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COAGULATION TREATMENT BY $Al_2 (SO_4)_3$ AND RESIDUAL Al DETERMINATION IN MEDJERDA WATER DAM (TUNISIA)

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ABSTRACT: The effect of pH, agitation speed and coagulant dosage on the coagulation performance of aluminium sulfate with respect to the treatment of Medjerda water was investigated in this paper. The measurement of residual aluminium speciation was also conducted. The evaluation of treatment efficiency of the optimization of coagulation process while was determined by measuring the reduction of turbidity, chemical oxygen demand (COD) and organic matter (OM). The optimal operational conditions are as follows: initial pH value of 6, concentration of aluminium sulfate of 30 $mg.L^{-1}$ and agitation speed of 80 rpm.

Keywords: Raw water, coagulation, Aluminium sulfate, chemical oxygen demand, organic matter.

RESUME : L'effet du pH, de la vitesse d'agitation et de la dose du coagulant sur le rendement de coagulation de l’eau du canal Medjerda ont été étudiés. La mesure d’aluminium résiduel et sa spéciation a également été menée. L'évaluation de l'efficacité du traitement de l'optimisation des processus de coagulation a été déterminée en mesurant la réduction de la turbidité, la demande chimique en oxygène (DCO) et de la matière organique (MO). Les conditions optimales sont les suivantes: pH optimum est égal à 6, la concentration optimale de sulfate d'aluminium est de l’ordre de 30 $mg.L^{-1}$ et la vitesse d'agitation est égale à 80 tours par minute.

Mots clés: Eau brute, coagulation, sulfate d’aluminium, demande chimique en oxygène, matière organique.

INTRODUCTION

Coagulation by metal salts such as aluminium sulfate is an important and widely applied process in water treatment. It is popular as a pre-treatment process for the removal of raw water turbidity (Tu), organic matter (OM), color, and microorganism [1-2]. Although effective for removing turbidity and organic materials, Al-based coagulants, particularly alum, may result in elevated concentrations of residual Al in finished water [3-4]. High concentrations of residual dissolved Al indicate incorrect coagulant dosing, inefficient use of the coagulant, or problems in the chemistry of treatment process. Thus, Al fractionation measurements can provide the treatment plant operator with valuable information about various aspects of plant performance [3].

Aluminium (Alum) determination at low level is of particular interest in potable water units because this metallic ion is commonly used as reactant for coagulation–flocculation in the treatment of raw waters to remove colloidal or suspended particles or to eliminate organic matter. At the outlet of these units, maximum tolerable level of this cation has been fixed to 200 µg L^{-1} by European Legislation [5]. This cation is associated with various health problems in numerous studies, from gastrointestinal damage and phosphate deficiency to dialysis encephalopathy, renal oestrodistrophy and Alzheimer’s disease [6-7]. In order to optimize coagulation process in drinking water plants and to minimise aluminium levels in finished water, monitoring of this metal contents during and after raw water treatment is there- fore needed. Up to now, the coagulant quantities are generally

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determined by the empiric Jar-test technique that induces problems of excess (or insufficient) reagent, particularly during period of fast variation in water quality [8-9].

The combination of coagulation with other appropriate physicochemical treatment processes such as water initial pH, coagulant dosage, and mixing conditions results in enhanced efficiency of the coagulation–flocculation process [10-11]. During raw water treatment, the determination of coagulant dosage is one of the most important factors among various works conducted in unit processes [12]. Other properties of the raw water such as influent turbidity, agitation speed, water initial pH, etc. affects the type of coagulant and its dosage [13-14].

The aim of this study was to optimize coagulation-flocculation. This study examined the individual and interactive influences of coagulation and flotation factors (i.e., speed agitation, coagulant dose, and pH) on the removal of turbidity, COD, and OM. The content and variation of different residual Al speciation in the water after coagulation with reference to the specific surface water treatment were systematically examined and analyzed.

2. MATERIALS AND METHODS

2.1. Materials

Analytically pure sodium hydroxide (NaOH) and hydrochloric acid (HCl) of concentration 0.50 $molL^{-1}$ reagents were used for regulating the pH of domestic sewage.

$Al_2 (SO_4)_3.18H_2O$ (Aldrich) has been used as coagulant. The initial $Al_2 (SO_4)_3$ solution was prepared by directly dissolving certain amount of $Al_2 (SO_4)_3.18H_2O$ to deionized water and it was used immediately after preparation.

2.2 COD (chemical oxygen demand) measurement

Sample for COD measurement was stored in acid- cleaned and muffled borosilicate clear glass vials with Teflon-lined caps, and 50 µl of 6 N HCl was added (pH < 2) to remove inorganic carbon and inhibit bacterial activity. COD samples were stored frozen until further processing. COD concentration was measured by high temperature combustion using a Shimadzu TOC-5000 as described in Burdige and Homstead (1994) [15].

2.3 Coagulation-flocculation experiments

All experiments were carried out on raw water collected from Medjerda dam (Tunisia) water quality shown in Table 1. Standard jar tests were performed using a program-controlled jar test apparatus with six flat impellers at a room temperature of 18.0–20.0 °C. The test water of 1.00 L was transferred into each 2.00 L plexiglass beakers. The initial pH was adjusted to the set value using 0.5 mol L^{-1} HCl and NaOH. The solutions were stirred rapidly at 200 rpm for 1min during coagulant addition, followed by slow stirring at 40.0 rpm for 15.0 min and quiescent settling for 30.0 min. After deposition, water samples were collected from 2.00 cm below the solution surface for subsequent measurements. The clarified water was extracted from the beaker to measure chemical oxygen demand (COD) residual turbidity (Tu) and permanganate oxygen demand (Organic matter: OM).

2.4. Measurement of residual Al content

In general, residual Al ratio represents the residual Al induced by coagulant itself and it is an important parameter of various coagulants in practical application [16-17].

The sample was acidified with nitric acid and was then analyzed. The Al concentration was analyzed using atomic absorption spectrometry (AAS Nova 410, NF EN ISO 12020).

3. RESULTS AND DISCUSSION

3.1 General water characterization

The inorganic content of the Medjerda water is depicted in Table I. Water taken from Medjerda dam has some high concentrations of chloride, sulfate and sodium ions. Nitrate, lead and Manganese concentrations were very low. The pH is slightly basic.

Iron (Fe) and Silicium (Si) are the most prevalent inorganic constituent in Medjerda water. Calcium (Ca) and sodium (Na) are the most abundant elements found in water.

Table I: Average characteristics of the raw water taken from Medjerda dam (Tunisia).

pH	Temperature (°C)	Turbidity (NTU)	Conductivity ($\mu S.cm^{-1}$)	Alkalinity (TAC) ($meq.L^{-1}$)	$KMnO_4$ oxidability ($mgO_2.L^{-1}$)
8.09	17. 5	4. 8	2560	128. 4	5.30
Chloride ($mg.L^{-1}$)	Fe ($mg.L^{-1}$)	Mn ($mg.L^{-1}$)	Cu ($mg.L^{-1}$)	Al ($mg.L^{-1}$)	Zn ($mg.L^{-1}$)
116. 79	0. 32	0.001	0	0.017	0. 03
Si ($mg.L^{-1}$)	Hg ($\mu g.L^{-1}$)	Na ($mg.L^{-1}$)	K ($mg.L^{-1}$)	Mg ($mg.L^{-1}$)	Ca ($mg.L^{-1}$)
2. 54	0.003	309.11	6. 05	61. 13	178.03
Nitrate ($mg.L^{-1}$)	Sulfate ($mg.L^{-1}$)	Pb ($\mu g.L^{-1}$)	Ag ($mg.L^{-1}$)		
3	204	0. 68	0.01		

3.2 Residual concentration of aluminium

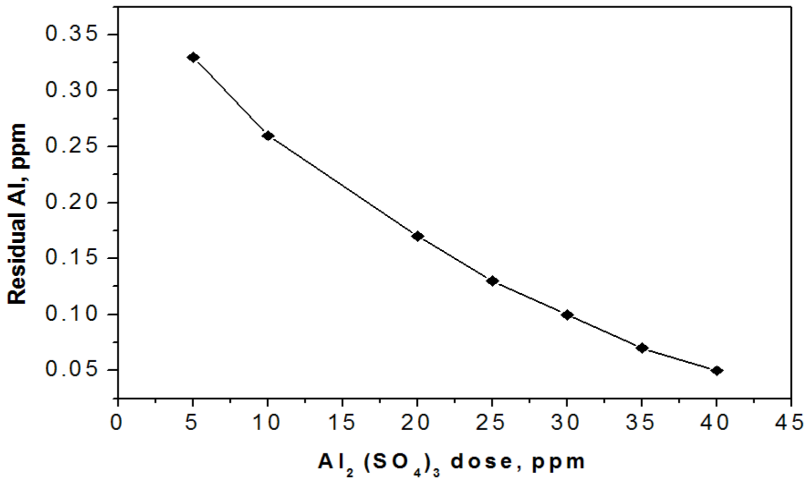

Figure 1: Variation of residual Al as a function of coagulant dose.

Residual aluminium concentration after sedimentation and filtration in the effluent must be taken into consideration because of the health effects of aluminium. The studies on health effects of aluminium in drinking water showed that high consumption of aluminium from drinking water may be a risk factor for Alzheimer's disease and a relationship exists between the number of diagnosed Alzheimer's disease cases and the level of aluminium present in the drinking water [18-19]. It has been supposed that overdose of aluminium sulfate may result in high residual aluminium [20-21].
Residual Al decreased straightly within the dosage investigated for $Al_2(SO_4)_3$. And there was very little amount of residual Al existed in the purified water (Figure 1).
Residual aluminium concentration was affected by concentration of coagulant dosage. Kang et al. [20] also noted that the highest soluble residual aluminium was found in the underdose aluminium-based coagulant range in sample water containing low turbidity. Because the maximum

contaminant level of aluminium in drinking water is 200 µg L^{-1}, aluminium sulfate was found as an effective and reliable coagulant due to required concentration and residual aluminium.

3.3 Optimization of coagulation-flocculation

3.3.1 Effects of water initial pH

In the coagulation-flocculation process it is very important to control pH. The aim of this experiment was to investigate the influence of water initial pH on coagulation efficiency at the pre-determined coagulant dosage and agitation speed of 40 $mg.L^{-1}$ and 100 rpm respectively. Water initial pH was adjusted in the range of 4 to 10 using 0.5 $molL^{-1}$ HCl and NaOH solutions.

Figure 2 illustrates the effect of water initial pH on coagulation efficiency. The result shows that the initial pH largely influenced both the organic matter (OM) and turbidity reduction.

The coagulant $Al_2(SO_4)_3$ was a monomeric salt, it hydrolyzed as soon as added into water and it would go through extremely rapid and uncontrolled hydrolysis when solution pH reached a certain value [22-23].

With the increase of initial pH, the turbidity value decreased noticeably until the pH value of 6, but increasing the pH above this point distinctly reduced the turbidity removal. Therefore, the optimum pH for turbidity and OM reduction was 6.0.

Figure 3 shows that the optimum water initial pH for COD reduction was 5.0.Based on the above consideration, the adopted optimum water initial pH was 6.0

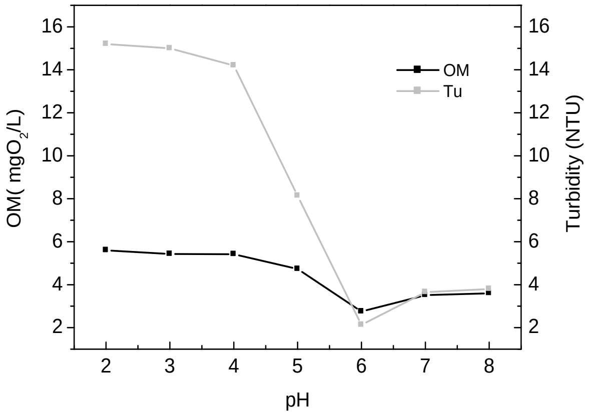

Figure 2: Variation of turbidity and OM as a function of pH.

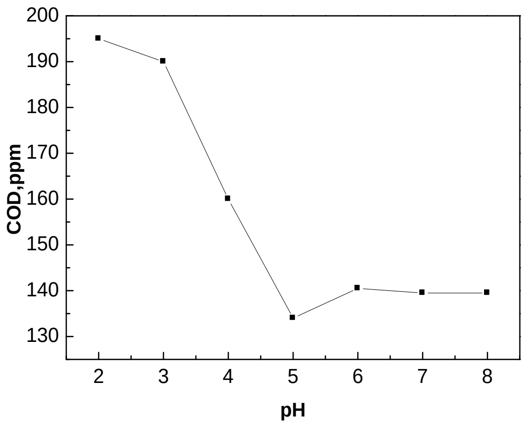

Figure 3: Variation of COD as a function of pH.

For aluminium hydroxide species at pH values between 4 and 6, the positively charged species are pre-dominant, while the range 5.5–7.5 is the best for $Al\,(OH)_3$ precipitate [24-25].

A spectroscopic study [26] suggested that at low pH values (< 4.5), organic matter formed soluble OM-Al complexes with $A1^{3+}$, while at higher pH values (pH >5), adsorption of OM on the surface of $Al(OH)_3$, crystals becomes dominant, leading to a maximum removal of the OM. With adsorption, the carboxylic group on a OM is first coordinated to the Al nuclei on the surface of $Al\,(OH)_3$, either by a ligand or by anion exchange; then further progressive adsorption of the rest of the molecule on the surface of $Al\,(OH)_3$, is brought up by physical and chemical forces such as van der Waals forces and H-bonding.

It can be seen that at pH 6 and above, the dominant mechanism was adsorption of organic species on precipitated $Al\,(OH)_3$ at pH 5.0 and below, the mechanism involved precipitation of soluble organic molecules by soluble cationic polymeric species; between pH 5 and 6, both mechanisms may occur simultaneously.

Under different conditions, the different mechanisms or their combination may be dominant. As indicated in the pH of raw, the effect of the initial pH on the particle and organic materials removal was correlated with the coagulant hydrolyzates. For $Al_2(SO_4)_3$, when pH was lower than 5.0, the polymerization of Al^{3+} was inhibited at a certain degree and the primary Al speciation was the positive monomer hydrolyzates, like $Al(OH)^{2+}$, $Al_2(OH)_2{}^{4+}$, and $Al_3(OH)_4{}^{5+}$,etc. [27-28]. These positive hydrolyzates were easy to neutralize the exterior negative charges of particle and organic materials in Medjerda water, and further destabilize the colloids.

When pH was higher than 8.0, the suspension system was difficult to be destabilized because the hydrolyzates were transformed to $Al\ (OH)_4{}^-$ [27-28].

3.3.2 Effects of coagulant dosage

In the coagulation flocculation process, coagulant dosage plays an important role in determining the coagulation efficiency. The experiment was conducted at the pre-determined water initial pH of 6 with an agitation speed of 100 rpm. The investigated coagulant dosages were in the range of 5–30 $mg.L^{-1}$.

Figure 4 shows the effects of coagulant dosage on OM (permanganat oxygen demand) and turbidity. The results indicate that OM and turbidity value decreased substantially with the increase of the coagulant dosage, .In the range of concentration used in this study (5-30 $mg.L^{-1}$) the turbidity and OM removal efficiency was achieved. The results also showed that at this range, the removal of COD was maximum (Figure 5).

The higher removal of COD under relatively higher coagulant concentration (30 $mg.L^{-1}$) could result from the sweep flocculation process [29] due to the fact that the concentration was close to the saturation level. Therefore, optimum coagulant dose was 30 $mg.L^{-1}$.

Indeed, the effect of the colloidal particles concentration in water is important because they serve as cores to the coagulation [30]. If the concentration of colloids is low, there are few particles to ensure good flocculation, regardless their neutralization.

The coagulation of OM by hydrolyzing metal salts is generally described as co-precipitation, charge neutralization and/or adsorption mechanisms, depending on the dose of coagulants and concentration of dissolved organic carbon [31]. However, other phenomena may involve chemical interactions between the metal ions and the functional groups of organic matter (MO) such as the formation of complexes [32].

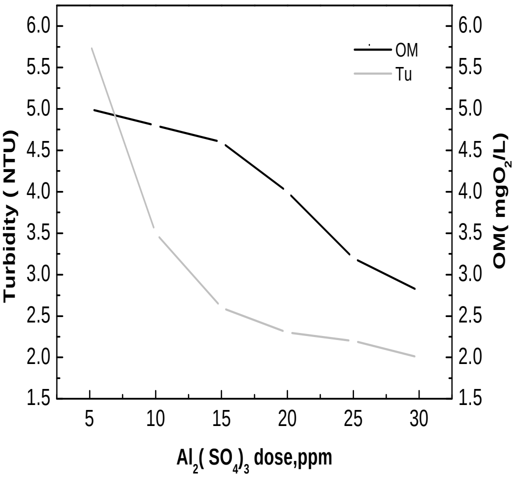

Figure 4: Effect of coagulant doses on permanganat oxygen demand and turbidity removal.

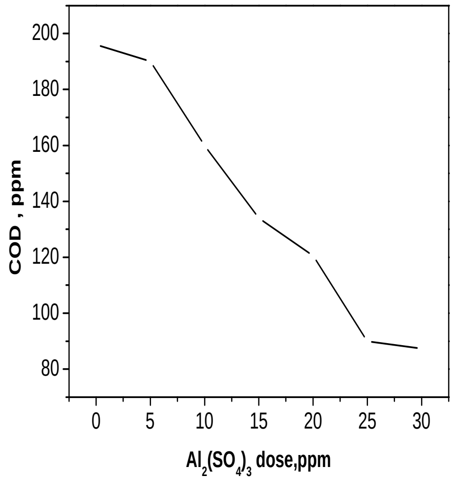

Figure 5: Effect of coagulant doses on COD removal.

3.3.3 Effects of agitation speed

Agitation speed is one of the important factors in achieving higher flocculation efficiency during the coagulation–flocculation process. In this experiment, the effects of agitation speed between 20–100 rpm with rapid mixing time of 1 min on reduction of turbidity, OM and COD was investigated. Figure 7 and 8 show the results from coagulation experiments carried out at the pre-determined optimum water initial pH and coagulant dosage. Figure 6 shows that the turbidity and OM value decreased with increasing agitation speed from 20 to 80 rpm. However, for a higher agitation speed (80 rpm), the result indicated a substantial reduction in turbidity and OM removal efficiency. Compared with the turbidity, there was a wider range of agitation speed that resulted in a decrease of the OM removal efficiency. The figure 7 shows that the COD removal efficiency decreased significantly between 40 and 80 rpm. Therefore, at a higher agitation speed, the coagulation efficiency was not improved. However, at the lower agitation speed of 20 rpm (less than 40 rpm), the flocs formed in coagulation-flocculation processes were easily broken and the removal efficiency would decrease. Based on the actual measurement, the optimum agitation speed was 80 rpm.

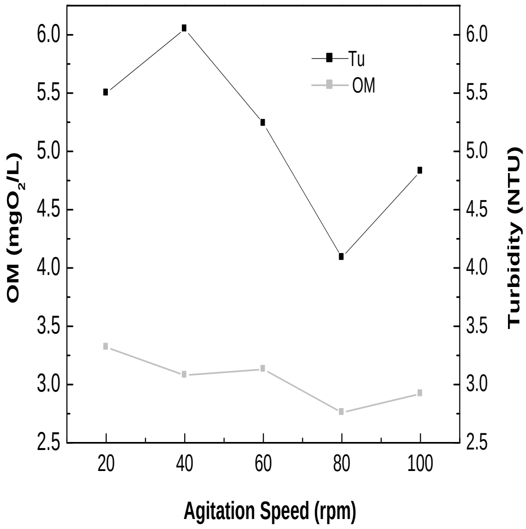

Figure 6: Effect of agitation speed on turbidity and OM removal.

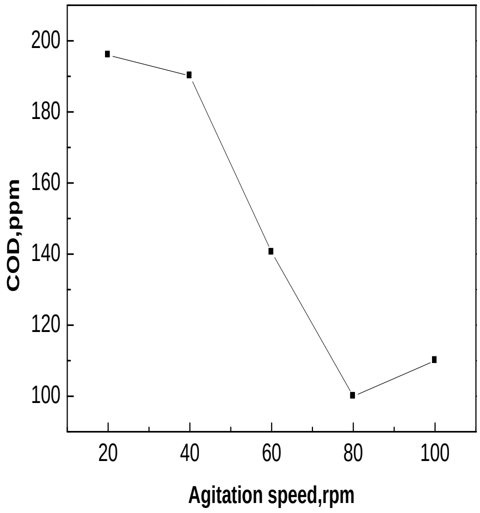

Figure 7: Effect of agitation speed on COD removal.

CONCLUSION

Coagulation-flocculation using aluminium sulfate is a suitable process for the removal of turbidity, organic matter and chemical oxygen demand when the operating parameters are optimized.

The optimal operational conditions are as follows: initial pH value of 6, concentration of aluminium sulfate of 30 mg.L^{-1} and agitation speed of 80 rpm. By applying these parameter values, maximal turbidity, organic matter and chemical oxygen demand removal has been predicted and confirmed experimentally. The obtained results are conform to legal Tunisian specification.

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