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Coagulation efficacy of a tannin coagulant agent compared to metal salts for paint manufacturing wastewater treatment

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ABSTRACT

Paint manufacturing wastewaters (PMW) contain highly toxic and organic biorefractory compounds and have adverse effects on human health. Jar-test experiments are conducted in order to assess the efficiency of natural and synthetic coagulants on the treatment of PMW. For this purpose a tannin-based polymer (TBP), iron chloride ($FeCl_3$), and aluminum sulfate ($Al_2(SO_4)_3$) have been used. The results indicate that TBP is more effective than coagulant salts. Coagulation–flocculation involving TBP does not require any pH adjustment either on raw or on treated wastewater. TBP achieves more than 87% of COD and 99% of color removal and produces less volume of decanted sludge than metal salts. The ranking of the efficiency of coagulant agents is as follows: TBP > $FeCl_3$ > $Al_2(SO_4)_3$. TBP as a natural coagulant can be a potential substitute for synthetic products on paint manufacturing wastewater treatment.

Keywords: Coagulation–flocculation; Paint manufacturing wastewater; Tannin-based polymer

1. Introduction

Wastewaters of paint manufacturing companies contain highly toxic and organic biorefractory compounds. They harm fish, wildlife, and contaminate the food chain if poured down a storm drain. These detrimental effects are more apparent and observable in developing countries due to their less stringent environmental regulations and difficulty in constructing, operating, and maintaining proper water or wastewater treatment systems due to high fixed costs, especially in the case of rural areas [1].

Industrial wastewater treatment involves many different techniques such as biodegradation, adsorption, membrane filtration, coagulation–flocculation, advanced oxidation processes, etc. [2–6]. Coagulation–flocculation has always attracted considerable attention as a simple and relatively cost-effective point-of-use technology [7] and for allowing high pollutant removal

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efficiency in wastewater treatment. Its application includes addition of conventional chemical-based coagulants, namely alum ($AlCl_3$), iron chloride ($FeCl_3$), and polyaluminum chloride (PAC). While the effectiveness of these chemicals as coagulants is well recognized, there are, nonetheless, disadvantages associated with usage of these coagulants such as ineffectiveness in low-temperature water [8], detrimental effects on human health, and production of large sludge volumes. It is therefore desirable to replace these chemical coagulants with natural-based agents to counteract the aforementioned drawbacks. Although many plant-based coagulants have been reported, only four types are generally well known within the scientific community, namely, nirmali seeds (*Strychnos potatorum*) [9], *Moringa oleifera* [10], cactus [11], and tannin [12].

Lab-scale experiments have demonstrated that it is possible to synthesize tannin-derived coagulant from several tannin feed stocks through a very simple procedure that involves Mannich base reaction. However, the chemical complexity of tannins, and the fact that they are usually taken from natural matrix without a very thorough purification, make knowing their structure a very difficult task. Tannins undergo Mannich aminomethylation by reacting with an aldehyde and an amine [13]. The resulting tannin Mannich polymer possesses a higher molecular weight due to formaldehyde and Mannich base cross linking, and also possesses ampholytic character due to the presence of both cationic amines and anionic phenols on the polymer.

The production process of this tannin-based polymer (TBP) is not completely known, but by following the rules of Mannich reactions, one can make an approach of its synthesis. In the case of diethanolamine (DEA), formaldehyde and the tannin extract mixture, the coagulant chemical formula may correspond to tannin $–[CH_2–NH–(CH_2–CH_2OH)_2]n$ and its probable expanded chemical structure is shown in Fig. 1 [7].

The purpose of this study is to assess the efficiency of natural and synthetic coagulant agents on the coagulation–flocculation process applied to paint wastewater. The coagulants used are TBP, iron chloride, and aluminum sulfate. This data provides new information about the role of natural polymeric coagulants in the industrial wastewater treatment operations, especially colored effluents.

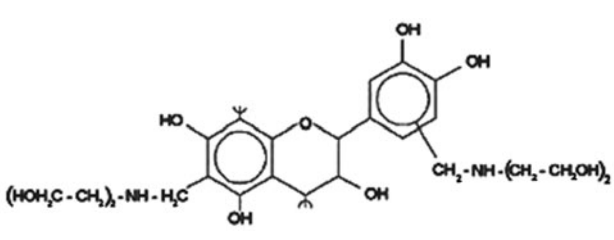

Fig. 1. Probable chemical structure of TBP [7].

2. Materials and methods

2.1. Paint wastewater source

The paint manufacturing wastewaters (PMW) are collected from the discharges of an aqueous emulsion paint manufacturing company in Casablanca city (Morocco). The samples are collected from equalization tank effluent. After in-site pH, conductivity, and turbidity measurements, the samples are transferred to the laboratory.

2.2. Coagulation–flocculation process

TBP is a natural organic polymer extracted from vegetable material. TBP has a viscosity between 10 and 50 cps and a density of 1.1 g cm^{-3} at 20°C.

Iron chloride ($FeCl_3$) and aluminum sulfate ($Al_2(SO_4)_3·18H_2O$) used in this study are supplied by SIGMA.

Jar-test experiments are conducted under controlled laboratory conditions using a standard jar-test apparatus. Four equal-volume polyethylene beakers are used to examine the four different dosages of coagulant in each run. The sample bottles are thoroughly shaken for resuspension of possibly settling solids, and then the appropriate volumes of sample are transferred to the corresponding jar-test beakers. The optimum coagulant was determined on the basis of color and chemical oxygen demand (COD) removal and the amount of decanted sludge. For each test, 1,000 ml of PMW were taken in a 1,000 ml working volume beaker and, after addition of coagulant, mixed for 5 min at 150 rpm to ensure complete dispersion. After rapid mixing, the slow mixing stage takes place for 15 min at 30 rpm. Finally, the beaker contents are transferred into Imhoff cones for a one-hour settling step. Thereafter, the volume of decanted sludge was determined, and the supernatant was carefully withdrawn for subsequent measurements of COD and color.

2.3. Analytical procedures

To assess the efficiency of coagulants on PMW treatment, the following parameters are considered: COD, color, and the amount of sludge.

2.3.1. Chemical oxygen demand

COD and other physical–chemical parameters for wastewater characterization measurement were performed according to standardized methods [14].

2.3.2. Color measurement

Prior to color measurement, the sample was filtered through a membrane filter (0.45 μm) to prevent turbidity. Color measurements are carried out with a spectrophotometer. Since the wastewater contains different kinds of pigments (depending on the production), the traditional method of applying the maximum absorbance is not used.

Color content is determined using an UV–visible spectrophotometer (Model 7800 UV–vis spectrophotometer) by measuring the absorbance at three wavelengths (436, 540, and 660 nm), and taking the sum of these absorbencies [15].

2.3.3. Amount of sludge

Once the experiment has been performed in the jar test, the beaker contents are transferred to special graduated conical containers (1 L Imhoff cones). After 1 h of settling, the sludge production is determined by direct reading as ml of sludge/L of wastewater treated.

3. Results and discussion

3.1. Wastewater characteristics

The paint wastewater is characterized by including substantial organic matter, high salinity, sulfate rich, and high suspended solid (Table 1). BOD/COD index [16] indicates that a biological treatment seems to be difficult, and thus a physicochemical process is required. The coagulation–flocculation process using iron chloride, aluminum sulfate, and TBP are used in the treatment of this effluent. Treatment efficiency is evaluated in terms of pollutant removal (COD and color) as well as in terms of sludge production.

Table 1
Characteristics of paint wastewater

	Min	Max	Average
pH	6.7	7.8	7.4
Conductivity (ms cm^{-1})	2.1	2.7	2.3
Turbidity (NTU)	452.0	3,020.0	1,178.7
Suspended matters (mg l^{-1})	1,655.0	13,350.0	8,701.6
Chloride (mg l^{-1})	177.7	355.0	266.3
Sulfate (mg l^{-1})	735.0	5,768.9	2,414.0
Total phosphorus (mg l^{-1})	1.4	16.1	7.5
TKN (mg l^{-1})	50.0	490.3	197.7
COD (mg l^{-1})	4,438.0	25,106.0	14,670.8
BOD (mg l^{-1})	960.0	1,968.0	1,465.2
BOD/COD	0.04	0.2	0.1

3.2. Initial and final pH of coagulation

3.2.1. Effect of coagulation pH

The pH solution is an important factor in the coagulation process, and the use of a coagulant at its optimum pH displays maximum pollutant removal. Chemical speciation of the coagulant, the surface charge of colloid and sometimes the charge of soluble molecule depends on pH. To optimize the coagulation pH, a known volume of prepared coagulant solution is added to a jar containing 1 l of wastewater at different pH values adjusted with concentrated H_2SO4 and NaOH. The effect of coagulation pH on the COD removal from jar tests for coagulation of PMW using 400 mg l^{-1} of the coagulant and an initial COD of 6,400 mg l^{-1} is shown in Fig. 2. COD removal rate decreases from 75 to 85% at coagulation pH 4–9 to 10–66% at coagulation pH 9–12 using $FeCl_3$ and $Al_2(SO_4)_3$. However, there is not much change observed in the COD removal rate for TBP, 67–69% at pH_i 4–12. Initial pH significantly affects iron and alum efficiency on COD removal; the best results are obtained in the acidic pH range. In the coagulation process, pH affects the surface charge of coagulant and also the stability of the suspension. Usually, salt coagulants charged positively tend to undergo a decrease in their cationic form at basic pH levels, and then electrostatic attraction between the cationic chains and the negatively charged pollutants becomes weak.

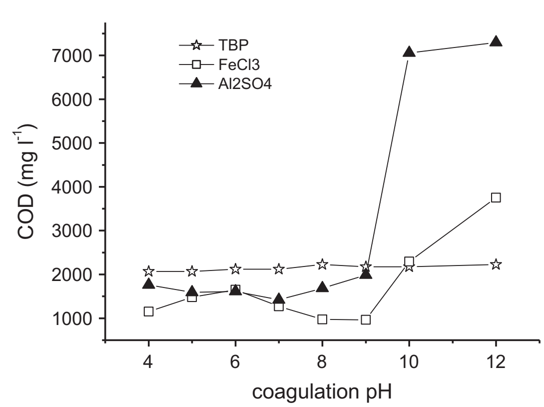

Fig. 2. Effect of coagulation pH on COD removal (coagulant = 400 mg l^{-1}).

It can be noticed that coagulation pH does not significantly affect TBP efficiency on COD removal (Fig. 2). Consequently, the process implicating TBP does not require coagulation pH adjustment. This non dependence on pH is an advantage in the coagulation–flocculation process.

3.2.2. Effect of coagulants on treated wastewater pH

pH of treated water is considered in this work as it may affect the economic feasibility of the proposed method. Fig. 3 depicts the effects of coagulant agents on treated wastewater pH. With iron and aluminum salts, the pH value decreases from 7 to 3.5 at 0–1,200 mg l^{-1} coagulant dosage. At optimum dosages of $FeCl_3$ and $Al_2(SO_4)_3$, the treated wastewater pH values are 5 and 4, respectively. The acidity of these two metallic ions (Lewis acid) explains this modification of pH. However, the use of TBP does not significantly affect pH of treated wastewater; pH value varies from 7 to 7.3 (Fig. 3). This pH range represents an optimal pH for water discharge or for a subsequent biological treatment.

It can be concluded that the process involving TBP does not require any pH adjustment, either on raw or on treated wastewater, as it is in coagulation–flocculation processes implicating alum or ferric salts. This is an advantage since the process efficiency is not pH dependent. In addition to financial gain, manipulation of TBP, as a natural agent, is much easier than classical coagulants.

3.3. Pollutant removal

The study of the effects of coagulant dosage on the COD and color removal has been undertaken by varying the amount of the coagulant in wastewaters, while keeping coagulation pH constant at its optimum value for each coagulant. For an initial COD of 6,400 mg l^{-1}, it is evident that for the quantitative removal of 81, 82, and 87% of COD, under experimental conditions of the coagulation test, the minimum concentrations of 800, 500, and 600 mg l^{-1} of $Al_2(SO_4)_3$, $FeCl_3$, and TBP are required, respectively (Fig. 4). Further increase in the coagulant dosage does not generate better removal rate. The coagulant dosage should be proportional to the quantity of colloids present. As seen in Fig. 4, a further increase in $FeCl_3$ concentration of more than 900 mg l^{-1} causes the restabilization of particles as the charge reversal on the colloids occurs [17]. However, the phenomenon is not observed with $Al_2(SO_4)_3$, at least at coagulant doses less than 1,200 mg l^{-1}; a better sweep coagulation with alum hydroxides due to greater interactions with macromolecules in the solution may explain this stability. In the same manner, the molecular weights of tannin are important and chemical flocculation is linked to a sweep coagulation mechanism.

Color and COD removal, as well as sludge production, corresponding to optimal doses of coagulants are shown in Table 2. Clearly, the process removes more color than COD, 81–87% of COD and 89–99% of color is removed. As the COD is linked to particular and soluble fractions, the difference in percentage removal between color and COD may be explained by the fact that in the soluble COD fraction, only some macromolecules are integrated in the flocculation process by sorption into the floc structure. However, color removal is mainly attributed to flocculated decolorization process. Through energetic and hydrophobic interactions, the molecules producing color, colloidal metallic hydroxides or organic compounds, intensively

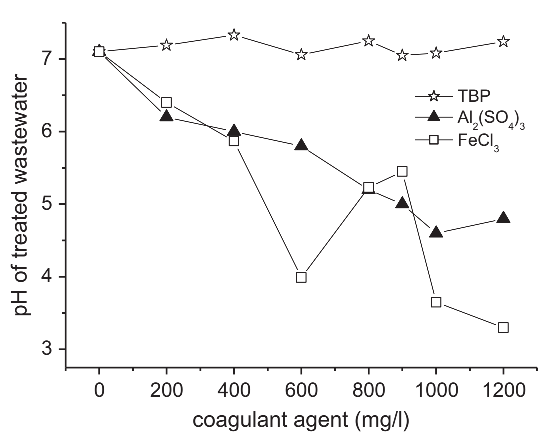

Fig. 3. Effect of coagulant agents on treated wastewater pH.

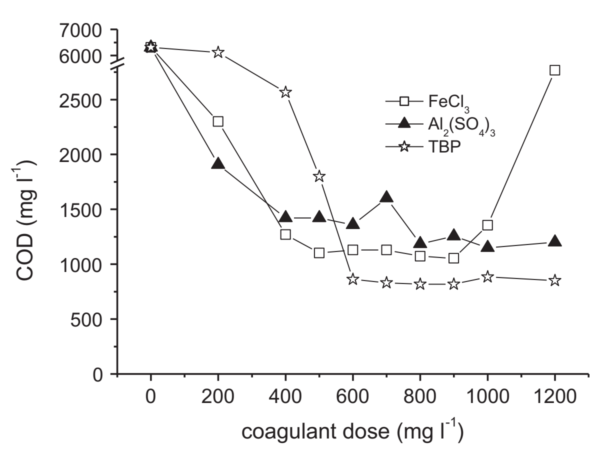

Fig. 4. Effect of coagulant dosage on COD removal.

Table 2
Pollutant removal and sludge production at optimal doses of coagulant agents

Coagulant agent	COD (%)	Color (%)	Sludge (ml l^{-1})
TBP	87	99	116
$FeCl_3$	82	89	172
$Al_2(SO_4)_3{\cdot}18H_2O$	81	89	220

bind with the flocculant [18], leading finally to color removal.

As seen in Table 2, TBP displays the maximum color and COD removal; 99% of color and 87% of COD are removed. The fact that this natural coagulant is more efficient than classical coagulants may be due to its ability to contribute to the three-dimensional network as a cross-linking agent. While iron chloride and aluminum sulfate are able to destabilize colloidal materials only by a coagulation mechanism, the biopolymer of TBP is involved in a second mechanism of flocculation [19,20].

The amine groups attached to the first and the last aromatic rings ($–CH_2–NH–(CH_2–CH_2OH)_2$), the oxygen atoms in the middle and the two N–H bonds, provide the polar propriety to this natural coagulant molecule (Fig. 1). Anionic colloid particles can then react with the coagulant's positively charged nitrogen atom to form a more complex molecule, and subsequently the colloidal structure is destabilized and if the size is large enough, settling operates [21]. Following this initial stage of floc formation, free-active centers on the floc surface can appear because of the large structure of the natural coagulant. The adsorption process occurs via electrostatic attraction between suspended colloids and the floc surface. The flocs begin to grow, and colloids removal increases [22].

3.4. Sludge production

One aspect to be considered for the choice of a coagulant, in addition to pollutant removal, is how much sludge it will produce. In the solid–liquid separation, sludge dewatering has been pointed out as one of the most expensive processes.

As is shown in Table 2, TBP produces less volume of decanted sludge compared to metal salts. However, the sludge produced using $Al_2(SO_4)_3$ is voluminous, resulting in an important sludge layer compared to the results obtained with TBP. At their optimum doses, TBP, iron, and alum produce 116, 172, and 220 ml l^{-1} of sludge, respectively. It appears that TBP has the highest dewatering efficiency of sludge than classical coagulants; it produced two times less sludge than alum. The use of $FeCl_3$ and $Al_2(SO_4)_3$ introduces an increase in the solid mass with hydroxide precipitation. However, when TBP was used, only initial suspended particles are agglomerated into larger and settleable flocs, but no additional precipitate is formed. Renault et al. [23] reported that organic polymeric compounds are advantageous over inorganic materials. The former possess several novel characteristics such as their ability to produce large, dense, compact flocs that are stronger, and have good settling characteristics.

In order to compare the results obtained with TBP and metal salts, we consider the ratios between the volume of sludge produced and the percentage of COD and color removal. These ratios have been estimated by taking into account the performances of the removal of organic and coloring matters (Fig. 5). The results indicate that the ratios obtained using TBP are markedly less than those obtained when the metal salts are used. The biopolymer produces the least amount of sludge for a given amount of COD and color removed in the treatment of this effluent. On the other hand, iron chloride produces a lower rate of sludge for the same amount of COD and color removal than aluminum sulfate.

The handling treatment and removal of the sludge generated in the coagulation–flocculation process are important aspects to consider when choosing the product to be used as coagulant. Considering the results obtained if a small amount of sludge is to be treated, the most suitable coagulant for the treatment of PMW would be TBP. The pollutant removal rate and the amount of the sludge produced during the coagulation–flocculation process are highly dependent on the specific coagulants used. The results indicate that the ranking of coagulant effectiveness is as follows: TBP > $FeCl_3$ > $Al_2(SO_4)_3$.

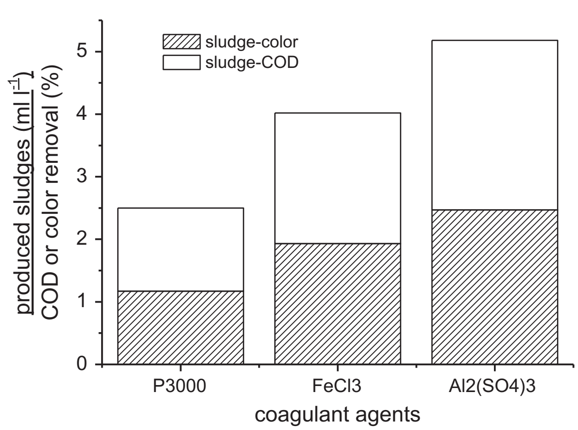

Fig. 5. Ratios between the amount of sludge produced and COD or color removal.

Moreover, natural polymeric coagulants form large and steady flocs via bridging effect with higher resistance to shear forces in a turbulent flow compared to non-polymeric coagulants such as iron chloride [24]. This implies that TBP can be used within a batch-stirred tank setup to treat PMW, since bridging linkages are more resistant to breakage at high shear levels.

TBP presents technical and environmental advantages. Technologically, the process involving TBP is much easier than the one implicating metal salts. pH adjustments of both raw and treated water, as well as further flocculant agents, are not needed (as it occurs with alum or ferric salts). TBP is completely natural, so several disadvantages linked to alum or ferric salts usage are avoided, particularly those associated with the use of aluminum [25].

TBP as a natural coagulant can be a potential substitute for synthetic products on paint manufacturing wastewater treatment. It can avoid the negative effects from residual metal salts and may produce biodegradable sludge. Furthermore, tannins are available and easy to store, and they only require a simple chemical modification. In addition, they can be a social change factor as they allow water treatment without coagulants and flocculants exterior dependence.

4. Conclusion

The efficiency of a TBP, iron chloride, and aluminum sulfate on paint manufacturing wastewater treatment are evaluated. TBP seems to be the most suitable combination for the treatment of PMW. It ensures the best pollutant removal results and produces the least amount of decanted sludges for a given amount of COD and color removal. Furthermore, the use of TBP does not require any pH adjustment, either on raw or on treated wastewater. In addition, TBP is technologically and environmentally better and it is a renewable resource. The improvement of pollutant removal and the amount of sludge produced depend on the specific coagulant used; the ranking of the coagulant agent's efficiency is as follows: TBP > $FeCl_3$ > $Al_2(SO_4)_3$.

References

[1] M. Montgomery, M. Elimelech, Water and sanitation in developing countries: Including health in the equation, Environ. Sci. Technol. 41 (2007) 17–24.

[2] F.M.S.E. El-Dars, M.A. Ibrahim, Adel M.E. Gabr, Reduction of COD in water-based paint wastewater using three types of activated carbon, Desalin. Water Treat. 52 (2014) 2975–2986.

[3] V.M. Daskalaki, H. Marakas, D. Mantzavinos, A. Katsaounis, P. Gikas, Use of seawater for the boron-doped diamond electrochemical treatment of diluted vinasse wastewater, Water Sci. Technol. 68 (2013) 2344–2350.

[4] M.A. Aboulhassan, S. Souabi, A. Yaacoubi, M. Baudu, Improvement of paint effluents coagulation using natural and synthetic coagulant aids, J. Hazard. Mater. 138 (2006) 40–45.

[5] M. Mamadiev, G. Yilmaz, Treatment and recycling facilities of highly polluted water-based paint wastewater, Desalin. Water Treat. 26 (2011) 66–71.

[6] B.K. Körbahti, A. Tanyolaç, Electrochemical treatment of simulated industrial paint wastewater in a continuous tubular reactor, Chem. Eng. J. 148 (2009) 444–451.

[7] J. Beltrán-Heredia, J. Sánchez-Martín, M.C. Gómez-Muñoz, New coagulant agents from tannin extracts: Preliminary optimisation studies, Chem. Eng. J. 162 (2010) 1019–1025.

[8] F. Xiao, J. Ma, P. Yi, J.C. Howard Huang, Effects of low temperature on coagulation of kaolinite suspensions, Water Res. 42 (2008) 2983–2992.

[9] G. Sarawgi, K. Kamra, N. Suri, A. Kaur, I.P. Sarethy, Effect of *Strychnos potatorum* Linn. seed extracts on water samples from different sources and with diverse properties, Asian J. Water Environ. Pollut. 6 (2009) 13–17.

[10] A.M. Thamer, H.M. Ezzuldin, M.J. Megat Mohd Noor, A.H. Ghazali, Coagulation activity of spray dried salt extracted *Moringa oleifera*, Desalin. Water Treat. 51 (2013) 1941–1946.

[11] Z.A. Zurina, N. Ismail, R. Yunus, I.S. Ahamad, A. Idris, A preliminary study on Jatropha curcas as coagulant in wastewater treatment, Environ. Technol. 32 (2011) 971–977.

[12] M.M. Kamel, A.M. Abd El-Mgeed, M.A.I. El-Hewaihy, Synthesis of a novel tannin-formaldehyde resin from Acacia nilotica fruit extract and its viability for adsorption of manganese from ground water, Water Sci. Technol. 13 (2013) 1236–1248.

[13] D.G. Roux, D. Ferreira, H.L. Hundt, E. Malan, Structure, stereochemistry, and reactivity of natural condensed tannins as basis for their extended industrial application, Appl. Polym. Symp. 1 (1975) 335–353.

[14] L.S. Clescen, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, twentieth ed., APHA, Washington, DC, USA, 1998.

[15] P. Aysegül, T. Enis, Colour removal from cotton textile industry wastewater in an activated sludge system with various additives, Water Res. 36 (2002) 2920–2925.

[16] Metcalf and Eddy Inc: Wastewater Engineering: Treatment, Disposal and Reuse, third ed., McGraw-Hill, New York, NY, 1985.

[17] J. Duan, J. Gregory, Coagulation by hydrolysing metal salts, Adv. Colloid Interface Sci. 100–102 (2003) 475–502.

[18] Y. Yu, Y.Y. Zhuang, Y. Li, M.Q. Qiu, Effect of dye structure on the interaction between organic flocculant PAN-DCD and dye, Ind. Eng. Chem. Res. 41 (2002) 1589–1596.

[19] N. Graham, F. Gang, G. Fowler, M. Watts, Characterisation and coagulation performance of a tannin-based cationic polymer: A preliminary assessment, Colloids Surf., A: Physicochem. Eng. Aspects 327 (2008) 9–16.

[20] T. Okuda, A.U. Baes, W. Nishijima, M. Okada, Coagulation mechanism of salt solution-extracted active component in *Moringa oleifera* Seeds, Water Res. 35 (2001) 830–834.

[21] Y.H. Kim (Ed.), Coagulants and Flocculants; Theory and Practice, Tall Oak Publishing, Littleton, USA, 1995.

[22] S. Bulatovic, Dispersion, coagulation and flocculation in: Handbook of Flotation Reagents, Elsevier, Amsterdam, 2007.

[23] F. Renault, B. Sancey, P.M. Badot, G. Crini, Chitosan for coagulation/flocculation processes—An eco-friendly approach, Eur. Polym. J. 45 (2009) 1337–1348.

[24] B. Bolto, J. Gregory, Organic polyelectrolytes in water treatment, Water Res. 41 (2007) 2301–2324.

[25] T.P. Flaten, Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking water, Brain Res. Bull. 55 (2001) 187–196.