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Scientific paper  
UDC:628.191/.196(497.11)

## Arsenic removal through coagulation and flocculation from contaminated water in Macedonia

*Arsenic removal from contaminated water from Kozuf mountain region in R. Macedonia was examined through application of processes of coagulation and flocculation with ferric ions in this work. The experimental results have shown that arsenic-borne coagulates produced by coagulation with ferric ions were filterable, so filtration (filter paper as filter medium) was needed to remove the coagulates from water. The coagulation followed by conventional filtration achieved a very high arsenic removal rate (over 90%) from contaminated arsenic water (0.4 mg/l arsenic concentration), producing cleaned water with the residual arsenic concentration of 0.02 mg/l. In the process of arsenic removal, a zero residual arsenic concentration was achieved through appropriate adjustment of pH value. The results of the research have established the relations between the added flocculants, the contact time, and the pH change and it has been found that in certain cases efficiency for arsenic removal of 100% can be achieved.*

**Key words:** coagulant, flocculent, arsenic, contact time, pH

### 1. INTRODUCTION

According to the WHO (World Health Organization) recommendations, the presence of arsenic in the water supply system or commercially used mineral water is extremely harmful and dangerous. Based on the WHO recommendations, EU directives and domestic regulations that correspond to above-mentioned recommendations, the maximal allowed concentration of total arsenic is 10 µg/l. Lately, the arsenic concentration in commercially used water and water used through the public water supply system on the territory of Republic of Macedonia often surpasses the MAC (Maximum Allowed Concentration) value [1-3]. Socio-economic conditions of R. Macedonia demand low-cost as well as efficient treatment systems that could be implemented in the rural areas or cities. The main arsenic species present in natural waters are arsenate ions  $\text{AsO}_4^{3-}$  (oxidation state V) and arsenite ions  $\text{H}_3\text{AsO}_3$ ,  $\text{H}_2\text{AsO}_3^-$  and  $\text{HAsO}_3^{2-}$

(oxidation state III). However, As(V) ions are most prevalent in oxygenated water while As(III) is found in anaerobic conditions, like in well water or in groundwater. The literature on arsenic concludes that the most common valence states of arsenic in well water are As(V) or arsenate, and As(III) or arsenite. In the pH range of 4–10, the trivalent As(III) species are neutral in charge, while the As(V) are negatively charged. The removal efficiency for arsenic is often much lower for As(III) than for As(V) by using anyone of the conventional technologies for elimination of arsenic from water [4, 5], so either elevation of pH [5] or oxidation of arsenite to arsenate [6] is considered a prerequisite for any treatment method to be efficient. Therefore, treatment of arsenic contaminated well water through appropriate technology is one option to mitigate the arsenic problem. Various technologies have been used for removing arsenic from groundwater. The most commonly used technologies include co-precipitation with alum or iron, adsorption onto coagulated floc, ion exchange resin, reverse osmosis and membrane techniques. A review of these technologies along with their distinct advantages and disadvantages is shown in Table 1 [7–14].

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Paper received: 25. 07. 2011.

Table 1 - Comparison of main arsenic removal technologies

Technologies	Advantages	Disadvantages	Removal (%)
<b>Oxidation/precipitation</b>			
Air oxidation	Relatively simple, low-cost but slow process In situ arsenic removal Also oxidizes other inorganic and organic constituents in water	Mainly removes arsenic (V) and accelerate the oxidation process	80
Chemical oxidation	Oxidizes other impurities and kills microbes Relatively simple and rapid process Minimum residual mass	Efficient control of the pH and oxidation step is needed	90
<b>Coagulation/co-precipitation</b>			
Alum coagulation	Durable powder chemicals are available Relatively low capital cost and simple in operation Effective over a wider range of pH.	Produces toxic sludges Low removal of arsenic Pre-oxidation may be required	90
Iron coagulation	Common chemicals are available More efficient than alum coagulation on weigh basis	Medium removal of As(III) Sedimentation and filtration needed	94.5
Lime softening	Most common chemicals are available commercially	Readjustment of pH is required	91
<b>Sorption techniques</b>			
Activated alumina	Relatively well known and commercially available	Needs replacement after four to five regeneration	88
Iron coated sand	Expected to be cheap No regeneration is required Remove both As(III) and As(V)	Yet to be standardized Produces toxic solid waste	93
Ion exchange resin	Well-defined medium and capacity The process is less dependent on pH of water Exclusive ion specific resin to remove arsenic	High cost medium Requires high-tech operation and maintenance Regeneration creates a sludge disposal problem As(III) is difficult to remove Life of resins	87
<b>Membrane techniques</b>			
Nanofiltration	Well-defined and high-removal efficiency	Very high-capital cost Pre-conditioning High water rejection	95
Reverse osmosis	No toxic solid waste is produced	High tech operation and maintenance	96
Electrodialysis	Capable of removal of other contaminants	Toxic wastewater produced	95

## 2. COAGULATION AND FLOCCULATION

Coagulation and adsorption processes are most promising for arsenic removal from high-arsenic water because of the low cost and high efficiency, and are widely used in the developing world. But, they have not been shown to deeply eliminate arsenic from water and to produce cleaned water with a very low arsenic concentration. Coagulation process is traditionally realized by adding ferric or aluminum ions [14]. In this process, fine particles in water first aggregate into coagulates because added ferric or aluminum ions strongly reduce the absolute values of zeta poten-

tials of the particles. Then, arsenic ions (arsenate or arsenite) precipitate with the ferric or aluminum ions on the coagulates, and thus concentrate in the coagulates. After that, the coagulates are separated from water through filtration, eliminating arsenic from the water. The coagulates are termed arsenic-borne coagulates. Coagulation with ferric ions for arsenic removal can be traced back to the late 1960s in Taiwan to treat deep-well water with naturally elevated arsenic concentrations [15]. Gullidge and O'Connor [16] also reported that arsenic could be readily removed from water to a high degree by conventional water treatment using ferric or aluminum ions as coagu-

lants. Since then, there have been a lot of reports on coagulation process for arsenic removal. It has been found that the coagulation is much more effective for the removal of As (V) than As (III). In the case when only As (III) is present, oxidation to convert As (III) to As (V) is needed prior to coagulation. The effective pH for arsenic removal was reported to be 5–7 with aluminum ions, and 5–8 for ferric ions [17]. Besides iron and aluminum compounds, manganese, calcium and magnesium compounds are also of effective coagulants for eliminating arsenic from water in neutral medium [18,19]. Arsenic removal from water achieved by coagulation process depends on initial arsenic concentration in water [19,20]. The arsenic removal could reach 99% (Jiang, 2001). Recently, it was reported that modified coagulation/filtration could give a residual arsenic concentration of 2 mg/l or less for treated well water [21,22]. The arsenic removal is also dependent on the pore size of the membrane filter disks used for coagulation process [21-25], since coagulates smaller than the pore can pass through the filter and remain in water. As it is known, in filtration, larger the filter pores, lower the capital and operation costs, and higher the separation efficiency. Therefore, there is a great significance in enlarging arsenic-borne coagulates in order to improve coagulation/filtration process for arsenic removal. However, there is little information in this regard, although there are numerous reports on coagulation process for arsenic removal from water. Usually, coagulations are enhanced by adjusting pH and electrolyte concentration to reduce the absolute values of zeta potentials of particles, and by optimizing coagulation kinetics.

### 3. EXPERIMENTAL PART

The contaminated arsenic water sample used in this work was originally collected from the Kozuf mountain region, located in Gevgelija municipality, southern part of R. Macedonia. The water was filtrated with an Ahlstrom Grade 610 filter paper (2.5 mm aperture) to remove solid contaminants. The water past the filter paper was used for the tests, which gave the initial arsenic concentration of 0.3-0.4 mg/l. The chemical composition and some properties of the water sample are listed in Table 2.

Ferric chloride  $\text{FeCl}_3$  concentration of 40% , was used as coagulant; hydrochloric acid (HCl) (Fremont, analytic purity) and sodium hydroxide (NaOH) (J. T. Barker, analytic purity) was used to adjust pH.

Arsenic water (1000-4000 ml) was first mixed with a given amount of ferric coagulant in a flask, and then was adjusted for pH with HCl or NaOH by using a potential meter (Orion 720-A). After that, it was stirred on a magnetic agitator (Digital hot plate/stirrer

04644) at 400 rev/min for 20 min, while temperature was kept at  $25 \pm 0.5$  °C. Arsenic-borne coagulates were formed during the agitation. After that, the suspension was filtrated through a Filtrak 391 filter paper (0.125 mm aperture). The filtrate was sent for arsenic analysis. Arsenic concentration was determined by rather fast and less accurate colorimetric method provided by MERCK, while more precise results for the remaining concentration of arsenic are obtained by hydride method provided by AAS (atomic absorption spectroscopy) conducted in AAS Model Varian Spectra AA 55 apparatus with hydride generator. Each test was duplicated. The arithmetic average result of the two tests was reported in this paper.

Table 2 - The chemical composition and some properties of the water sample

Parameter	Quantity units	Sample
pH		6.6
blur	NTU	0.45
Electrical conductivity	$\mu\text{S}$	1316
dry residue	mg/l	766.5
bicarbonate	mg/l	951.6
alkalinity		156
hardness	°Dh	38.57
calcium	mg/l	205.1
Magnesium	mg/l	42.33
iron	mg/l	0.0
Manganese	mg/l	0.0
sodium	mg/l	32.7
arsenic	mg/l	0.3-0.4
Chromium	mg/l	<0.005
Chloride	mg/l	9.0
sulfate	mg/l	22.52
silicates	mg/l	24.0
Nitrate	mg/l	0.26
nitrite	mg/l	0.0
ammonia	mg/l	0.0
Consumption of permanganate	mg/ $\text{IO}_2$	2.5

### 4. RESULTS AND DISCUSSION

#### 4.1. Application of ferric chloride as a flocculent depending on the starting concentration

Experimental results regarding the application of ferric chloride in various concentrations as flocculants and the resulting effects are presented in Table.3.

Four concentrations of ferric chloride solution were used - 7.43 mg/l; 9.9 mg/l; 14.9 mg/l and 29.7 mg/l. Experimental reaction time was 5 minutes.

Table 3 – Removal of arsenic with flocculent  $FeCl_3$  (output concentration of arsenic)

Series 1 - Working volume 1000 ml with flocculent concentration 0.0272 g/l  $FeCl_3$

Series 2 - Working volume 2000 ml with flocculent concentration 0.0149 g/l  $FeCl_3$

Series 3 - Working volume 3000 ml with flocculent concentration 0.0099 g/l  $FeCl_3$

Series 4 - Working volume 4000 ml with flocculent concentration 0.00743 g/l  $FeCl_3$

time (min)	Series 1 As [mg/l]	Series 2 As-[mg/l]	Series 3 As-[mg/l]	Series 4 As-[mg/l]
0	0.38	0.35	0.35	0.33
3	0.009	0.01	0.025	0.025
5	0.004	0.006	0.025	0.025

#### 4.2. Application of ferric chloride as a flocculent depending on pH value

According to literature, it is evident that the pH value of the treated water has certain influence on the removal efficiency of both forms of arsenic. A group of experiments was conducted in order to determine ferric chloride's efficiency of arsenic removal depending on various pH values and flocculent concentration. The results of these experiments are given in Table 4.

Series of experiments were conducted with ferric chloride concentrations of 9.9 mg/l; 14.9 mg/l and 27.2 mg/l, and pH values of 5.5; 6.5; 7.5; and 8.5. Experimental reaction time was set for 20 minutes.

Table 4 - Removal of arsenic with flocculent  $FeCl_3$  with change of the Ph value

Series 1 - Working volume 1000 ml with flocculent concentration 0.0272 g/l  $FeCl_3$

Time (min)	As [mg/l] pH=5,5	As [mg/l] pH=6,5	As [mg/l] pH=7,5	As [mg/l] pH=8,5
0	0.4	0.4	0.4	0.4
1	0.0	0.002	0.023	0.09
3	0.0	0.0	0.023	0.039
5	0.001	0.001	0.01	0.039
10	0.0	0.0	0.01	0.03
20	0.0	0.0	0.005	0.027

Series 2 - Working volume 2000 ml with flocculent concentration 0.0149 g/l  $FeCl_3$

time (min)	As [mg/l] pH=5,5	As [mg/l] pH=6,5	As [mg/l] pH=7,5	As [mg/l] pH=8,5
0	0.4	0.4	0.4	0.4
1	0.0	0.001	0.05	0.15
3	0.001	0.001	0.02	0.1
5	0.0	0.0	0.035	0.15
10	0.0	0.001	0.025	0.1
20	0.0	0.001	0.025	0.1

Series 3 - Working volume 3000 ml with flocculent concentration 0.0099 g/l  $FeCl_3$

time (min)	As [mg/l] pH=5,5	As [mg/l] pH=6,5	As [mg/l] pH=7,5	As [mg/l] pH=8,5
0	0.4	0.4	0.4	0.4
1	0.004	0.005	0.025	0.18
3	0.002	0.004	0.058	0.24
5	0.001	0.002	0.025	0.16
10	0.0	0.002	0.025	0.16
20	0.0	0.002	0.025	0.1

#### 4.3. Analysis of the obtained results:

a. Examinations were performed through discontinuous setup of the experiments.

b. Application of ferric chloride as a coagulant/flocculent.

- Four concentrations of ferric chloride were utilized - 7.43 mg/l; 9.9 mg/l; 14.9 mg/l and 29.7 mg/l.
- The 90% or more arsenic removal in the experimental batch reactor was usually completed within 3min or less for most experiments.
- Following arsenic removal efficiency results were detected 92.4%, 92.9%, 98.3%, and 98.9%, accordingly.
- High removal efficiency was achieved in all the experiments, which resulted in decrease of the arsenic concentration in the treated water samples. Experimental results regarding the 2 cases of water samples containing higher concentrations of arsenic suggest decrease below MAC values.

c. Usage of ferric chloride as a coagulant/flocculent at different pH values.

- Four different pH values were adjusted – 5.5, 6.5, 7.5 and 8.5.
- The 90% or more arsenic removal in the experimental batch reactor was usually completed within 60s or less for most experiments.
- According to several literature sources, the pH value has a significant impact on the arsenic removal efficiency, especially regarding  $As^{3+}$  and  $As^{5+}$  [22-24].
- At higher pH values, only the highest concentration of ferric chloride stimulates the arsenic removal efficiency. This is evident from Table.4.
- On the other hand, decrease of arsenic concentration below MAC is achievable only at acidic or neutral pH values. This cannot be achieved at higher pH values.

## 5. CONCLUSIONS

Obtained results from conducted experiments indicate that the applied ferric ions can be efficiently used as a coagulant/flocculent. The coagulation/flocculation followed by conventional filtration achieved a very high arsenic removal rate from contaminated arsenic water (0.4 mg/l arsenic concentration), producing a cleaned water with no residual arsenic concentration (0.0 mg/l). The experimental results have shown that the process of coagulation/flocculation was finished in 60s or less. Furthermore, system's pH value has significant influence on the arsenic separation from its aqueous solutions, where higher efficiency and better results are obtained for mildly acidic pH values as well as for neutral value.

Therefore, high arsenic removal efficiency can be accomplished by appropriate setup of the process parameters and in certain cases efficiency of 100% can be achieved.

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## IZVOD

## UKLANJANJE ARSENA PUTEM KOAGULACIJE I FLOKULACIJE IZ KONTAMINIRANIH VODA MAKEDONIJE

*Uklanjanje arsena iz zagađene vode iz planinskog regiona Kozuf u R. Makedoniji je ispitan u ovom radu primenom procesa koagulacije i flokulacija sa feri jonima. Eksperimentalni rezultati su pokazali da se arsen zgrušava pri koagulacije sa feri jonima, tako da je potrebno izvršiti filtraciju vode i očistiti je od koagulanata. zgrušava. Konvencionalna filtracijom koagulanata ostvario se veoma visok stepen uklanjanja arsena (preko 90%) od kontaminiranog arsena u voda (0,4 mg / l, koncentracija arsena), i proizvedena je očišćena voda sa rezidualnom koncentracijom arsena od 0,02 mg / l. U daljem procesu uklanjanja arsena, nula rezidualna koncentracija arsena je ostvaren kroz odgovarajuće podešavanje pH vrednosti vode. Rezultati istraživanja su uspostavili odnos između dodatka flokulanta i vreme kontakta, kao i promene pH, pri čemu je uočeno da u nekim slučajevima može se postići efikasnost za uklanjanje arsena od 100%.*

**Ključne reči:** koagulant, flokulanti, arsen, kontaktno vreme, pH

Rad primljen: 25.07.2011.

Originalni naučni rad