]. The bentonite clay was subjected to XRD and XRF analyses to determine its mineralogical and elemental composition.

B. *Characterization of RO blow down and raw water*

The RO blow down and raw water fed to the Komati power plant were characterized by means of ICP analyses, to determine the metals present, as well as measurement of the temperature, pH, conductivity, sulphate and turbidity.

TABLE I

WATER CHARACTERIZATION

Source	pH	Conductivity (mS)	Sulphate (mg/L)	Temperature (C)	Alkalinity (mg $CaCO_3$/L)	Chloride (mg Cl^-/L)	Turbidity (NTU)
RO blowdown	7.80	5.15	3315	18.3	156	350	0.85
Raw water	8.04	0.234	55	18.6	26	41.67	1.55

C. *Coagulation and flocculation experiments*

In this experimental setup, the 6-beaker jar test apparatus, complete with stirring paddles and control settings, was used. 200 mL of the sample was poured into six 600 mL glass beakers. The six beakers were placed in the jar test apparatus, then the rapid mixing (160 rpm) was carried out for 1 minute and thereafter the slow mixing (50 rpm) was conducted at varying time intervals of 5, 10, 15 and 30 minutes to obtain optimal conditions. The samples were then allowed to settle for 1.5 hours after which the characterization was conducted. The main objective was to obtain the optimum concentration of the PAC, Bentonite and PEI as well as optimum time interval at which pollutants can removed. The concentrations of the PAC and PEI was varied between 5 mg/L, 10 mg/L, 15 mg/L and 25 mg/L, with the bentonite concentration being varied between 100 mg/L, 200 mg/L, 400 mg/L, 800 mg/L. As soon as optimization was completed, these optimum conditions were used to find optimum combinations between the PAC, PEI and bentonite clay. The parameters measured for the water analysis of the pre- and post-samples were the pH, electrical conductivity (EC) and temperature using a portable Lovibond SensoDirect 150 multi-parameter water quality meter, the turbidity was measured using a Hanna Turbidity Meter, the sulphate content was measured using COD and Multiparameter Bench Photometer HI 83099 (Hanna Instruments Inc., USA), chloride and alkalinity were measured by titration.

III. RESULTS AND DISCUSSION

A. *Mineralogical and elemental analysis of bentonite clay*

The following tables illustrate the mineralogical and elemental composition of the bentonite clay as analyzed by XRD and XRF respectively.

TABLE II
ELEMENTAL COMPOSITION OF BENTONITE

Element	Weight %	Compound %
C	17.94	65.74
Na	0.24	0.33
Mg	0.68	1.13
Al	2.62	4.96
Si	11.03	23.59
K	0.54	0.65
Ca	0.25	0.35
Ti	0.28	0.47
Mn	0.13	0.17
Fe	2.04	2.63
O	64.24	

TABLE III
MINERALS PRESENT IN RAW BENTONITE DETERMINED BY XRD ANALYSIS

Phase name	Figure of merit
Quartz	0.259
Bentonite	1.614
Albite	0.671

B. Effect of PACl, PEI and bentonite on certain parameters of the RO blow-down and raw water samples

The following graphs illustrate the impact each flocculant had on the water sample`s turbidity. From this, the optimum slow mixing time was determined for the next phase of the experiments. The sulphate removal from RO blowdown and raw water in Figures 1 and 2 respectively show similar trend as it is observed that PEI achieves better removal of sulphate followed by PAC and lastly bentonite; the percentage removal of sulphate increases with slow mixing time and more sulphate is removed from raw water than from the RO blowdown.

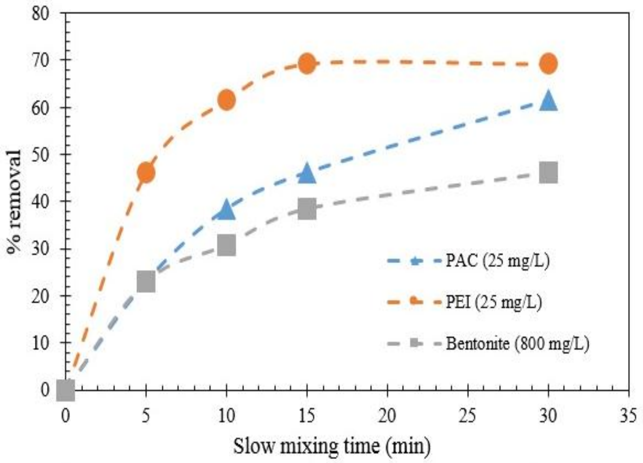

Fig. 1: Sulphate removal % versus slow mixing time (RO blow-down)

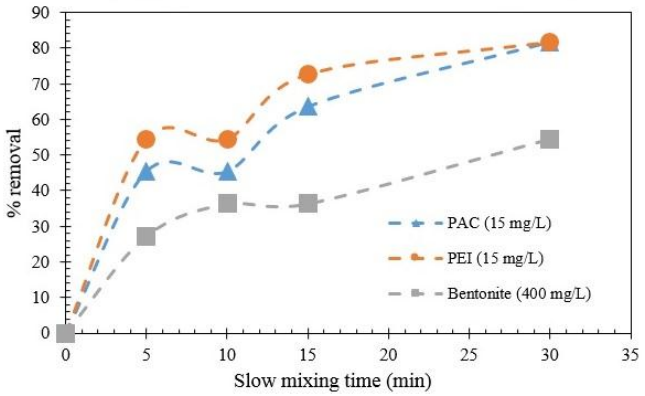

Fig. 2: Sulphate removal % versus slow mixing time (raw water)

Figures 3 and 4 show the effect of each flocculant on the turbidity removal from RO blow-down water sample. As seen, the PACl, and bentonite increased the turbidity greatly, while the turbidity remains almost constant when PEI is used as coagulant.

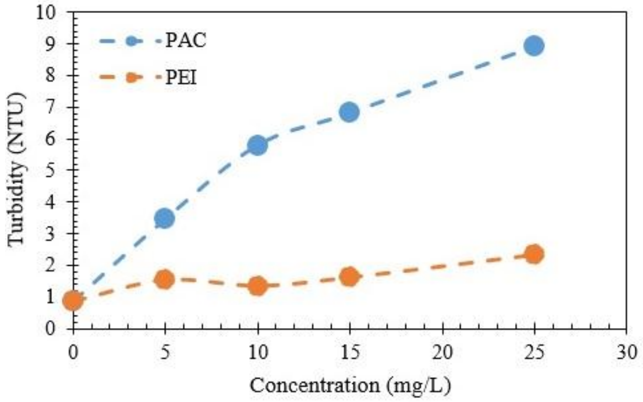

Fig. 3: Effect of PACl, PEI to turbidity on RO blow-down sample

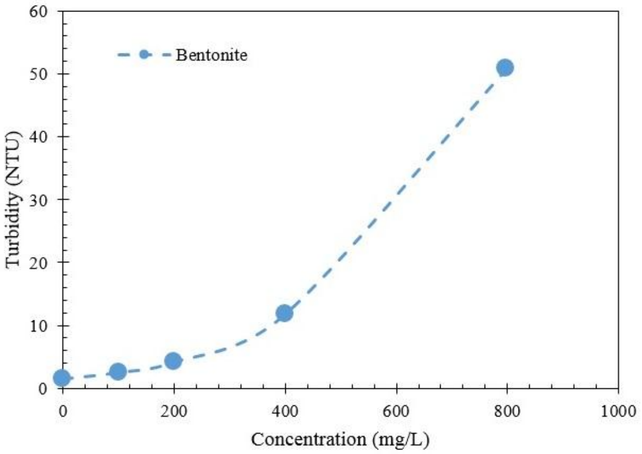

Fig. 4: Effect of bentonite to turbidity to RO blow-down sample

The removal of turbidity from the raw water sample using PACl, PEI and bentonite is shown in Figures 5 and 6. The same trend of results was observed as the addition of PACl or bentonite results mostly into the increase of turbidity while PEI maintain the same level of turbidity. The possibility is there that the increase in turbidity could be because of impurities that could exist in the PAC created. This could have had secondary reactions, forming more colloidal substances when added to the water.

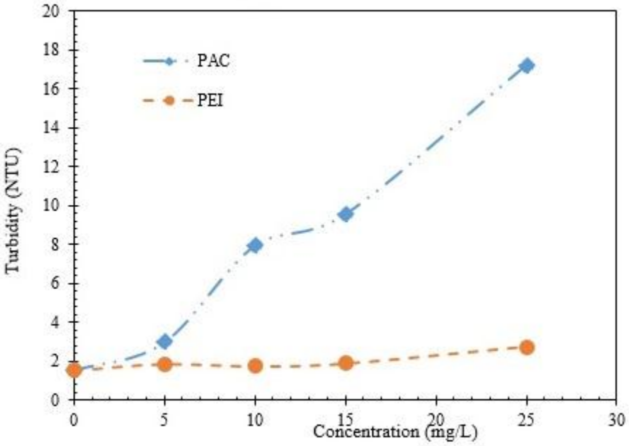

Fig. 5: Effect of PACl, PEI on turbidity of raw water

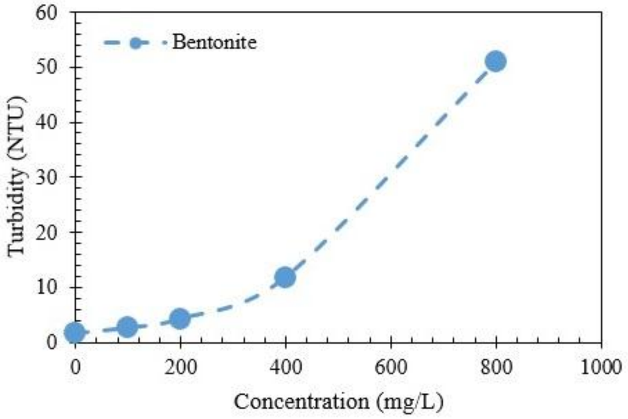

Fig. 6: Effect of bentonite to turbidity of raw water

The effect of the PACl, PEI and bentonite`s on the turbidity removal at varying slow mixing time is represented in Figure 7 and Figure 8 for the RO blow-down and raw water respectively. It can be observed that none of the coagulant reduces the turbidity; apart from the PEI which tend to maintain the turbidity constant, addition of bentonite mostly result into an increase in turbidity which remains high and constant over the range of slow mixing time.

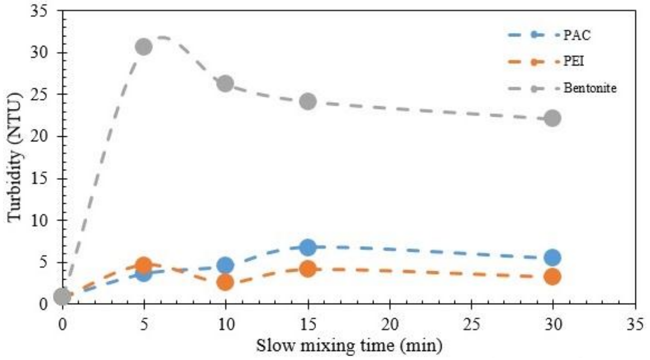

Fig. 7: Turbidity versus slow mixing time for RO blow-down

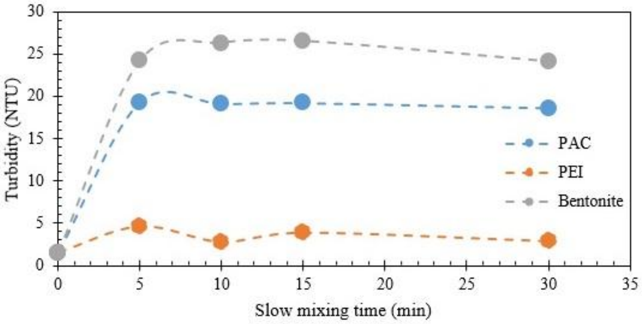

Fig. 8: Effect of slow mixing time of PACl, PEI and bentonite on the turbidity

Figures 9 and 10 depict the effect of flocculant on the pH of RO blow-down and raw water respectively. Addition of bentonite or PEI in the RO blow-down water resulted into insignificant increase in pH. The PACl however decreased the pH drastically. This can be due to the addition of the counter ions of H^+. This could also be the reason for the decrease in pH, which in turn led to the increase in turbidity when PAC was introduced. The same was observed for the raw water sample.

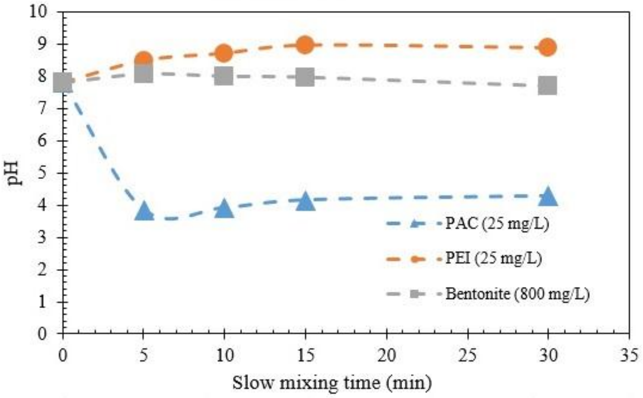

Fig. 9: Influence on pH of PACl, PEI and bentonite on RO blow-down as a function of slow mixing time

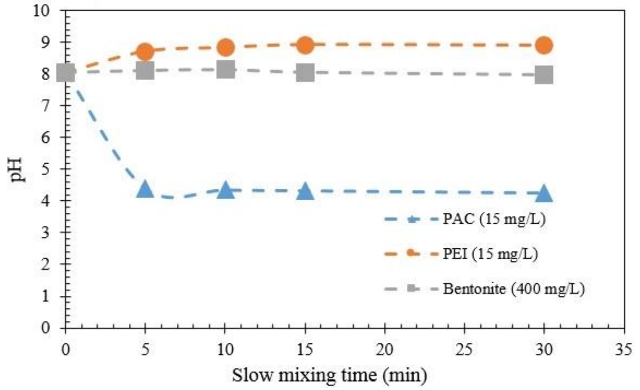

Fig. 10: Influence on pH of PACl, PEI and bentonite on raw water as a function of slow mixing time

C. Performance of PACl in combination with bentonite and PEI

Tables 4 and 5 show the results obtained from the use of combined flocculants for the treatment of RO blow-down and raw water respectively. As seen in Table 4, the sulphate content was lowered significantly from 3315 mg/L to 510 mg/L when using PACl and PEI in combination; the same combination allowed to mitigate the impact of PACl on the pH, resulting to a nearly neutral pH value of 6.25; lower turbidity was also recorded. This implies that the combination PACl and PEI is the best for the treatment of the RO blow-down. In Table 5, it can be observed that all the combinations of coagulants performed better than the single coagulants, with the combination PACl + PEI + bentonite achieving an acceptable pH close to neutrality of a value of 6.57.

TABLE IV
PERFORMANCE OF COMBINED FLOCCULANTS (RO REJECT)

Combination	pH	Conductivity (mS)	Sulphate (mg/L)	Temperature (C)
PACl+PEI	6.25	7.79	510	18.7
PACl+Bentonite	6.43	7.30	765	18.7
PEI+Bentonite	6.05	5.32	1020	18.7
PACl+PEI+Bentonite	6.62	8.64	765	18.7

Combination	Turbidity (NTU)
PACl+PEI	15.3
PACl+Bentonite	89.1
PEI+Bentonite	15.2
PACl+PEI+Bentonite	66.7

TABLE V
PERFORMANCE OF COMBINED FLOCCULANTS (RAW WATER)

Combination	pH	Conductivity (mS)	Sulphate (mg/L)	Temperature (C)
PACl+PEI	5.85	2.38	10	18.7
PACl+Bentonite	5.92	1.89	15	18.7
PEI+Bentonite	5.86	0.23	20	18.7
PACl+PEI+Bentonite	6.57	2.88	15	18.7

Combination	Turbidity (NTU)
PACl+PEI	20.3
PACl+Bentonite	77.4
PEI+Bentonite	19.6
PACl+PEI+Bentonite	63.7

Overall it was observed that the combination of coagulants performed well when compared to the coagulants added individually. A significant lowering in sulphate content was observed in both the RO blowdown and raw water. No significant change in conductivity was observed.

D. Alkalinity and Chloride

The addition of bentonite and PEI to the PACl had a good impact on lowering of alkalinity of the RO blow-down with values decreasing from 156 (mg $CaCO_3$/L) to 54, 38 and 104 when adding PACl+PEI, PACl+bentonite and PEI+bentonite respectively. A slight decrease of alkalinity was also recorded when treating raw water, starting with 26 mg $CaCO_3$/L, and resulted in 18, 24 and 12 mg $CaCO_3$/L respectively. This slight decrease can be due to the fact that the initial alkalinity was relatively low. The intial chloride concentration in the RO blow-down and raw water was recorded as 350 mg Cl^-/L. and 41,67 mg Cl^-/L respectively. No significant reduction was observed for the instances where PACl was added. This is due to the addition of Cl^- ions added by means of the PACl. As for the combination of PEI and bentonite, chloride was reduced to 240 mg Cl^-/L for RO blow-down.

IV. CONCLUSION

PACl demonstrated great removal effectiveness alone and, when used in combination with bentonite and PEI, produced good results. It can be derived from the above mentioned data that PACl in combination with bentonite clay and supplemented by the cationic organic polymer, PEI, is an effective method for the desalination of the processed and raw water from the Komati power plant. There is however a concern related to the considerable decrease of pH due to the addition of PACl, as well as the relative increase of turbidity during all the possible treatment investigated. Future studies will aim at addressing such concerns.

ACKNOWLEDGMENT

The authors are grateful to the sponsor from ESKOM, the North-West University and the National Research Foundation (NRF) in South Africa. Any opinion, findings and conclusions or recommendations expressed in this material are those of the authors and therefore the NRF does not accept any liability in regard thereto. The contribution of N. Lemmer is acknowledged and greatly appreciated.

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