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An Efficient Removal of Arsenic from Industrial Effluents using Electro-coagulation as Clean Technology Option

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ABSTRACT: This paper is a preliminary communication of a study on removal and recovery of heavy metals from industrial waste waters using electro-coagulation (EC) technique. The larger study envisages use of solar energy for producing the D.C. current, and simple chemical methods of standard methods in chemistry like use of hydrochloric acid, hydrogen sulfide, collection of precipitate, incineration and getting metal oxides in the most economical way of metal recovery. However, this paper reports on the removal of Arsenic (As) from industrial effluent using electro-coagulation (EC) technique. The optimization has been performed to increase the removal efficiency of As by varying initial pH (2-10), time of electrolysis (5-30min) and current density (0.8-4.8 A/dm^2). For the first time, we notice that the current density 4.8 A/dm^2 has been observed to produce the quickest removal (99.9%) within 10min. The phenomenal COD reduction from 400mg/l to 30mg/l with electrolysis time of 15min is a significant finding, to achieve this type of COD reduction by the existing methods generate huge quantities of sludge. The sludge formed in the reaction vessel also have been Investigated.

Key words: Combined Al-Fe electrode system, Wastewater, Initial pH, Current Density, Electrolysis tim, COD

INTRODUTION

Over the past decades, researchers are focusing their attention towards the removal of toxic metals from different products which spread to all branches of environmental and life science due to its severe maladies in human immune systems (Huang & Poynton, 2004; Naim *et al.*, 2011; Heidari *et al.*, 2011; Li *et al.*, 2011). Amongst, Arsenic has found to be one of the most toxic heavy metal (Ashan and Del Valls, 2011). Its toxicity solely depends up on its oxidation state. Trivalent arsenic has 100 times more toxic than the pentavalent state. If Arsenic is ingested to the human body, there is severe health disorder occurred in the risk of bladder and prostate cancers, decrease in hearing ability, skin thickening and disturbance to the nervous system (Pickering & Prince, 2000). The serious problems have encountered in many regions of the world such as Argentina, Bangladesh, Chile, India, Mexico, Mongolia, Myanmar, Nepal, New Zealand, Thailand, Taiwan, Turkey and Vietnam, when arsenic concentration in ground water and/or surface water have exceed the international drinking water standards (permissible limit of 10μgL^{-1}). Earlier report states that the ground water in Rappel (north Belgium) an industrial site polluted with arsenic contains upto 31,000mg/L (Cappuyns & Van Herreweghe, 2002). Thus, arsenic is one of the important toxic carcinogen and mutagen (Kobya & Can, 2003). In environmental view, industrial activities cause serious pollution problems regarding the groundwater and streams (Rameshraja and Suresh, 2011; Ajibola and Ladipo, 2011; Haruna *et al.*, 2011; Norris and Titshall, 2011; Nasrabadi *et al.*, 2010). In connection to this, it is expedite to look forward to renunciation the toxic metals from drinking water and industrial effluents from the severe health problems. Various techniques have been employed for the treatment of heavy metals, including ion exchange and reverse osmosis (Chen, 2004), precipitation (*Rajeshwar & Ibanez, 1994)*, absorption (Dabrowski & Curie-Sklodowska, 1999) and electrocoagulation (Golder & Samanta, 2007). Amongst, electro-coagulation (EC) is an unprecedented clean water technology for the removal of toxic heavy metals containing solutions (Picard & Galhalifaud-Feuiltade, 2000). Earlier research reports showed that the EC is most promising method for the removal of pollutants (Holt & Barton, 2002;

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Barrera-Diaz & Roa-Morales, 2006; Jiang & Graham, 2002). Recently, Jewel. A. G. Gomes et al reported the removal efficiency varied from 78.9% to more than 99.6% at different initial concentration (1.42 - 123ppm) when Al-Fe electrode was used (Gomes & Daida, 2007). Here, we report on the efficient removal efficiency of arsenic (92 to 99.9%) in drinking water and industrial effluents by varying initial pH (2-10), time of electrolysis (5-30min) and current density (0.8-4.8 A/dm^2). We used different combination of electrodes for the removal of As, amongst, Iron electrodes are found to be ideal. The results are discussed in detail.

MATERIALS & METHODS

All the required chemicals are in analytical grade. Stock synthetic solution of 1000mg/L arsenic has prepared by dissolving 1.734g of sodium arsenite ($NaAsO_2$) in 1000 ml of double distilled water. Lower concentration solutions have prepared by suitable dilution. The pH of the solution is adjusted to the required value with 10^{-2}M hydrochloric acid and/or 10^{-2}M sodium hydroxide. Al-Fe, Al-Al and Fe-Fe plates (100mm×50mm×0.5mm) of 99.9% purity have been used as electrodes.

EC has been performed at ambient temperature (25^{o}C) on synthetic and real industrial waste water. The detailed experimental setup is presented in Fig.1 (a). The synthetic and industrial waste water is taken in 1000ml beaker. The electrodes are carefully dipped in the synthetic and industrial waste water then the electrodes are connect to radiometer potentiostat/ galvanometer (Model: RPS-302 D [AQUILA]) is used in Galvan static mode to supply the constant current. One electrode functioned as a sacrificial anode (active surface = 50cm^2) and other acts as cathode. After completion of the treatment, sample is taken from the reactor and filtered to elim-inate sludge formed during electrolysis. The change in electrode has observed after the EC which showed in Fig.1(b). The residual concentration of metal ions is estimated by using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP - OES) (Model: Thermo Electron Corporation model IRIS Intrepid II XSP). COD estimated by COD reactor.

RESULTS & DISCUSSION

In order to evaluate the effect of pH, a series of experiments have been carried out using different combinations (Al-Fe, Al-Al and Fe-Fe) of electrodes. A series of 10mg l^{-1} of As(III) and As(V) solutions were adjusted pH between 2-10 and used for EC experiments. The removal of arsenic % at different initial pH in the range of 2-10 using different electrodes is displayed in Fig. 2. From the Fig. 2, it is obvious that the removal efficiency of arsenic ions have significantly been increased with increase of initial pH in the range of 2-10. After 15min of electrolysis at 0.8A, the removal efficiency of arsenic reached to 99.9% at initial pH=8. The removal percentage of arsenic is the increased with pH could cause the formation of $Al(OH)_4$ and $Fe(OH)_4$. During the formation, all the aluminum cations produced at the anode and formed polymeric species Al^{3+}, precipitated as $Al(OH)_3$ leading to a more effective treatment in the removal of arsenic. Earlier reports showed that there is significant change have been noticed in the final pH compared with initial pH (2-10) after the EC (Vik & Carlson, 1984; Do & Chen, 1994). This is due to the excess of hydroxyl ions generated at

Fig.1(a): Electro-coagulation Unit

Fig.1(b) : Electrodes after Electro coagulation

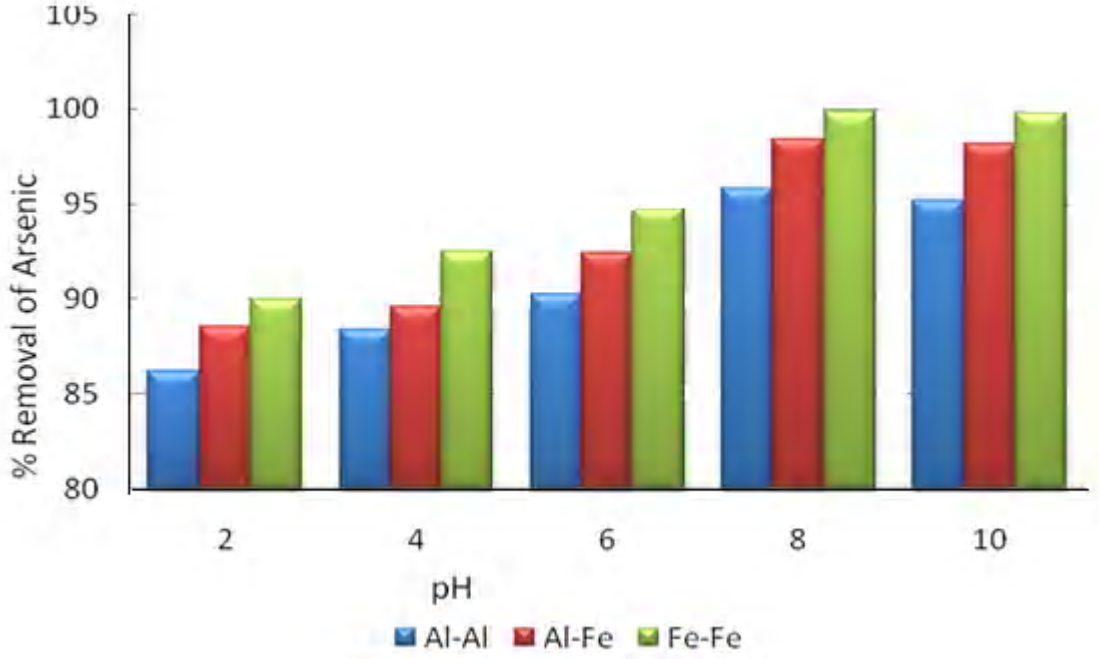

Fig. 2. Removal of arsenic at different initial pH using different electrodes

cathode and the exchange of Cl^{-1} with OH^- in $Al(OH)_3$ and $Fe(OH)_3$ in acidic conditions. The initial pH is above 9, slight decrease in the final pH could be due the formation of $Al(OH)_4$ and $Fe(OH)_4$.

A series of experiments have been performed to investigate the removal efficiencies on solutions containing As (III) and As (V) with current density varied from 0.8 to 4.8A/dm^2 is shown in Fig. 3.The removal rate of arsenic metal ions have successfully been enhanced with enhance the current density. The highest removal percentage of arsenic (99.9%) is achieved in just 10min at the current density of 4.8 A/dm^2. This startling behavior could be due to increase of coagulant and bubbles generation rate; resulting more efficient and faster removal is possible with increase current density. According to Faraday's law, Aluminum and hydroxide ions generated at a given time in the EC cell are depending on the current flow. It is very interesting to know that, the bubble sizes reduced with increase of current density, this is beneficial in the separation process. Furthermore, the amount of oxidized aluminum and the charge loading is enhanced as time progress. It is note that these parameters are kept at low level to achieve a low cost treatment. The effect of current density on the removal of arsenic at pH=6 is tabulated in Table 1.The results showed that the removal rate of arsenic is attained to 99.4% at 20 min and the volumetric electrical charges ensuring 98% removal of arsenic at 9.2mFl^{-1} using iron electrodes. The bubble density and upward flux increases at high current thus faster removal of the coagulant by flotation. Hence, As reduction in the probability of collision between the coagulant and targeted pollutants. From these observations, it is infer that the quickest removal rate is prevailed at highest current.

The effect of metal ion concentration presented in the wastewater as function of removal percentage of arsenic is displayed in Fig.4. The metal ion concentrations are in the range of 2-25mg/l at different times of electrolysis. From Fig.4, It is clear that the charge loading increase linearly with initial concentration. The results demonstrate that the amount of aluminum delivered per unit of pollutant is not affected by the initial concentration. Further, the charge loading play very important role in the removal of arsenic to the admissible level.

The removal percentage of arsenic from industrial effluents using various electrodes as shown in Fig 5. The residual concentrations of arsenic with COD are measured at different electrolysis times. From the Fig.5, it is obvious that the initial concentrations of As (6 mg/L) exceeded the legal limits. Further the COD content of the wastewater (400 mg/L) is found to be more than three times the authorized limit; indicating the presence of some organic compounds in the wastewater. From the Fig. 5, it is noticed that the residual concentration of arsenic decreases slowly and reached to the 0.005 mg/L after the electrolysis time of 25min. The removal rate of As from the industrial effluents seems to be relatively slow as compared with the removal of As from synthetic wastewater. This

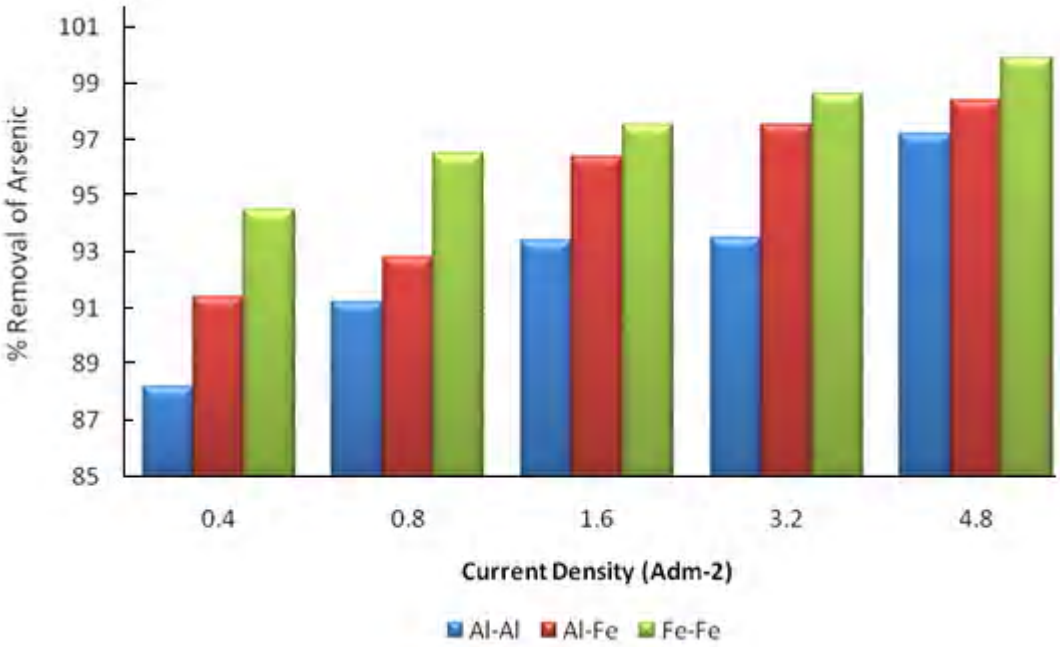

Fig. 3. Removal of Arsenic as function of current density using different electrodes

Table.1. Effect of current density with contact time on removal of arsenic (Surface area 50 cm^2, electrodes Fe/Fe, pH=6)

Contact time(min)	Residual concentration (in ppm)			
	0.8 A/dm^2	1.6 A/dm^2	3.2 A/dm^2	4.8 A/dm^2
5	0.58	0.46	0.39	0.31
10	0.44	0.36	0.27	0.25
15	0.39	0.34	0.22	0.12
20	0.22	0.18	0.12	0.06
30	0.14	0.11	0.08	0.006
40	0.11	0.07	0.008	0.004
50	0.006	0.002	0.001	0.001

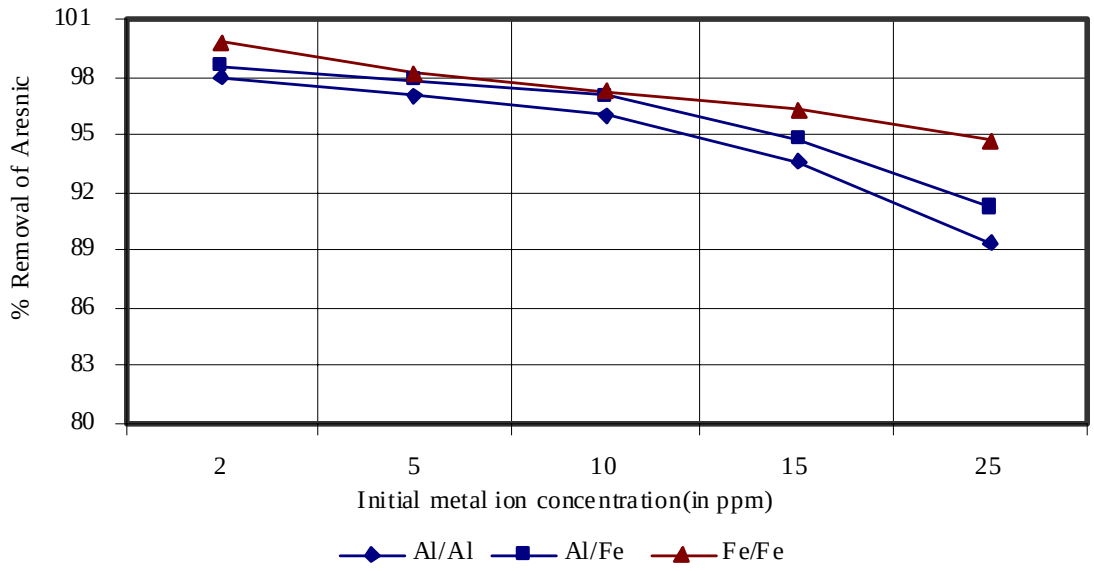

Fig. 4. Removal of arsenic as function of metal ion concentrations using different electrodes

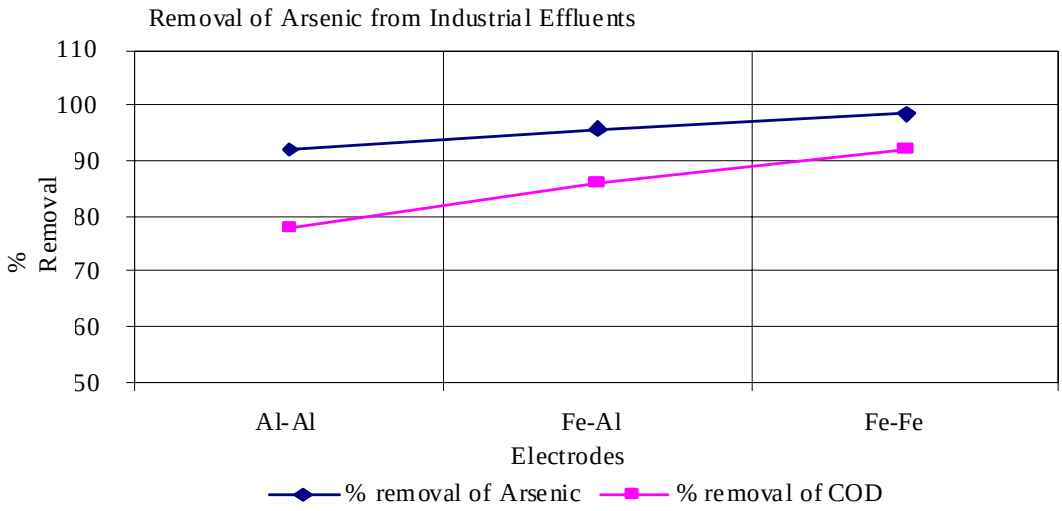

Fig. 5. Removal of Arsenic from Industrial Effluent

could be due to the presence of organic compounds in the industrial effluents; the organic compounds might adsorb on $Al(OH)_3$ coagulants which lead to as substantial reduction of metal ions. The COD reduced from 400 mg/l to 30mg/l at 15min; the removal efficiency at this condition is found to be 92%. Beyond the 15min, the residual COD reached to a plateau and remains nearly constant.

In the EC process sludge formation is primarily due to formation of denser fine metallic particulates, further separate from liquid to settle bottom of the reaction vessel due to gravity (sometime, magnetic separation) the characteristics of sludge produced form the effluents are listed in the Table 2. The sludge formation details with treatment costs are given in the Table 2. In our EC experimental setup, removal of one kg As produces 3.1 kg of sludge meanwhile it is much less than 36kg of sludge generated in iron sulphate precipitation method. These results disclose that the iron electrodes are more reliable than aluminum and hybrid Al/Fe electrodes in the removal of As from industrial effluents. This metaphor is due to the formation of Fe-As complex which is more stable than Al-As complex. The sludge production is proportional to characteristics of raw wastewater. Settable solids and matter destabilized by coagulation and

Table 2. The sludge formed after Electro-coagulation and Operating cost

Electrodes	pH	Electrolysis Time (min)	% Removal of Arsenic	Sludge formed (kg/m^3)	Operating cost $\$/m^3$
Fe-Fe	2	20	98.4	0.034	0.0222
	4	15	99.2	0.041	0.0220
	6	15	99.8	0.048	0.0196
	8	10	99.9	0.056	0.0184
	10	10	99.9	0.054	0.0168
Al-Fe	2	25	95.2	0.025	0.0198
	4	20	96.8	0.028	0.0218
	6	20	98.2	0.032	0.0229
	8	15	98.6	0.036	0.0237
	10	15	98.4	0.035	0.0179
Al-Al	2	30	95.4	0.019	0.0226
	4	25	96.2	0.021	0.0232
	6	25	97.8	0.027	0.0246
	8	20	98.4	0.034	0.0252
	10	20	98.4	0.032	0.0198

concentration flocculent and has also proportional to current density and electrolysis time (Gomes & Daida, 2007; Kobya & Can, 2003; Do & Chen, 1994). The sludge was analyzed by SEM has been observed in Fig. 6 (a) and 6(b). The removal of arsenic percentage (99.9%) is evident from the EDS spectrum which is shown in Fig. 7.

From the results, it is evident that the electro coagulation method is an efficient clean technology for the removal of heavy metals from industrial wastewater by using Fe electrodes. The removal efficiencies of heavy mental ions from the industrial wastewater are being possible to fine optimization of external parameters. The pharmaceutical waste water samples have been treated by Electrocoagulation results are given in Table 3. Operating conditions for the removal of As from pharmaceutical wastewaters using EC has given detail results in Table 4.

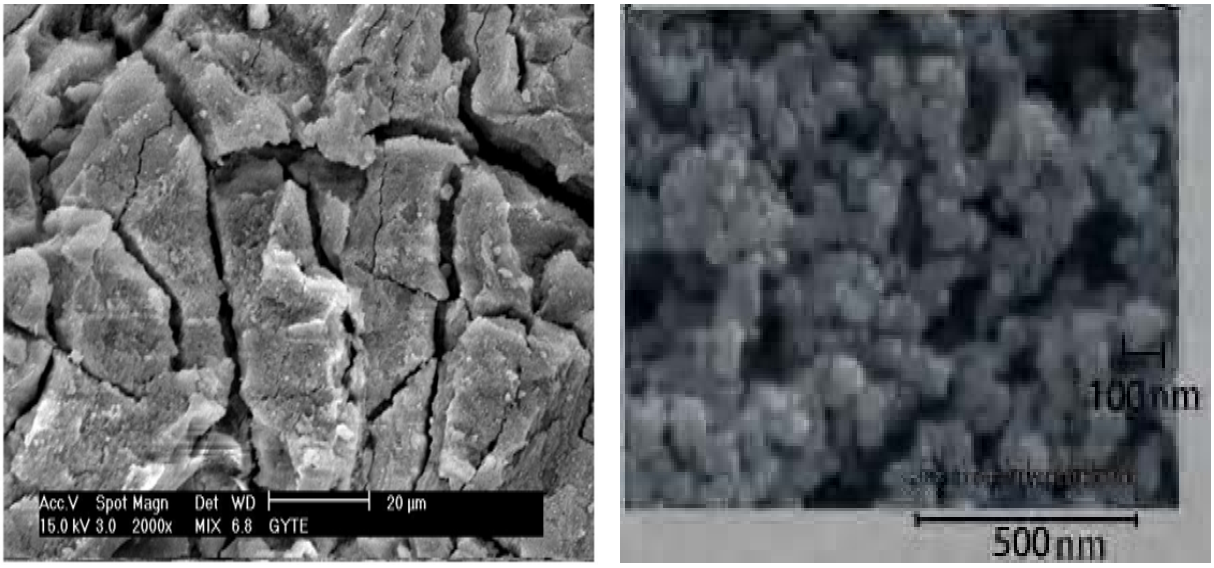

Fig 6(a) Fig 6(b)

Fig. 6. SEM images of sludge are represented with two magnifications

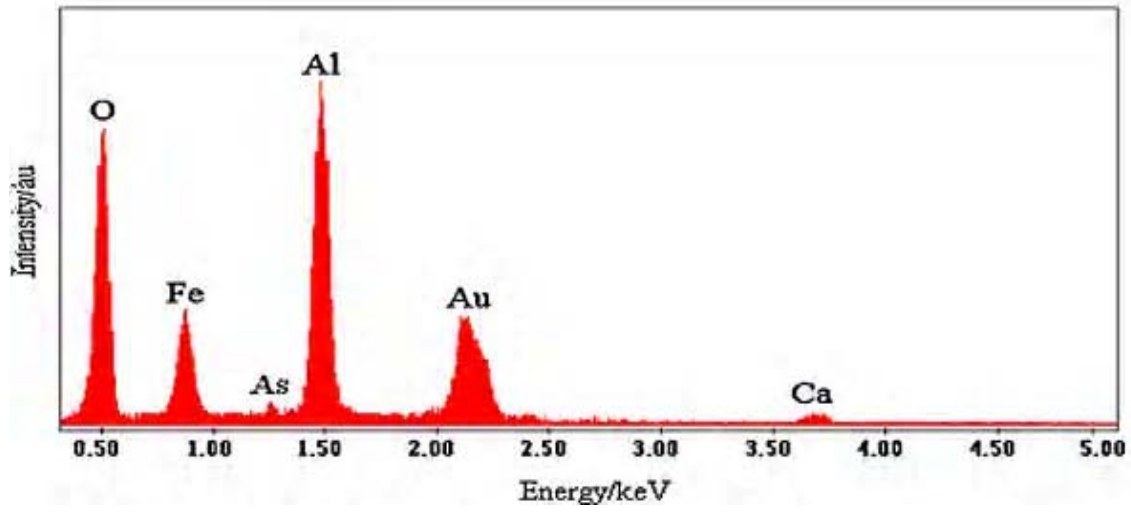

Fig.7. EDS spectra for the concentration of elements in the samples

Table 3. COD reduction after Electro-coagulation pharmaceutical effluents(Initial concentration of As, 6 mg/ L; current density, 4.8 A/dm^2; contact time, 10 min)

Parameters	Final concentration of COD and Arsenic		
	Al/Al electrode	Al/Fe electrode	Fe/Fe electrode
COD	85.68	53.04	32.64
Arsenic	0.528	0.258	0.005

Table 4.Operating conditions for removal of As from pharmaceutical wastewaters using EC

Environmental Parameter	Initial concentration	Effluents before primary treatment treated with EC		
		5 min.	20 min	30 min
pH	6.8±0.2	7.2±0.1	7.3±3.56	7.2±0.1
TDS, mg/L	1270±12.6	246±8.3	58±4.29	18±1.67
COD, mg/L	300±4.8	32±2.1	28±1.2	7±0.83
BOD, mg/L	30±1.4	11±0.94	7±0.81	4±0.58
As, mg/L	20±0.97	1.26±0.03	0.09±0.01	0.01±0.006
Environmental Parameter	**Initial concentration**	**Effluents before primary treatment treated with EC**		
		5 min.	**20 min**	**30 min**
pH	5.2±0.2	7.0±0.1	7.3±0.1	7.2±0.1
TDS, mg/L	5480±42	1210±7	980±6.1	895±3.8
COD, mg/L	2250±9	320±4	285±2.6	252±1.2
BOD, mg/L	110±6	53±2.8	36±1.1	20±0.9
As, mg/L	93±9	10.8±0.6	5.73±0.2	4.12±0.11
Environmental Parameter	**Initial concentration**	**Effluents before primary treatment treated with EC**		
		5 min	**20 min**	**30 min**
pH	6.9±0.2	7.3±0.1	7.2±0.1	7.5±0.2
TDS, mg/L	90±2.68	61±1.26	29±0.92	21±0.81
COD, mg/L	72±2.43	46±1.08	10±0.84	8±0.61
BOD, mg/L	28±1.23	13±0.93	5±0.09	ND
As, mg/L	6±0.91	0.9±0.01	0.01±0.001	0.006±0.001

CONCLUSIONS

In summary, it could be concluded that EC is an ideal method for the removal of arsenic from the drinking water and industrial effluents by using different electrodes. The removal capacity of arsenic is enhanced by monitoring the external parameters such as initial pH, current density, treatment rate and metal ion concentration. The removal percentage of arsenic metal ions have enhanced with enhance the current density and finally reached to 99.9 % within 10 min at the current density of 4.8 A/dm^2. The charge loading increases almost linearly with initial concentration and plays an important role in the removal of arsenic to the admissible level. The COD content of the wastewater (400 mg/L) is found to be more than three times the authorized limit; indicating the presence of some

organic compounds in the industrial effluents. The removal rate of As (0.005mg/L after the electrolysis time of 25 min) from the industrial effluents seems to be relatively slow as compared with the removal of As from synthetic wastewater. This could be due to the presence of organic compounds in the industrial effluents; the organic compounds might adsorb on Al $(OH)_3$ coagulants which lead to as substantial reduction of metal ions. Iron electrodes are found to be most ideal electrode compared with aluminum and hybrid Al/Fe electrodes in the removal of arsenic using clean water technology.

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