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Removal of Aqueous Natural Organic Pollutants Using Mixed Mining Solid Wastes: Coal Fly Ash and Iron Sludge

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Abstract. A new coagulant (ash sludge) has been developed from a mixture of mining solid wastes (coal fly ash and iron sludge). The chemical composition of the coal fly ash and iron sludge was characterised by X-ray fluorescence (XRF). The effectiveness of the coagulant was tested on the removal of aqueous natural organic matter and its improvement on total hardness, conductivity and turbidity of water under different pH and adsorbent dosages. The coagulant contains a high composition of Al^{3+} and Fe^{3+} ions. Ash sludge uses a lower optimum dosage (40 mgL^{-1}) compared to the conventional coagulant, alum (55 mgL^{-1}). At optimum pH 8, ash sludge removed 80.2% of the aqueous natural organic matter while alum removed 70.9%. Under optimised pH and coagulant dosage, alum coagulated water showed a higher total hardness (166 mgL^{-1}) compared to ash sludge (155 mgL^{-1}). Compared to alum, ash sludge exhibits an excellent potential in the removal of organic materials and gives water with better qualities.

Keywords: alum, coagulant, demineralisation, flocculation, natural organic pollutants.

1. INTRODUCTION

The presence of natural organic pollutants (NOM) in raw water has a negative effect on the operation of demineralisation plants. These organic pollutants slip onto the anion bed of the demineralisation plant leading to resin fouling (Cornelissen et al., 2008). Interaction of NOM with the resin results in numerous problems such as increased resin regeneration frequency, increased operation costs due to high consumption of regeneration chemicals, slippage of silica into high pressure boilers causing damage and boiler corrosion by acidic organics (Beril et al., 2005; Basheer et al., 2011). Resin fouling causes overall reduction in capacity and life expectance of resin.

To overcome these problems, organic loading in water is reduced using conventional treatment processes (Bachir, 2008). These conventional treatment processes which have now been adopted by most industries involve coagulation and flocculation (Mesdaghinia et al., 2005) of raw water followed by clarification, sand filtration and finally demineralisation through cation and anion exchange resins. Coagulation is an established process of transforming small particles into larger aggregates that

can be removed in subsequent sedimentation and filtration stages (Shaw, 1992). The process of coagulation is commonly done by alum ($Al_2(SO_4)_3 \cdot 14H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$) (Edzwald and Tobiason, 1999). The advantages of using alum as a coagulant are that it readily dissolves in water and it does not stain equipment reddish brown like ferric sulphate. However alum has a limited working pH range (Johnson and Amirtharajah, 1983; Świetlik and Sikorska, 2005). Organic matter in water mainly consists of humic substances which are removed using alum through two mechanisms namely binding to metal species or anionic sites (Randtke, 1988) and adsorption on amorphous metal hydroxide precipitates (Mesdaghinia et al., 2005).

In addition to alum, other salts such as sodium aluminate, ferric chloride, ferric sulphate and cationic polymers (Gregory and Duan, 2001; Asaari and Zahari, 2007) have been used as coagulants. A significant advantage of iron salts over alum is a broader coagulation pH range thus the treatment of soft coloured water could result in the colour being preferably removed under acidic conditions (Zhao et al., 2011).

In this study, a new coagulant from coal fly ash and iron sludge wastes is prepared. These toxic wastes are produced in large quantities from a local power station and iron smelting company. Coal fly ash and iron sludge contain three coagulating constituents namely aluminum, iron and carbon. The use of these wastes will reduce their accumulation and toxicity to the environment. The new coagulant will be economical since it eliminates costs incurred in procuring conventional coagulants. The water treated by the new coagulant will be strictly used for boiler operations since ash contains some toxic compounds such as arsenic and mercury which are carcinogenic (Page et al., 1979). The residual inorganic compounds in the ash and iron slag will be removed by the demineralisation anionic and cationic resins. The iron sludge and ash contain high levels of Al^{3+} and Fe^{3+} and is therefore expected to be an effective coagulant. Studies on the use of coal fly ash as a coagulant have been reported in literature (Sha et al., 2013, Moyo et al., 2012). To the best of our knowledge no studies on the combined use of these wastes to make a coagulant have been reported in literature.

2. MATERIALS AND METHODS

2.1. Sample preparation

Iron sludge was collected from Zimbabwe Iron Steel mine smelting dumping site, pulverised and screened through a 300 μm mesh. The coal fly ash was collected from dumping sites of a coal mine, Hwange Colliery in Zimbabwe. The coal fly ash samples were dried at 105 ºC for 2 h. The samples were ground and sieved to a particle size of between 50-150 μm. Elemental analyses of the powdered samples were done by X-ray fluorescence (Philips PW1606).

Coal fly ash and iron sludge were prepared according to a previously reported procedure (Rao, 2006). Powdered coal fly ash (60 g) and iron sludge (30 g) were mixed in a 500 mL beaker. This was followed by addition of 150 mL of 3.5 M H_2SO_4 under continuous stirring. The solution was gently heated on an electric hot plate for 2.5 h and allowed to cool to room temperature. The mixture (ash sludge coagulant) was dried for 5 h in an oven at 60 ºC.

2.2. Water analysis

Raw river water (Gweru river, Zimbabwe) was collected from a special sampling point along the main line feed to the clarifier using the grab sampling method. The sampling container was pretreated with concentrated nitric acid and rinsed thoroughly with distilled water to remove any contaminants before collecting water. The pH, turbidity, total hardness, conductivity and UV-Vis absorbance (Shimadzu 1601) of the raw water was determined at 254 nm. The total hardness was determined using complexometric titrations (Betz and Noll, 1950).

2.3. Batch studies

2.3.1. Effect of pH of solution

Raw water (500 mL) at different pH (2-10) was transferred into 10 beakers. Samples of alum and ash sludge were separately added into each beaker to make 10 mgL^{-1} coagulant dosages. Each of the 10 beakers was stirred for 60 seconds and allowed to flocculate for 1 h. The water was then filtered to remove the floc and large particles. The coagulated water was analysed on a UV-Vis spectrometer at 254 nm.

2.3.2. Effect dosages of alum and ash sludge

Separate dosages of alum and ash sludge were added to beakers containing 500 mL raw water adjusted to pH 8 to make coagulants dosages in the range 10-70 mgL^{-1}. Each of the beakers was stirred vigorously (300 rpm) for 1 minute to spread the coagulant throughout the water. The mixture was left to settle for 1 h and filtered. The water was analysed for pH, turbidity, total hardness, conductivity, UV-Vis absorption and residual metal ion content.

Table 1: Chemical compositions of iron sludge and coal fly ash

Compound	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	MgO (%)	C (%)
Coal fly ash	50.65	18.65	20.17	3.16	2.35	5.02
Iron sludge	15.82	4.82	41.76	5.76	1.64	30.2

Table 2: Effect of coagulant dosage on floc formation and settling time

Dosage (mgL^{-1})	Floc formation time (s)		Floc settling time (s)	
	Alum	Ash sludge	Alum	Ash sludge
10	3000	20	3910	2100
25	2715	10	3620	900
40	2740	5	3336	300
55	1800	5	3002	420
70	1531	3	3306	1200

Table 3: Residual Al^{3+} and Fe^{3+} ions in water at optimum coagulant dosages and pH 8

Coagulant	Residual Al^{3+} (ppm)	Residual Fe^{3+} (ppm)
Alum	0.23	-
Ash sludge	0.13	0.15

3. RESULTS AND DISCUSSIONS

3.1. Chemical composition of wastes

The chemical compositions of the wastes are shown in Table 1. The most prevalent coagulating compounds in iron sludge and coal fly ash are Fe_2O_3 and Al_2O_3 respectively. A high percentage of SiO_2 in coal fly ash is not a cause for concern since it is removed in the filtration bed and in the anion resin. Carbon found in these wastes participates in coagulation through adsorption of the organic and inorganic compounds (Namasivayam et al., 2007). A combination of iron sludge and fly ash has a high potential of producing an effective coagulant.

3.2. Effect of solution pH

The effect of the solution pH on the removal of NOM during coagulation and flocculation is illustrated in Fig. 1. The maximum removal of NOM was observed at pH 8 for both coagulants. At optimum pH, 32 and 44% of NOM were removed using alum and ash sludge respectively. At this pH, NOM will be in anionic form and the metal coagulants are cationic metal hydroxides (Ma et al., 2001).

There is low removal of NOM at low pH due to partially ionised anionic NOM sites resulting in weak bonding and formation of small flocs (Bachir, 2008). Above pH 8, there is a reduction in NOM removal due to neutralisation of the positive charge on the metal hydroxides coagulant as more OH$^-$ ions are added (Bachir, 2008). On the other hand, NOM will increasingly become ionised due to proton loss at higher pH, hence a need for higher coagulant dosages (Shaw, 1992).

3.3. Effect of coagulant dosage

Table 2 shows the floc formation and settling times of the coagulants at pH 8 and coagulant dosages of 55 mgL^{-1} and 40 mgL^{-1} for alum and ash sludge respectively. The larger black ash sludge flocs settle faster than the smaller brown alum flocs. The faster formation time of flocs from ash sludge is attributed to the combined coagulant effects of iron and aluminum. Iron and aluminum form cationic hydroxides in water which bind the negatively charged NOM at pH 8 (Rebhun and lurie, 1993). Porous carbon adsorbs the organic and inorganic compounds in water (Bachir, 2008; Shaw, 1992). Previous studies done by Bachir (2008), comparing the floc formation and settling times of alum and iron sulphate coagulants show that iron sulphate forms flocs in 10 minutes while alum formed flocs in 35 minutes because of higher Al^{3+} charge density.
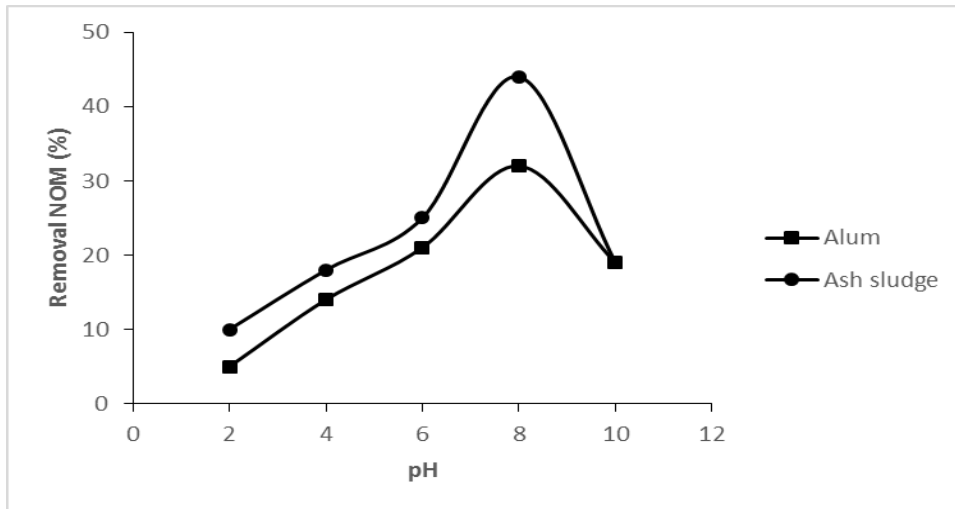
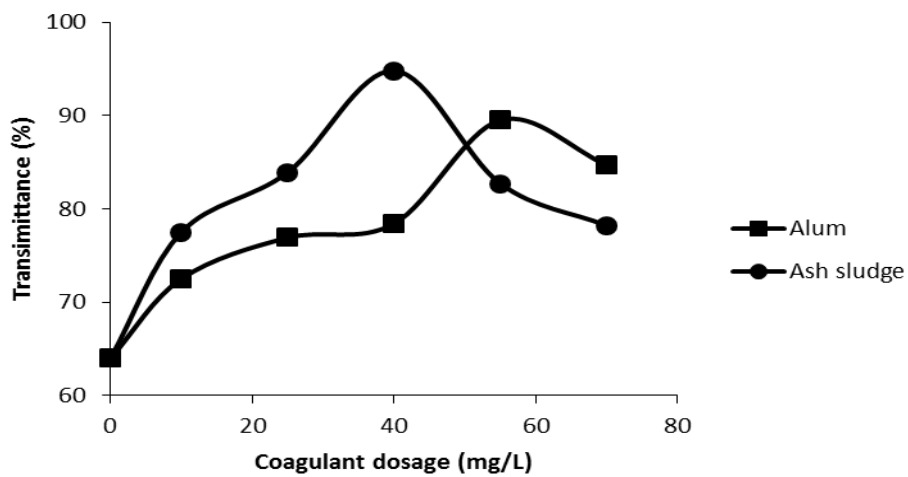**Fig. 1:** Effect of change in pH on the removal of organics by coagulants

Fig. 2: Effect of coagulant dosage on turbidity removal at pH 8
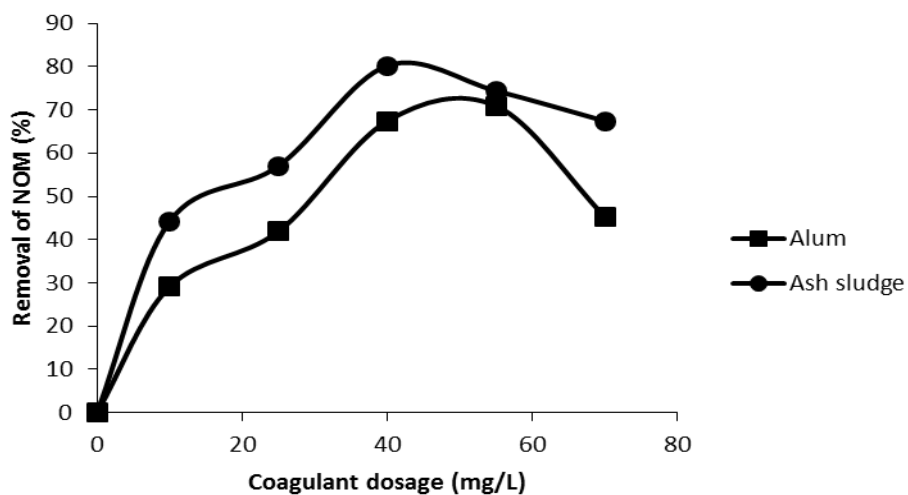

Fig. 3: Effect of coagulant dosage on NOM removal at pH 8

Turbidity in water is caused by suspended particles and colloidal matter and is an expression of the optical property of light that scatter rather than transmit (Davies-Colley and Smith, 2001). Fig. 2 shows the effect of coagulant dosages on turbidity removal at pH

8. The optimum dosage for turbidity removal was 40 mgL^{-1} and 55 mgL^{-1} for the ash sludge and alum respectively. The optimum coagulant dosage was defined as the coagulant that gave the highest filtered water turbidity transmittance. The water transmittance

increased from 60% (raw water) to 94.8% and 89.5% at optimum dosages of ash sludge and alum respectively. As the coagulant dosage increases the water gets less turbid until optimum dosage is attained. At a point of complete charge neutralization, the colloids agglomerate to give bigger flocs that readily settle at the bottom and leave the water clear with no notable suspended particles which signals the optimum conditions for turbidity removal. Addition of excessive coagulant results in adsorption of coagulant metal ions causing reversal of the net charge on the colloidal particles and colloidal restabilisation. Restabilisation of colloids by charge reversal allows greater amounts of small particles to remain in solution, thus reducing the transmittance and increasing the suspended solids content in the treated water (Kretszchmar et al., 1997). This trend is more pronounced in ash sludge than in alum. The effect of coagulant dosages on the removal of NOM is shown in Fig. 3. At optimum dosages of alum (55 mgL^{-1}) and ash sludge (40 mgL^{-1}), 70.9 and 80.2% of NOM respectively were removed.

Fig. 4 shows the effect of increasing coagulant dosages on water conductivity. The conductivity decreases with increase in coagulant dosage until optimum dosages are attained. At optimum dosage, water containing alum and ash sludge recorded conductivities of 178 and 176 µS respectively. An increase in coagulant dosage increases removal of inorganic compounds. Ash sludge coagulant adsorbed more inorganic compounds than alum due to presents of both Al^{3+} and Fe^{3+} ions compared to only Al^{3+} in alum. Beyond optimum dosages, there was an increase in conductivity due to adsorption of excess coagulating metal ions on larger flocs resulting in reversal of net charge and restabilisation of colloidal particles (Kretszchmar et al., 1997). Beyond optimum dosage the higher conductivity of water was observed using alum compared to the use of ash sludge. This observation confirms that restabilisation of colloidal particles was faster in alum water than in water containing ash sludge.

Total hardness is a measure of the amount of calcium and magnesium ions in water (Fritz, 1969). The effect of coagulant dosages on the removal of total hardness from water is shown in Fig. 5. Maximum total hardness removal occur at optimum coagulant dosages. At optimun dosage, alum was less effective in removing total hardness (166 mgL^{-1}) compared to ash sludge (152 mgL^{-1}). Total hardness decreased with increase in coagulant dosage until the optimum coagulant dosages are attained. Ash slugde was more effective than alum in removing calcium and magnesium ions. This attributed to a greater number of coagulant species in ash sludge compared to alum. An increase in total hardness beyond optimum coagulant dosages is attributed to net charge reversal and restabilisation of colloidal particles.

Table 3 shows the concentrations of residual coagulant metal ions. High concentrations of residual Al^{3+} and Fe^{3+} ions in water after enhanced coagulation enhance exhaustion of the cationic resin (Beril et al., 2005). Carbon in ash sludge adsorbs inorganic compounds which accounts for lower residuals Al^{3+} in water using ash sludge. The maximum allowable residual metal ion content in water is 0.3 ppm (Furlan et al., 2009). Therefore the residual metal ions were below the maximum permissible levels.
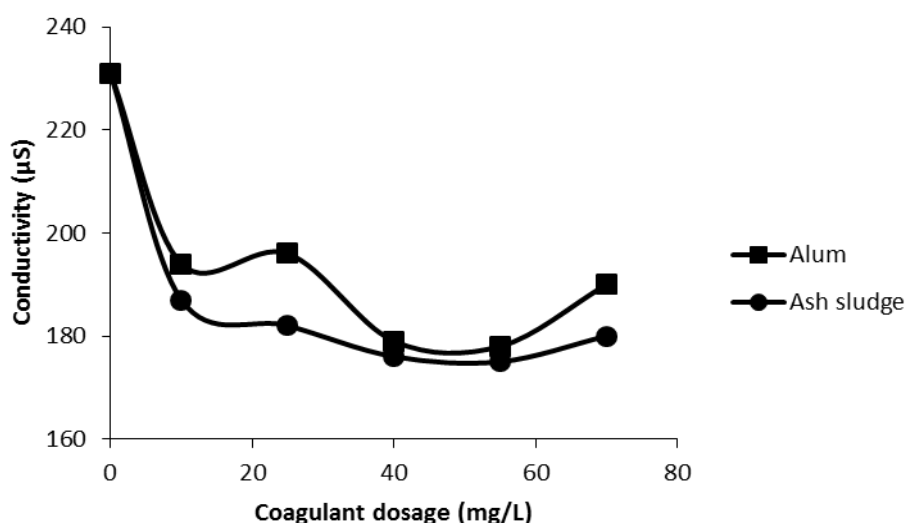

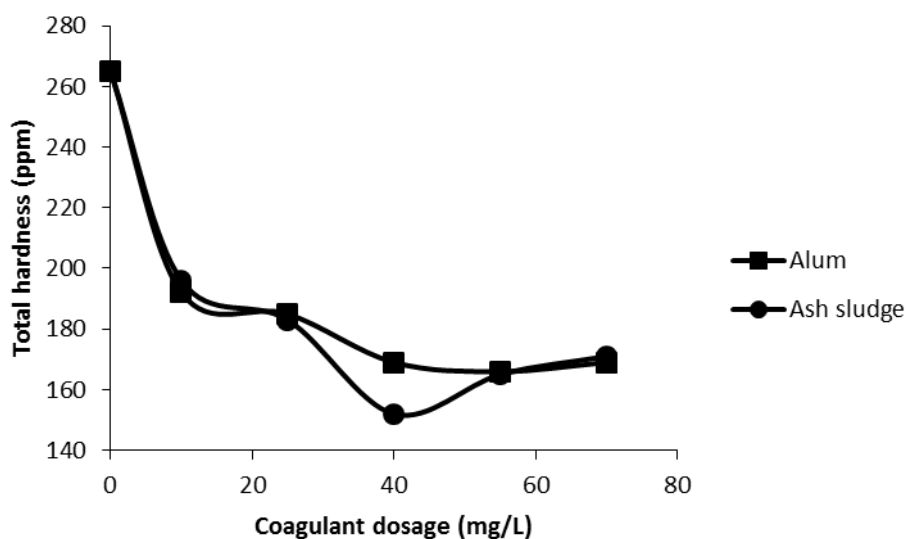**Fig. 4:** Effect of coagulant dosage on water conductivity at pH 8

Fig. 5: Effects of coagulant dosages on total hardness

4. CONCLUSION

The ash sludge coagulant was successfully synthesised using coal fly ash and iron sludge. The overall performance of ash sludge was superior to alum in all aspects. Ash sludge has a higher percentage removal of NOM at lower coagulant compared to alum. The new coagulant has shown great potential in reducing accumulation of environmental waste through economic utilisation of toxic wastes. Future work on the effect of varying proportions of fly ash and iron sludge could further increase the percentage removal of NOM. Further study on the effectiveness of ash sludge in removing heavy metal pollutants is in progress.

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