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Removal of sulfide, sulfate and sulfite ions by electro coagulation

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Abstract

The removal of various species of sulfur from beamhouse of tannery wastewater and also from synthetic samples was studied by electro-flotation technique. Consumable anodes of iron and aluminum and insoluble anode of titanium were tested as anodes. It was found that iron and aluminum anodes were effective for the removal of suspended solids, sulfide, sulfite and sulfate. Progress of simultaneous coagulation of suspended solids during electro-flotation was measured using particle size analysis. Coagulation was found to be essential for effective flotation of suspended solids. Metal ions generated in situ by electrolytic oxidation of anode were found to react with dissolved sulfide ions. Metal sulfides thus formed as colloidal suspension were coagulated and floated simultaneously by hydrogen bubbles generated from cathode. Simultaneous occurrence of precipitation, coagulation and flotation was observed during electro-flotation. X-ray diffraction studies were conducted to identify the nature of sulfide phase formed during electrolytic precipitation. The effect of pH, current density and initial concentration of pollutants was studied and the results are discussed. The removal of sulfite and sulfate ions is explained by zeta-potential measurements.

Keywords: Electroflotation; Tannery effluent; Separation; Sulfur species

1. Introduction

Wastewater from the leather industry is known to be heavily contaminated with inorganic and organic pollutants. The effluent emanating from beamhouse of tannery industry contains high concentration of sulfide ions. Since these effluents are toxic to aquatic environment, it is essential to neutralize them and bring the discharge levels of these species to below the toxic limit. The acute toxicity of inhaled H_2S and its effect on respiratory, cardiac and nervous systems have been well documented [1–3]. While soluble sulfides are completely hydrolyzed in body fluids, H_2S linked to lipophilic molecules are able to diffuse across membranes including the skin [1]. Diffusion of absorbed H_2S in blood plasma to bones, spleen, lungs, liver, kidneys, pancreas and small intestine has also been reported. Toxic effects were attributed due to deactivation of enzymes either by cleavage of their disulfide bridges or by binding of sulfide to metal. Degradation of key enzymes, such as cytocrome oxidase, alkaline phosphates and carbonic-anhydrate in the presence of H_2S are also reported [3]. Kotronarou and Haffmann [4] have reported the conversion of sulfides to H_2SO_4 by biological oxidation. Structures submerged in such effluent water are frequently damaged due to corrosion. Hence, the removal of sulfide ions from the effluents is essential.

Hydrogen sulfide in aqueous environment is generally controlled by oxidation methods. Several oxidants, such as molecular oxygen [5], hydrogen peroxide [6], hypochlorites, chlorine and $KMnO_4$ [7] have been tried to eliminate H_2S from wastewater. Selective electrochemical oxidation of sulfide compounds in the presence of organic matter, Mn^{2+} and Cr^{3+} was also studied by Rajalo and Petrovskaya [8]. Removal of sulfide from seawater using hydrous Fe(III) oxides was examined and found to be suitable [9]. Bagreev and Bandosz [10] have recently demonstrated the effective adsorption of H_2S and $SO_4{}^{2-}$ on ‘Terrene’, a material obtained by pyrolysis of sewage sludge. Further, samples of activated carbon of different origin were tested and proved to be effective for the removal of H_2S [11]. In practice, H_2S is typically removed from wastewater by aeration or chemical oxidation. Aeration devices, such as simple air diffusers, mechanical aeration and complex packed tower aerators with different configuration are being used in wastewater treatment plants. During aeration, free H_2S to the extent of 0.05 mg/l is gen-

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erally carried to atmosphere along with air. Thus, the atmosphere surrounding the treatment plant is often charged with H_2S. Because of this, plant operators and people around the treatment plant frequently complain of headache and nausea. Sulfate content in effluents is deleterious since SO_4^{2-} ions hydrolyze to form H_2SO_4 that is highly corrosive. Thus, there is an urgent need to develop a suitable technique for the purification of wastewater containing sulfides.

In the present investigation, the electro-flotation technique is explored for instantaneous and effective removal of sulfide, sulfite and sulfate ions. The technique of electro-flotation has been adopted extensively in Russia for the treatment of various industrial effluents. An electro-coagulation process has been adopted for potable water production wherein Mo content was brought down to 0.006 mg/l from 9.95 mg/l and Fe to 0.015 mg/l from 130 mg/l [12]. Separation of oil from emulsion [13], purification of textile water [14], removal of metal ions [15] and nitrogen from industrial wastewater [16] have been studied by the electro-flotation process. The sulfide ions in the aqueous effluent could be precipitated as metal sulfides by the metal ions released from anode. The precipitate thus formed could be simultaneously removed by flotation using hydrogen bubbles generated at the cathode. The generation of SO_4^{2-} ions as a secondary pollutant could be avoided by this technique.

2. Experimental

2.1. Electro flotation Cell

An electro flotation cell measuring 15 cm × 15 cm × 15 cm fabricated using perspex material was used in the present study. The front side of the cell was provided with a lip so that the floated material could be scooped out through this lip. The effective volume of the cell was about 3.0 l. Metallic rods with a diameter of 0.6 cm were used as electrodes. The anode assembly comprises of six rods, each with a length of 11 cm connected perpendicularly to a common rod. A similar arrangement was adopted for the cathode assembly. A set of electrodes comprises both anode and cathode rods arranged parallel to each other. A schematic of the cell assembly is given in Fig. 1. The gap between the anode and cathode was maintained at 2 mm to avoid short-circuiting and to minimize ohmic losses. The entire electrode assembly was placed on non-conducting wedges fixed to the bottom plate of the cell.

2.2. Flotation

A measured quantity of the effluent sample/synthetic solution at desired pH and concentration was carefully transferred into the electroflotation cell. All synthetic solutions were prepared in 0.04 M NaCl solution to achieve the desired conductivity. pH of the effluent sample was adjusted using dilute HCl and NaOH. The electrodes were connected to the respective anode and cathode leads of the DC rectifier and energized for a required duration at a fixed current. After completion of the experiment, the power to the cell was switched off and the electrodes were disconnected. The floated solid was carefully scooped out onto a tray and the purified water was separately drawn into a beaker for subsequent analysis. The electrodes were thoroughly cleaned before each experiment.

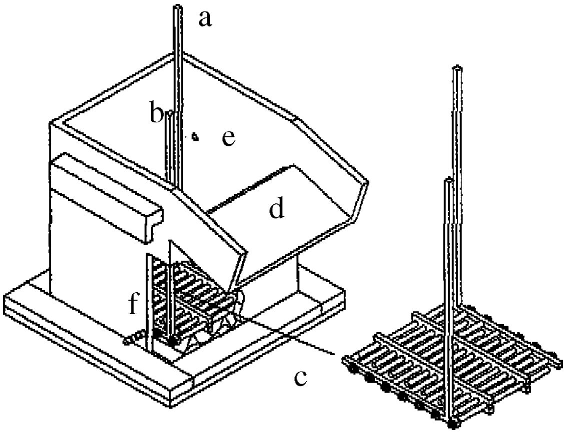


Fig. 1. Electroflotation cell: (a) anode lead; (b) cathode lead; (c) electrodes assembly; (d) froth lip; (e) inlet and (f) outlet.

2.3. Chemical and X-ray diffraction analysis

Standard methods suggested by American Public Health Association [17] were adopted for the estimation of sulfide, sulfite, sulfate, COD, BOD and suspended solids. Sulfate ion (SO_4^{2-}) was precipitated in an acetic acid medium with barium chloride and estimated by turbidimetric method. Iodometric method was followed for the estimation of sulfite (SO_3^{2-}) and sulfide (S^{2-}) content. Open reflux method was adopted for the estimation of COD content. The sample was refluxed in a strongly acid solution with a known excess of potassium dichromate and the remaining unreduced potassium dichromate was titrated with ferrous ammonium sulfate. Estimation of 5-day BOD, suspended solids and chlorides was carried out as per the procedures suggested by American Public Health Association [17].

X-ray diffraction analyses of precipitates formed during electroflotation were carried out using Siemens D500 diffractometer using Co Kα radiation.

All the chemicals used in this study were of analytical grade.

2.4. Physical characterization

Zeta potential measurements and particle size analysis were conducted using a zeta-meter (3.0 + model of zeta-meter Inc., USA) and a particle size analyzer (CILAS-1180, France), respectively. Precipitates of metal hydroxides/oxides were obtained by using the respective metal rods as anodes. After immersing the electrodes in a 0.04 M NaCl solution, electrodes were energized at a fixed current and duration. The metal hydroxide/oxide precipitate that formed instantaneously was siphoned out into a beaker and equilibrated with respective solutions of SO_3^{2-} and SO_4^{2-} before measuring the zeta-potential. Each sample was equilibrated for half an hour. The equilibrated slurry was injected into the micro-electrophoresis cell using disposable syringes. A minimum of three readings with a standard deviation of <2% was taken and the mean value was reported. A similar procedure was adopted to study the zeta potential of aluminum hydroxide precipitate in the presence of sulfate and sulfite. Prior to each measurement, the electrophoresis cell was thoroughly washed and rinsed with de-ionized water followed by rinsing with the sample solution to be measured.

3. Results and discussion

The effluent sample collected from the beamhouse of a tannery was subjected to electro-flotation using different materials as anode. The characteristics of the raw and treated effluents are shown in Table 1. It is observed that around 90% COD and BOD are removed by using iron or aluminum as anodes. In the presence of iron as anode, a black color precipitate typical of iron sulfide appeared soon after the electrodes were energized. This clearly indicates that the sulfide is converted to iron sulfide. It was also observed that the removal of sulfidic sulfur (∼75%) was slightly better with the use of Fe anode and removal of suspended solids (>95%) is superior in the presence of Al anode. Although a decrease of 50% in sulfidic sulfur was observed in the presence of titanium anode, an equivalent increase in sulfate sulfur was observed. This suggests the oxidation of S^{2-} to SO_4^{2-} with the use of titanium anode. Oxidation of sulfide to sulfate in the presence of Ti anode was reported by Rajalo and Petrovskaya [8]. Therefore, it is disadvantageous to use a titanium anode as it only converts sulfide ion to another form, which remains as a secondary pollutant.

Table 1
Effect of anodic material on the removal of pollutants

Parameter	Raw sample	After electrocoagulation (anode)			
		Fe	Al	Ti	Fe and Al
pH	11.86	11.78	11.78	11.59	11.52
Conductivity (μmho/cm)	9540	3970	3920	9420	3980
Sulfide (mg/l)	108	29	34	56	28
Sulfate (mg/l)	54	31	35	93	22
Chloride (mg/l)	30	29	30	21	30
Suspended solids (mg/l)	1078	270	24	687	24
Total dissolved solids (mg/l)	3470	–	1924	–	1878
COD (mg/l)	1314	84	75	1210	67
BOD (mg/l)	766	55	–	–	41

Experimental conditions: current density, 47 mA/cm^2 and electroflotation time, 1200 s.

3.1. Effect of electrode material on coagulation and flotation

Electro flotation tests were conducted on beamhouse effluent in the presence of different anodes at a current density of 47 mA/cm^2. The duration of electro flotation was maintained for 900 s in all the experiments. Though the bubble size and the flux are almost identical, floatability of suspended solids is observed to be better in the presence of iron and aluminum anodes and poor in the presence of titanium. The results of the same are presented in Fig. 2. In order to understand the effect of the anode material on flotation, size analysis of suspended solids was carried out using a particle size analyzer. The duration of electro flotation was varied from 2 to 15 min at a fixed current density of 47 mA/cm^2. After the experiment, the froth phase was subjected to mild agitation so that the entire solid phase is detached from the bubbles. The samples thus obtained were analyzed for particle size distribution and results obtained are presented in Fig. 3. The size of suspended solids in the raw effluent was found to vary from 0.04 to 180 μm with a mean diameter of 18.75 μm. With the use of aluminum and iron anodes, a gradual increase in size of the solids is evident as the duration of electroflotation is increased. Colloidal size solids are coagulated within 600 s and the size of the coagulum remains almost constant thereafter. Mean diameter of the solids increased to 34 μm with iron as anode and 61 μm with the use of aluminum as anode. This clearly suggests the coagulation of colloidal solids in the presence of Al^{3+} and Fe^{3+} ions released from the anode. These ions are generally preferred in the coagulation process because of their multivalent character and low solubility ($k_s = 10^{-32.7}$) of their hydroxides. Al or Fe ions dissolved from anode form a range of coagulant species that destabilize and aggregate the suspended solid particles and precipitates. Thus the suspended solids were simultaneously coagulated and floated effectively in the presence of soluble anodes. In the conventional treatment, sulfate ions from alum and iron salts leads to secondary pollution. This could be avoided by the electro flotation technique as the metal ions dissolved from the respective anodes act as coagulant. It has been reported that the electro-coagulation process consumes less coagulant [18] and has an advantage of removing small colloidal particles because the applied electric field accelerates the motion, thereby facilitating the coagulation.

It is well established that the mono and polymeric aluminum hydroxyl species thus formed can in-turn interact with particles of opposite charge by electrostatic attraction and form a coagulum. Coagulated solids are subsequently lifted to the surface by hydrogen and oxygen bubbles generated electrolytically. Better floatability of coagulated particles could be attributed to favorable hydrodynamics. From the point view of hydrodynamics, the probability of

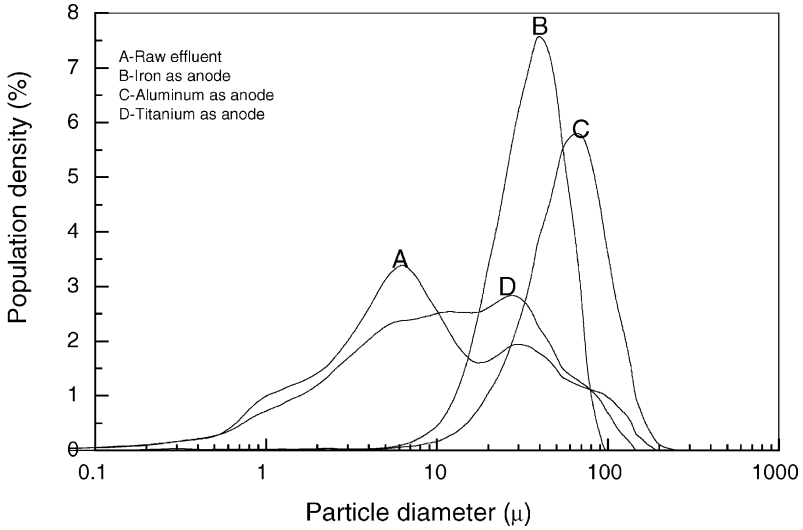
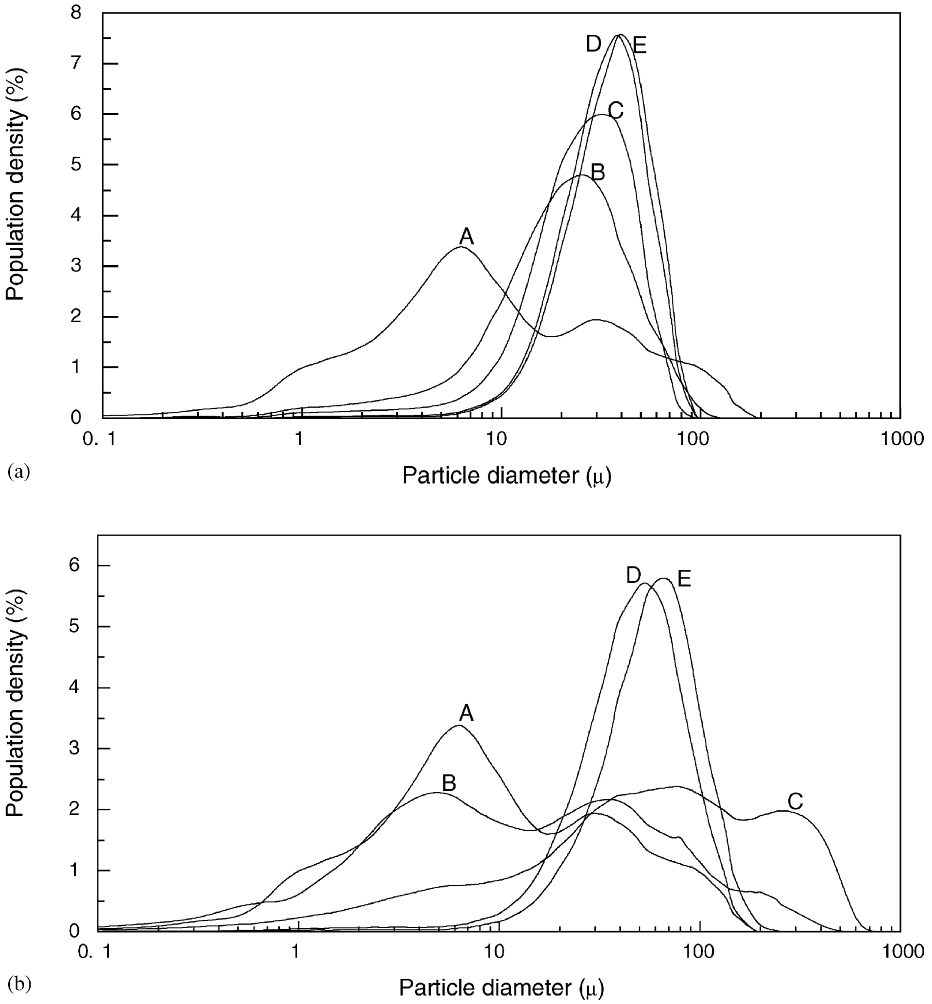


Fig. 2. Electro-coagulation of suspended solids in the presence of different anodic materials.



(a)

(b)

Fig. 3. Progress of coagulation with reference to electro flotation time in the presence of (3a) iron, (3b) aluminium as anodes: (A) raw effluent, (B) 120 s (C) 300 s, (D) 600 s, (E) 900 s.

particle-bubble collision is better if the bubble size and particle size are approximately the same [19]. Glembotskii et al. [20] have reported that the bubbles generated by electrolysis of water are very small and generally vary from 15 to 80 μm depending on pH and current density. It may be noted that the size of the coagulated solids and the size of electrolytic bubbles are in the same range. Generally, the surface of solid should be hydrophobic to facilitate bubble attachment. However, bubbles generated by electrolysis are able to float even hydrophilic precipitates. This is attributed to high capillary pressure inside the bubbles. At the moment of bubble formation, the pressure inside the bubble is estimated to be around 1.45×10^6 Pa [21]. Bubbles with high pressure could spread even on hydrophilic surface and establish micro contact [22].

3.2. *Effect of initial concentration of pollutant on recovery*

Electro flotation tests were conducted on synthetic effluent solutions prepared from pure sodium salts of sulfide, sulfite and sulfate. Separate solutions of Na_2S, Na_2SO_4 and Na_2SO_3 with different initial concentrations were taken and subjected to electro flotation using iron as anode. The results of the tests shown in Fig. 4 indicate that the extent of removal of sulfur species decreases with increasing concentration. Sulfide removal was much higher and almost complete at low concentrations (100 mg/l) compared to sulfite and sulfate. The sulfidic sulfur was removed in the form of metal sulfide in the presence of iron or aluminum anode. The metal ions (aluminum/iron) generated in situ by electrolytic oxidation in turn react with S^{2-}, SH^- ions and form metal sulfide precipitate. The anodic dissolution of metal ions and the evolution of hydrogen from cathode can be represented as

$$Fe \rightarrow Fe^{2+} + 2e^-, \qquad E^0 : +0.440\,V \tag{1}$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^-, \qquad E^0 : -0.771\,V \tag{2}$$

$$Al \rightarrow Al^{3+} + 3e^-, \qquad E^0 : +1.677\,V \tag{3}$$

$$H_2O + e^- \rightarrow \tfrac{1}{2}H_2(g) + OH^-, \qquad E^0 : -0.828\,V \tag{4}$$

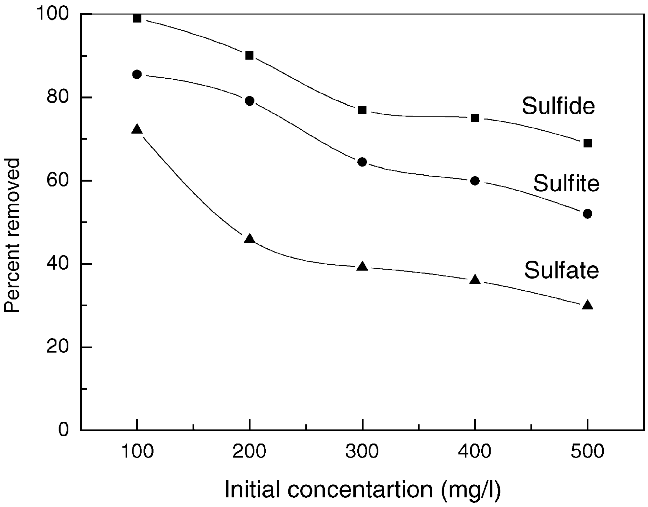


Fig. 4. Effect of initial concentration of sulfide, sulfite and sulfate vs. percent removal (anode: Fe, flotation time: 600 s, pH of suspension: 7.0, current density: 32 mA/cm^2 in the case of sulfide and 62 mA/cm^2 in the case of sulfite and sulfate).

Depending on the pH, sulfide ion exists as H_2S, HS^- and S^{2-} (pK_1: 7.02, pK_2: 13.9). Interaction between Fe^{2+} ions and H_2S, HS^- and S^{2-} species leads to the formation of FeS precipitate that is insoluble. Because of auto-oxidation, ferrous ions are converted to stable ferric ions. Further, small amount of chlorine liberated from anode due to secondary reaction is expected to oxidize ferrous ions to ferric. Since experiments were conducted in a basic environment, simultaneous formations of ferric hydroxide/oxides are also expected. Precipitates of iron(III) hydroxides thus formed are also converted to FeS by sulfide ions by reductive dissolution mechanism [9,23]. Better floatability of metal sulfides can be attributed to the inherent hydrophobic character of iron sulfides. On the other hand, sulfite and sulfate ions cannot be precipitated like sulfide ion. These ions only form respective metal salts that are highly soluble in water. Sulfite and sulfate ions are getting removed possibly by adsorption on metal oxides/hydroxides. The possible interaction of these ions with metal hydroxy species is explained at a later stage along with zeta-potential measurements.

3.3. *Effect of current density on removal of sulfur species*

Electro flotation tests also were conducted at various current densities and the results are presented in Fig. 5. It is apparent that by increasing the current density from 12 to 62 mA/cm^2, the removal of sulfur species also increases. S^{2-} ions could be removed up to 90% even at low current densities whereas removal of sulfite and sulfate ions is comparatively poor. By increasing the current density, the bubble flux and in turn the collision probability is increased. At the

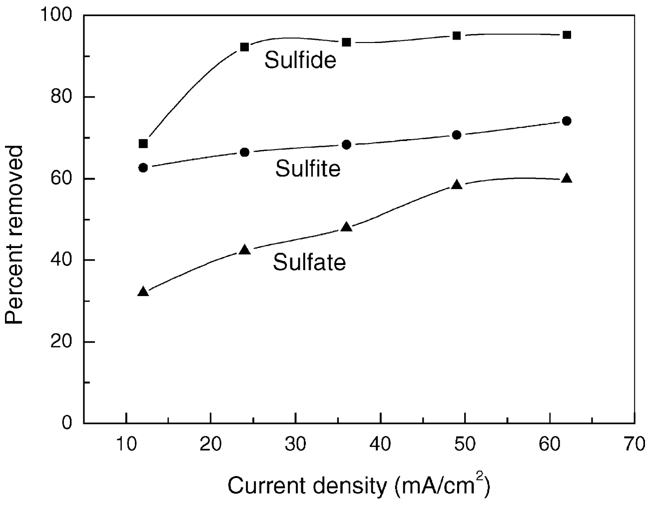


Fig. 5. Effect of current density on the removal of sulfur species (anode: Fe, flotation time: 600 s, initial concentration: 100 mg/l).

same time, the dissolution of anode and in turn concentration of metal ions also increases. At higher current densities the consumption of electrodes is high. Thus current density plays an important role in achieving optimum results.

3.4. Effect of pH on sulfate removal

Synthetic effluent solutions containing sulfate were taken and subjected to electro flotation at different pH values and the results obtained are shown in Table 2. It is seen that the sulfate removal is better at slightly acidic conditions. In order to explain these results and also to understand the removal of sulfite and sulfate ions, zeta-potential measurements were carried out on the oxy-hydroxides of iron and aluminum formed during electrolysis. From the results plotted in Figs. 6 and 7, the iso-electric point (iep) of iron oxide/hydroxide and aluminum oxide/hydroxide was observed at a pH of 7.7 and 8.8, respectively. These values are in accordance with the values reported by earlier researchers [24,25]. Below the pH of iep, precipitates of oxy-hydroxides are positively charged. From the results it is apparent that the magnitude of positive zeta-potential of iron and aluminum oxy-hydroxides reduces in the presence of sulfate and sulfite ions without any shift in iep. This clearly indicates that there is no chemical interaction between these ions and metal hydroxy precipitates. At the same time, decrease in the magnitude of zeta-potential of metal hydroxides in the presence of these ions clearly suggests an electrical interaction. This reduction in positive charge may be due to weak electrical interaction between negatively charged sulfite and sulfate ions and positively charged oxy-hydroxy species of iron and aluminum. Generally, the involvement of sulfate radical in electrical double layer is considered to be negligible. Sulfite and sulfate ions are possibly enmeshed in the porous metal oxide/hydroxide precipitate. Transmission electron microscopic (TEM) studies conducted by earlier researchers [26] have revealed that at a pH of 6.0, the aggregated Fe $(OH)_2$ colloids exist as three dimensional (branched or spread out) porous sponge-like precipitate. Thus, better removal at slightly acidic conditions can be explained in the light of the zeta-potential results. Adsorption of phosphate ions on iron precipitate was explained in terms of the inclusion of small Fe/phosphate containing agglomerates in the chain-like colloidal structure [27]. Under an applied electric field, motion of oppositely charged ions will become faster that could facilitate adsorption.

Table 2
Effect of solution pH on sulfate removal

pH of suspension	Concentration of SO_4^{2-} (mg/l) after electro-coagulation		SO_4^{2-} removal (%)	
	Fe anode	Al anode	Fe anode	Al anode
5.5	32	28	68	72
7.0	35	33	65	67
8.5	41	49	59	41
9.5	59	73	41	27
10.5	78	80	22	20

Experimental conditions: initial concentration: 100 mg/l, current density: 62 mA/cm^2 and electroflotation time: 600 s.

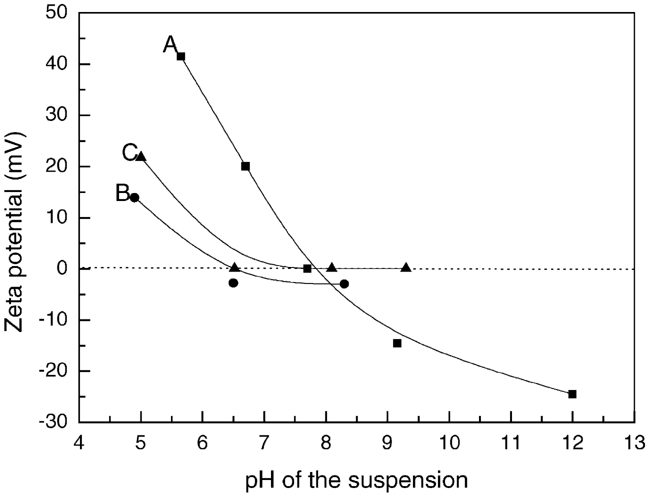


Fig. 6. Zeta-potentials of iron oxide/hydroxide in the presence of sulfite and sulfate ions: (A) pure iron oxide/hydroxide; (B) in the presence of sulfate and (C) in the presence of sulfite ions.

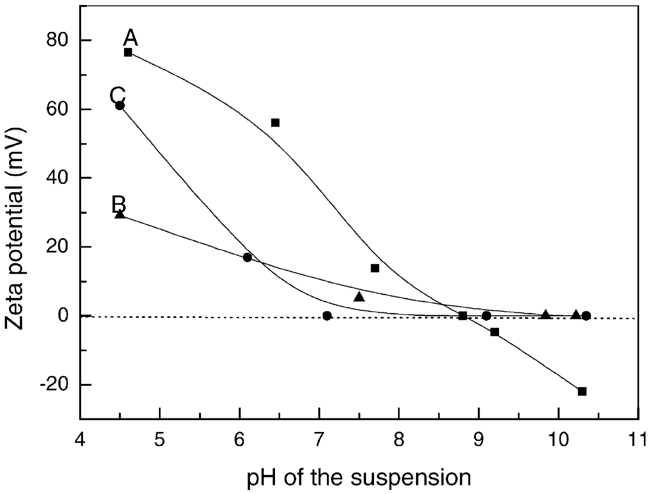


Fig. 7. Zeta-potentials of aluminum oxide/hydroxide in the presence of sulfite and sulfate ions: (A) pure aluminum oxide/hydroxide; (B) in the presence of sulfate and (C) in the presence of sulfite ions.

3.5. Effect of anode material on S^{2-} removal

Iron and aluminum sulfide precipitate formed during the experiments were separated and X-ray diffractograms were taken to identify the nature of the phases (Table 3). The precipitates formed during electrolysis exhibited several peaks confirming the heterogeneity of the samples. X-ray diffraction studies confirm the presence of iron and aluminum oxide/hydroxide as major phases in both the samples. Since a neutral pH was maintained in the solution, iron and aluminum ions released from anode are expected to form respective hydroxides. Ferric iron that is more stable

Table 3
XRD data of sulfide precipitate in the presence of Fe and Al anodes

Precipitate in the presence of Fe anode			Precipitate in the presence of Al anode		
D (Å)	I/I^0	Phases	*D* (Å)	I/I^0	Phases
6.253	77	FeO(OH); L,	3.204	46	Al_2S_3, S, AlO(OH)
5.409	85	Na_2S_5	2.822	100	Al_2S_3, S
5.212	81	Na_2S_5	2.356	35	Al_2S_3, AlO(OH)
4.94	100	FeO(OH)	1.993	52	Al_2S_3, S, AlO(OH)
4.418	83	Na_2S_5	1.856	30	Al_2S_3, S, AlO(OH)
4.268	81		1.63	24	Al_2S_3
4.121	88	Fe_2O_3	1.435	19	AlO(OH)
3.959	77	Fe_2O_3	1.306	15	AlO(OH)
3.795	80	Na_2S_5	1.261	18	
3.646	79	Na_2S_5			
3.452	83	FeS_2(M)			
3.23	98	FeO(OH), S			
3.115	84	FeS_2(P), Fe_7S_8, $Fe_{1-x}S$, FeS, Fe_3S_4			
2.867	75	Fe_7S_8, S, Na_2S_5, FeS, Fe_3S_4			
2.681	70	FeO(OH), S, FeS_2(M), FeS_2(P), Fe_7S_8, $Fe_{1-x}S$, Fe_2O_3, Na_2S_5			
2.585	66	FeO(OH), Na_2S_5, FeS			
2.314	61	FeS_2(M), FeS			
2.246	67	FeO(OH), Fe_2O_3, S			
2.201	69	FeO(OH), FeS_2(P), Fe_2O_3, S			
2.062	67	Fe_7S_8, $Fe_{1-x}S$, S			
1.992	69	S Fe_3S_4			
1.925	69	FeO(OH); L, FeS_2(M), FeS_2(P), Fe_2O_3 Fe_3S_4			
1.895	71	FeS_2(P), Fe_2O_3, S			
1.813	58	FeO(OH); L, S, FeS			

FeS_2(M): marcasite, FeS_2(P): pyrite, FeO(OH); L: lepidocrosite.

will be formed both due to auto oxidation of Fe^{2+} and because of anodic dissolution as shown in Eq. (2). The formation of FeO(OH) from ferric hydroxide and AlO(OH) from aluminum hydroxide can be represented as:

$$Fe(OH)_3 \rightarrow FeO(OH) + H_2O \tag{5}$$

$$Al(OH)_3 \rightarrow AlO(OH) + H_2O \tag{6}$$

In addition to the above oxide phases, sulfide phases, such as pyrite, marcasite, makhinawite and greigite, elemental sulfur and aluminum sulfide were observed. Both, bulk and surface reactions between S^{2-} and Fe^{2+}/Fe^{3+} are expected under experimental conditions.

Reactions that occur in solution phase are

$$Fe^{2+} + H_2S \rightarrow FeS + 2H^+ \tag{7}$$

$$Fe^{2+} + HS^- \rightarrow FeS + H^+ \tag{8}$$

$$Fe^{2+} + S^{2-} \rightarrow FeS \tag{9}$$

$$2Al^{3+} + 3S^{2-} \rightarrow Al_2S_3 \tag{10}$$

In the case of iron, in addition to monosulfides, FeS_2 formation by polysulfide-pathway was also suggested [27,28] according to the following equation.

$$FeS(s) + S^0(s) \rightarrow FeS_2(s) \tag{11}$$

Elemental sulfur is formed due to oxidation at anodic site and also by Fe^{3+} reduction. HS^- is oxidized to either elemental sulfur or $SO_4{}^{2-}$ according to the following equations:

$$HS^- + OH^- \rightarrow S^0 + H_2O + 2e^- \tag{12}$$

$$HS^- + 9OH^- \rightarrow SO_4{}^{2-} + 5H_2O + 8e^- \tag{13}$$

$$FeS_2 \rightarrow Fe^{2+} + 2S^0 + 2e^- \tag{14}$$

$$FeS_2 + 8H_2O \rightarrow Fe^{3+} + 2SO_4{}^{2-} + 16H^+ + 15e^- \tag{15}$$

However, the above reactions are more favorable with the use of stable electrodes, such as titanium. Conversion of nearly 50% of sulfide to sulfate (Table 1) in the presence of titanium electrode can be explained by Eq. (13). Conversion of S^{2-} to elemental sulfur is also advantageous as it can be removed by flotation.

Removal of sulfide in the presence of iron oxides by reductive dissolution mechanism was suggested by Santos et al. [23]. In the presence of oxidized sulfur species, iron mono sulfides are unstable and are readily converted to pyrite. However, they can remain intact under reducing H_2S environment [27]. The presence of minor quantity of makhinawite and griegite along with pyrite indirectly suggests pyrite formation through makhinawite and greigite route suggested in the earlier studies [28].

4. Conclusions

Separation of pollutants from tannery wastewater and also from synthetic effluents containing sulfide, sulfite and sulfate was studied by electro flotation technique. Soluble anodes like Fe and Al are found to be effective both for the removal of sulfur species and suspended solids. Sulfide ions are precipitated as metal sulfides and simultaneously coagulated by metal ions generated in situ by electrolytic oxidation of anode. Hydrogen bubbles simultaneously emanating from cathode were used to remove coagulated solids. Stable electrodes like titanium are found to be disadvantageous since they merely converts sulfide ions to sulfate ions. Separation of sulfite and sulfate was found to be a physical process wherein these ions are enmeshed in coagulant molecules.

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References

[1] R.E. Gosselin, R.P. Smith, H.C. Hodge, in: R.E. Gosselin (Ed.) Clinical Toxicology of Commercial Products, fifth edition, Wilkins, Baltimore, MD, 1984.
[2] S. Tabacova, NeuroToxicology 7 (2) (1986) 421.
[3] National Research Council of Canada, Hydrogen sulfide in the atmospheric environment: scientific criteria for assessing its effects on environmental quality. NRCC NO 18467, Associate Committee on Scientific Criteria for Environmental Quality, Ottawa, 1981.
[4] A. Kotronarou, M.R. Haffmann, Environ. Sci. Technol. 25 (6) (1991) 1153.
[5] M. Tomar, T.H.A. Abdulah, Water Res. 28 (12) (1994) 2545.
[6] F.J. Millero, A. Le ferriere, M. Fernandez, S. Hubinger, J.P. Hershey, Environ. Sci. Technol. 23 (2) (1989) 209.
[7] F. Cadena, R.W.J. Peters, J. Water Pollut. Control Fed. 60 (1988) 1259.
[8] G. Rajalo, T. Petrovskaya, Environ. Technol. 17 (1996) 605.
[9] W. Simon Poulton, D. Michael Krom, J. Van Rijn, R. Raiswell, Wat. Res. 36 (2002) 825.
[10] A. Bagreev, J.T. Bandosz, J. Colloid Interf. Sci. 252 (2002) 188.
[11] A. Bagreev, F. Adip, J.T. Bandosz, Carbon 39 (2001) 1897.
[12] D. Mills, J. AWWA 92 (6) (2000) 34.
[13] A.Y. Hosny, Sep. Technol. 6 (1996) 9.
[14] S.H. Lin, C.F. Peng, Wat. Res. 28 (2) (1994) 277.
[15] L. Alexandrova, T. Nedialkova, I. Nishkov, Int. J. Miner. Process. 41 (1994) 285.
[16] L. Szpyrkowicz, Z. Naumczyk, F. Zilio-Grandi, Wat. Res. 29 (2) (1995) 517.
[17] S. Lenore Clesceri, E. Arnold Greenberg, D. Andrew Eaton, Standard Methods for the Examination of Water and Waste Waters, 20th edition, American Public Health Association, Washington, DC 20, USA, 1998.
[18] A. Eilen Vic, A. Dale Carlson, S. Arild Eikum, T. Egil Gjessing, Wat. Res. 18 (1984) 1355.
[19] V.A. Glembotskii, A.A. Mamokov, A.M. Romanov, V.E. Nenno, in: Proceedings of the XIth International Mineral Processing Congress, Cagliari, 1975, pp. 561–582.
[20] V.A. Glembotskii, A.A. Mamokov, V.N. Sorokina, Electronnaja Obrabotka Materialov. 5 (1973) 66.
[21] V.I. Melic-Gaikazyan, N.P. Emelianova, V.T. Pronin, All Union Conference on Physico-Chemistry of Waste Free Technology of Refining of Minerals, Nauka, Alma-Ata, 1981, p. 7 (in Russian).
[22] C. Manohar, V.K. Kelkar, J.V. Yakhmi, J. Colloid Interf. Sci. 89 (1982) 54.
[23] M. Dos Santos Afonso, W. Stumm, Langmuir 8 (1992) 1671.
[24] W. Rudzinski, R. Charmas, S. Partyka, S. Thomas, J.Y. Bottero, Langmuir 8 (1992) 1154.
[25] M. Syed Ahmed, in: P. Somasundaran, R.B. Grieves (Ed.), Advances in interfacial phenomena of particulate/solution/gas systems, Application to Flotation Research, vol. 75, AIChE Symposium Series, 150, AIChE, New York, 1975, pp. 110–117.
[26] Q.H. He, G. Gary Leppard, C.R. Paige, W.J. Snodgrass, Water Res. 30 (6) (1996) 1345.
[27] R.T. Wilkin, H.L. Barnes, Geochim. Cosmochim. Acta 60 (1996) 4167.
[28] G. Liane Benning, T. Rick Wilkin, H. L Barnes, Chem. Geol. 167 (2000) 25.