

Effect of coagulant treatment on the metal composition of raw water

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Abstract

This study reports the results of an investigation on the use of two coagulants, namely $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ which were investigated for their capabilities to reduce the metal levels of raw river water samples when treated. Generally, the percentage removal of the metals from raw water samples increased with mg/l dosage of either coagulant used. Although both coagulants were efficient in removing Cr and Ni, generally $Fe_2(SO_4)_3$ was proved to be the more efficient coagulant for the removal of all the metals studied. $Fe_2(SO_4)_3$ was 89.58% efficient in removing Cr and 99.73% efficient in removing Ni. It was 68.42% efficient in removing Zn, 40.14% efficient in removing Mn and 35.29% efficient in removing Cd (all at 13 mg/l dosage of coagulant). Judging from these results and taking into consideration the potential health threat to man from the possible Al contamination of treated water from the use of aluminium-based coagulants, the use of $Fe_2(SO_4)_3$ as coagulant in water treatment for the removal of suspended matter was preferred and would be highly recommended.

Introduction

Heavy metal removal is an important step in water-treatment processes. The aim of water treatment is to achieve the required standard of final water quality regardless of the quality of the source water. However, the extent of water treatment for domestic use will depend on the freshwater source quality. Some sources, such as rivers, require more extensive treatment than others, such as deep borehole water (Rossi and Ward, 1993). Many coagulants are widely used in conventional water-treatment processes for potable water production. Coagulants can be classified into inorganic coagulants, synthetic organic polymer and naturally occurring coagulants. They are used for various purposes depending on their chemical characteristics. An inorganic polymer 'PAC' (polyaluminium chloride) is the most widely used coagulant in water treatment (Van Benchosten and Edzwald, 1990; Boisvert et al., 1997; Najm et al., 1998; Okuda, et al., 1999, 2001).

Though aluminium-based coagulants are frequently used in water treatment there are fears that aluminium (the major component of PAC and alum) may induce Alzheimer's disease (Crapper et al., 1973; Miller et al., 1984; Martyn, et al., 1989) and that they exhibit strong carcinogenic properties (Dearfield et al., 1964; McCollister et al., 1964; Mallevalle et al., 1984). Some domestic tap waters may contain aluminium in relatively high concentrations because aluminium has been added as a flocculant during the purification process (DWAf, 1996). The implication of this may be serious since aluminium ions have been demonstrated to be toxic especially in individuals with impaired renal function (Savory and Wills, 1991).

Coagulation or chemical precipitation has been known since the previous century when it became widely used in England where lime was used as coagulant alone or with calcium chloride or magnesium (Genovese and Gonzale, 1998). Removal of turbidity by coagulants however, depends on the type of colloids in suspension,

pH, chemical composition of the water, the type of coagulant and coagulant aid, and the degree and time of mixing provided for chemical dispersion and floc formation (Rossi and Ward, 1993). Furthermore, Cheng et al. (1995) studied the coagulation mechanism by using $Al_2(SO_4)_3$, a cationic polymer and $FeCl_3$. They found two main mechanisms of coagulation: At a relatively high coagulant dosage and higher pH, the adsorption of particles onto a floc of aluminium hydroxide or ferric hydroxide predominates, while the formation of insoluble complexes in a way that is analogous to that of charge neutralisation predominates at low coagulation dosage and lower pH values.

Findings on various coagulation processes have been reported in literature. These include addition of fish scales to enhance the solids removal by dissolved air flotation (Genovese and Gonzalez, 1998); coagulation of liquid effluent from fish-meal processing by heat and pH changes (Civit et al., 1982); effect of dosage and mixing conditions on the flocculation of concentrated suspensions using polymeric coagulants (Gregory and Guibai 1991); phosphate adsorption in flocculation processes of $Al_2(SO_4)_3$ and polyaluminium-silicate sulphate (Boisvert et al., 1997), to mention but a few.

In this study, two coagulants, namely $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ were investigated with the aim of determining their capabilities to reduce metal levels (Cd, As, Cr, Ni, Mn, Cu and Zn) of raw river water samples. The interest in coagulation processes and hence the removal of the metals lies in the fact that these metals may constitute a threat to human health particularly when they occur in levels above the minimum allowable threshold in water intended for human consumption (Cd, 5 µg/l, Cr (VI), 0.05 mg/l, As, 10 µg/l, Zn, 3.0 mg/l, Cu, 1.0 mg/l and Mn, 0.05 mg/l) (DWAf, 1996).

Materials and methods

Method

Raw water from Tyume River in Alice was filtered through an acid-washed glass-wool plug to remove large particulates. A 250 ml sample of filtered water was placed in a 500 ml beaker and stirred

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Al ₂ (SO ₄) ₃ as coagulant				Fe ₂ (SO ₄) ₃ as coagulant			
Dose (mg/l)	pH	Change in conc. of Cd (mg/l)	% Removal	Dose (mg/l)	pH	Change in conc. of Cd (mg/l)	% Removal
0	6.8	0.51	0	0	6.8	0.51	0
3	7.3	0.51	0	3	7.2	0.50	1.96
5	7.4	0.50	1.96	6	7.2	0.50	1.96
6	7.4	0.50	1.96	9	7.2	0.49	3.92
8	7.5	0.49	3.92	12	7.3	0.47	7.84
10	7.6	0.48	5.88	13	7.4	0.33	35.29

Al ₂ (SO ₄) ₃ as coagulant				Fe ₂ (SO ₄) ₃ as coagulant			
Dose (mg/l)	pH	Change in conc. of Cr (mg/l)	% Removal	Dose (mg/l)	pH	Change in conc. of Cr (mg/l)	% Removal
0	6.8	0.48	0	0	6.8	0.48	0
3	7.3	0.38	20.83	3	7.1	0.34	29.17
5	7.4	0.29	39.58	6	7.2	0.20	58.33
6	7.4	0.21	56.25	9	7.2	0.07	85.42
8	7.6	0.09	81.25	12	7.4	0.05	89.58
10	7.7	0.07	85.42	13	7.4	0.05	89.58

Al ₂ (SO ₄) ₃ as coagulant				Fe ₂ (SO ₄) ₃ as coagulant			
Dose (mg/l)	pH	Change in conc. of As (mg/l)	% Removal	Dose (mg/l)	pH	Change in conc. of As (mg/l)	% Removal
0	6.8	0.054	0	0	6.8	0.054	0
3	7.3	0.054	0	3	7.1	0.054	0
5	7.4	0.054	0	6	7.2	0.053	1.85
6	7.4	0.054	0	9	7.2	0.052	3.70
8	7.6	0.053	1.85	12	7.3	0.051	5.56
10	7.7	0.052	3.70	13	7.4	0.051	5.56

continuously using a magnetic stirrer at a speed of 100 r/min, and 0.1 M H₂SO₄ or 0.2M NaOH as appropriate was added to achieve the required pH. The water samples were coagulated with different doses of Al₂(SO₄)₃, namely 3, 5, 6, 8 and 10, mg/l Al₂(SO₄)₃; pH ranged between 7.3 and 7.8. Similarly, other water samples were coagulated also with different doses of Fe₂(SO₄)₃, namely 3, 5, 6, 8 and 10 mg/l Fe₂(SO₄)₃; pH ranged between 7.1 and 7.5. After coagulant in solution had been added, the stirring rate was accelerated

removal from raw water samples during the water treatment. Cd, As and Ni have been shown to have mutagenic, carcinogenic and teratogenic effects (Friberg et al., 1986; Fishbein, 1987; Stara et al., 1980; Fern and Harton, 1983; Ou et al., 1980). The genotoxicity of Cr has also been indicated (Bianchi and Levis, 1987; Bianchi and Levis, 1988). The major effect of the presence of Mn in domestic water is of aesthetic value. Though Zn, Cu, As and Cr are essential elements they could be harmful if present at undesirably high levels

to 300 r/min for 1 min and then reduced to 100 r/min and continued for 15 min. Any floc formed was allowed to settle for 30 min after stirring had been completed; 25 ml of the resultant solution was taken from 10 mm below the water surface, filtered through filter paper and analysed by Unicam Solar 969 Atomic Absorption Spectrophotometer (DWAF, 1992). For quality control, triply distilled water samples were spiked with a known amount of standard Cd, Cr, As, Ni, Mn, Cu and Zn, respectively, and the recoveries of the elements were measured using the above procedures for the parameters (DWAF, 1992). Blank determination was done with triply distilled water using the same procedure (DWAF, 1992) to establish blank levels.

Results and discussion

The percentage recoveries obtained for the elements were Cd, 66%, Cr, 78%, As, 69%, Ni, 84%, Cu, 62% and Zn, 73%, which validated the experimental procedures used for the chemical analysis. The results of the blank determinations for the metals showed clean blank levels. The levels of heavy metals in the river water samples before treatment with coagulants were: Cr, 0.48 mg/l; Cd, 0.51 mg/l; As, 0.054 mg/l; Ni, 0.75 mg/l; Mn, 1.42 mg/l; Cu, 1.08 mg/l and Zn, 0.38 mg/l. These values seem very high and might be due to effluents from diffuse sources such as rural and agricultural runoff and from point sources such as effluent from Alice Sewage Works, which are usually partially treated.

The results of the removal of metals from raw water samples using Al₂(SO₄)₃ and Fe₂(SO₄)₃ as coagulants respectively are shown in Tables 1 to 7. The metals, e.g. Cd, As, Cr and Ni can be extremely toxic to man even at low concentrations in domestic water supply when consumed (Stoepller, 1991; Leonard, 1991; Gauglhofer, 1991; Sunderman and Oskarsson, 1991) hence the need for their effective

in treated water samples (DWAf, 1996).

The results of Cd removal from raw water samples after coagulant treatments are shown in Table 1. Levels of Cd in water samples dropped from 0.51 mg/l at 0 mg/l $Al_2(SO_4)_3$ dosage to 0.48 mg/l at 10 mg/l $Al_2(SO_4)_3$ dosage (i.e., 5.88% removal; pH, 7.6) whilst after $Fe_2(SO_4)_3$ treatment the level fell to 0.33 mg/l at 13 mg/l dosage (i.e. 35.29% removal; pH, 7.4). The change in concentration of Cd after the coagulant treatments is not very significant and the final concentrations after the treatments were still higher than the South African water quality guideline of 5 µg/l Cd in water intended for domestic use.

The results for Cr removal from raw water samples by coagulants are shown in Table 2. The levels of Cr dropped from 0.48 mg/l at 0 mg/l $Al_2(SO_4)_3$ dosage to 0.07 mg/l at 10 mg/l $Al_2(SO_4)_3$ dosage (i.e., 85.42% removal; pH, 7.7). With $Fe_2(SO_4)_3$ treatment, Cr levels in water fell to 0.05 mg/l at 13 mg/l dosage (i.e. 89.58% removal; pH, 7.4). Significant removal of Cr from water was achieved with both coagulants but the removal was much more significant with $Fe_2(SO_4)_3$. The new level of Cr in water after $Fe_2(SO_4)_3$ treatment fell to within the South African water quality guideline of 0.05 mg/l in water intended for domestic use (DWAf, 1996).

The range of As removals from water after the $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ treatments, respectively, are shown in Table 3. Levels of As dropped from 0.054 mg/l at 0 mg/l $Al_2(SO_4)_3$ dosage to 0.052 mg/l at 10 mg/l $Al_2(SO_4)_3$ dosage (i.e. 3.70% removal; pH, 7.7). With $Fe_2(SO_4)_3$ treatment, the level fell to 0.051 at 13 mg/l dosage (i.e., 5.56% removal; pH; 7.4). The removals of As by either coagulant were very small and not significant. The level of As in water after coagulant treatments was still higher than the South African water quality guideline of 10 µg/l in water intended for domestic use (DWAf, 1996).

The change in concentrations of Ni in the river water samples after treatments with coagulants is shown in Table 4. Levels of Ni dropped from 0.75 mg/l at 0 mg/l $Al_2(SO_4)_3$ dosage to 0.34 mg/l at 10 mg/l $Al_2(SO_4)_3$ dosage (i.e. 54.67% removal; pH, 7.8) whilst its level fell to 0.002 mg/l at 13 mg/l $Fe_2(SO_4)_3$ dosage (i.e. 99.73% removal; pH 7.5). The percentage removal of Ni from water by $Fe_2(SO_4)_3$ is very significant. There is no South African guideline for Ni in water intended for domestic use (DWAf, 1996).

$Al_2(SO_4)_3$ as coagulant				$Fe_2(SO_4)_3$ as coagulant			
Dose (mg/l)	pH	Change in conc. of Ni (mg/l)	% Removal	Dose (mg/l)	pH	Change in conc. of Ni (mg/l)	% Removal
0	6.8	0.75	0	0	6.8	0.75	0
3	7.3	0.71	5.33	3	7.1	0.71	5.33
5	7.5	0.69	8.00	6	7.2	0.54	28
6	7.6	0.58	22.67	9	7.4	0.39	48
8	7.6	0.40	46.67	12	7.5	0.24	68
10	7.8	0.34	54.67	13	7.5	0.002	99.73

$Al_2(SO_4)_3$ as coagulant				$Fe_2(SO_4)_3$ as coagulant			
Dose (mg/l)	pH	Change in conc. of Mn (mg/l)	% Removal	Dose (mg/l)	pH	Change in conc. of Mn (mg/l)	% Removal
0	6.8	1.42	0	0	6.8	1.42	0
3	7.3	1.26	11.27	3	7.1	1.24	12.68
5	7.4	1.26	11.27	6	7.2	1.08	23.94
6	7.4	1.17	17.61	9	7.2	1.02	28.17
8	7.6	1.08	23.94	12	7.3	1.00	29.58
10	7.8	1.00	29.58	13	7.4	0.85	40.14

$Al_2(SO_4)_3$ as coagulant				$Fe_2(SO_4)_3$ as coagulant			
Dose (mg/l)	pH	Change in conc. of Cu (mg/l)	% Removal	Dose (mg/l)	pH	Change in conc. of Cu (mg/l)	% Removal
0	6.8	1.08	0	0	6.8	1.08	0
3	7.3	1.06	1.85	3	7.1	1.05	2.78
5	7.4	1.06	1.85	6	7.2	1.04	3.70
6	7.4	1.06	1.85	9	7.2	1.04	3.70
8	7.6	1.06	1.85	12	7.3	1.04	3.70
10	7.7	1.03	4.63	13	7.4	1.02	5.56

The removals of Mn from water samples after treatment with coagulants are shown in Table 5. Levels of Mn dropped from 1.42 mg/l at 0 mg/l $Al_2(SO_4)_3$ dosage to 1.00 mg/l at 10 mg/l $Al_2(SO_4)_3$ dosage (i.e. 29.58% removal; pH, 7.8). With $Fe_2(SO_4)_3$ treatment, the levels fell to 0.85 mg/l at 13 mg/l dosage (i.e., to 40.14%; pH, 7.4). The removal of Mn from water by $Fe_2(SO_4)_3$ was significant, though the level was still higher than the 0.05 mg/l Mn South African water quality guideline for water intended for domestic use (DWAf, 1996).

TABLE 7
Removal of Zn from river water after treatment with coagulants

Al ₂ (SO ₄) ₃ as coagulant				Fe ₂ (SO ₄) ₃ as coagulant			
Dose (mg/l)	pH	Change in conc. of Zn (mg/l)	% Removal	Dose (mg/l)	pH	Change in conc. of Zn (mg/l)	% Removal
0	6.8	0.38	0	0	6.8	0.38	0
3	7.3	0.27	28.95	3	7.1	0.19	50
5	7.4	0.27	28.95	6	7.2	0.16	57.89
6	7.4	0.24	36.84	9	7.2	0.15	60.53
8	7.6	0.24	36.84	12	7.3	0.14	63.16
10	7.8	0.20	47.37	13	7.4	0.12	68.42

The removal of Cu from raw water samples using Al₂(SO₄)₃ and Fe₂(SO₄)₃ as coagulants, respectively, are shown in Table 6. Levels of Cu dropped from 1.08 mg/l at 0 mg/l Al₂(SO₄)₃ dosage to 1.03 at 10 mg/l coagulant dosage (i.e. 4.63% removal; pH, 7.7) whilst the level fell to 1.02 at 13 mg/l Fe₂(SO₄)₃ dosage (i.e. 5.56% removal; pH, 7.4) which was very insignificant. However, the level of Cu in the river water after the coagulant treatments was close to the South African water quality guideline of 1.0 mg/l Cu for water intended for domestic use (DWAf, 1996)

The change in concentrations of Zn in water samples after the coagulant treatments is shown in Table 7. The levels of Zn fell to 0.20 mg/l at 10 mg/l Al₂(SO₄)₃ dosage (i.e., 47.37% removal; pH, 7.8) from 0.38 mg/l at 0 mg/l dosage. The levels using Fe₂(SO₄)₃ as coagulant dropped from 0.38 mg/l to 0.12 mg/l at 13 mg/l (i.e., 68.42% removal; pH, 7.4). This change in Zn concentration is very significant and the new level after Fe₂(SO₄)₃ treatment is much less than the South African water quality criterion of 3.0 mg/l Zn in water intended for domestic use (DWAf, 1996) (Table 7).

Generally, the percentage removal of the metals from raw water samples increased with mg/l dosage of coagulant used. Though both coagulants were efficient in removing Cr and Ni, Fe₂(SO₄)₃ was a more efficient coagulant for the removal of all the metals than Al₂(SO₄)₃. Judging from these results and taking into consideration the potential health threat to man from possible Al contamination of potable water produced with Al-based coagulant (Alfery et al. 1976; Savory and Wills, 1991), the use of Fe₂(SO₄)₃ as coagulant in water treatment is highly recommended for water of similar characteristics especially when coagulant dosing is used as the sole treatment.

Conclusion

Two coagulants, namely Al₂(SO₄)₃ and Fe₂(SO₄)₃ were investigated for their efficiency in removing metals from raw river water samples during treatment. The percentage removal of the metals from raw water samples increased with mg/l dosage of either coagulant used. Apart from removing suspended matter which is the primary purpose of adding coagulant to water, both coagulants have the additional advantage of being capable of removing metals. However, Fe₂(SO₄)₃ proved to be the more efficient coagulant in this regard. Taking into consideration the potential health threat to man from the possible Al contamination of potable water produced with Al-based coagulant, the use of Fe₂(SO₄)₃ as coagulant in water treatment would be highly recommended for water of similar characteristics and when coagulant dosing is used as the sole treatment.

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