

## Removal of Arsenic, Fluoride, and Lead from Wastewater Using Novel Polyinorganic Coagulants

Fathy M. M. Ahmed<sup>1,\*</sup>, Khaled A. Falous<sup>2</sup>, and Moktar M. Aburzeza<sup>2</sup>

<sup>1</sup> Faculty of Marine Resources, Alasmarya Islamic University, Libya.

<sup>2</sup> Faculty of Science, Alasmarya Islamic University, Libya.

\*Corresponding author: fathy732005@yahoo.com

### إزالة الزرنيخ والفلور والرصاص من المياه الملوثة باستخدام عديد متخن

#### غير عضوي جديد

فتحي محمد محمد أحمد<sup>1</sup>، خالد أحمد الفلوس<sup>2</sup>، مختار المبروك أبورزينة<sup>2</sup>

<sup>1</sup> كلية الموارد البحرية، الجامعة الأسمرية الإسلامية، ليبيا.

<sup>2</sup> قسم الكيمياء، كلية العلوم، الجامعة الأسمرية الإسلامية، ليبيا.

#### Abstract

The present study highlights to the removal of some dangerous pollutants such as lead, arsenic, and fluoride from wastewater. Treatment using a novel polyinorganic coagulants, the eight novel polyinorganic coagulants were prepared, and characterized namely, poly aluminum chloride (PACl) polyaluminum chloride silicate (PAClSi), polyaluminum hydroxy sulphate (PAHS), polyaluminum hydroxy sulphate silicate (PAHSSi), polyferric chloride (PFeCl), polyferric chloridesilicate (PFeClSi), polyaluminum ferric chloride (PAIFeCl), and polyaluminum ferric chloride silicate (PAIFeClSi). The application was carried out for the removal of pollutants from wastewater using these novel polyinorganic coagulants. It was found that the maximum percentages of removal of  $Pb^{2+}$ ,  $As^{3+}$ , and  $F^-$  ions from wastewater reached 99.98, 97, and 99%, using novel polyinorganic coagulants PAHSSi, PAIFeClSi, and PAIFeClSi respectively. Therefore, polyinorganic coagulant impregnated with silica was considered as a good coagulant for wastewater treatment due to its low cost and good efficiency in this application, as well as it will solve the problem of water shortage and to sustains a non-conventional water resource.

**Keywords:** Rice husk ash, Active silica, Sodium silicate, Polyinorganic coagulants, Pollutants removal.

#### الملخص

تسلط الدراسة الضوء على إزالة بعض الملوثات الخطيرة مثل الزرنيخ، والفلور والرصاص من المياه الملوثة باستخدام عديد المتخن الغير عضوي الجديد، عدد ثمانية من عديد متخن غير عضوي جديد تم تحضيرها وتوصيفها وهي عديد كلوريد الألمونيوم، عديد كلوريد الألمونيوم والسيلكون، عديد كبريتات الألمونيوم الهيدروكسيلية، عديد كبريتات الألمونيوم الهيدروكسيلية والسيلكون، عديد كلوريد الحديد، عديد كلوريد الحديد والسيلكون، عديد كلوريد الألمونيوم والحديد، عديد كلوريد الألمونيوم والحديد والسيلكون، التطبيقات تم إجراؤها على إزالة الملوثات من المياه الملوثة ووجد أن أقصى إزالة للرصاص، الزرنيخ و الفلور من المياه الملوثة سُجلت 99.98 و 97 و 99% من المياه الملوثة على التوالي باستخدام عديد المتخن الغير عضوي لكبريتات الألمونيوم الهيدروكسيلية والسيلكون، وكلوريد الألمونيوم والحديد والسيلكون وكلوريد الألمونيوم والحديد والسيلكون على التوالي. وبناءً على هذه النتائج فإن عديد

المشحن الغير عضوي المطعم بالسليكا يعتبر من المتخينات الجيدة في معالجه المياه الملوثة لتكلفته الصغيرة، وكفاءته العالية في هذا التطبيق بالإضافة إلى إسهامه في حل مشكله نقص المياه من خلال استدامته في المحافظة على مصادر المياه الغير تقليديه.  
الكلمات الدلالية: رماد قش الأرز، السليكا المنشطة، سيليكات الصوديوم، عديد المشحن الغير عضوي، إزالة الملوثات.

## 1. Introduction

The presence of heavy metals like, lead, arsenic and some anions such as nitrate and fluoride in aquatic systems is a very earnest problem and related to the prevalence some diseases like renal failure, liver cirrhosis, hair losses, cancer and chronic diseases. Heavy metals are dangerous for living organisms because of their stability, toxicity and tendency to accumulating in the environment. The industrial wastewaters are considered to be the main source of heavy metal impurities. Iron and aluminum co-precipitation/adsorption are a well-accepted process for removal of heavy metals from wastewater. Arsenic is the twentieth most abundant element in the earth's crust, fourteenth in the seawater and the twelfth most abundant element in the human body (Gupta, 2002).

Rice husk is a by-product from rice mill that has been used as an energy source in many industries such as biomass power plant and rice mill. Burning rice husk generates rice husk ash (RHA) which is rich in silica and can be an economically valuable raw material for production of natural silica (Kalapathy et al., 2000). There are several methods for the extraction of silica from biomass (Riveros and Garza, 1986; Yalcin and Sevinc, 2001; Krishnarao et al., 2001; and Della et al., 2002), the studies have suggested that acid preliminary treatment before thermal treatment is a reasonable method for natural silica extraction. The high purity of silica and low mineral impurity are retrieved by boiling in hydrochloric acid solution for 1 hr followed by burning in the atmosphere at 650-700°C for 4 hr. By means of this method, the extracted silica was found in the form of amorphous structure which is the most reactive form for silylation reaction (Yalcin and Sevinc, 2001).

Sodium silicate, the precursor for silica production, is currently manufactured by smelting quartz sand with sodium carbonate at 1300°C (Foletto et al., 2006). This conventional technology requires high energy costs, produce considerable air pollution, impurity of the product and need to maintenance of the oven due to attack of base. It could be avoided by processing rice husk silica, instead of sand, by ambient temperature methods. Rice husk ash is produced commercially by husk combustion and contains over 60% silica and is an economically viable raw material for the production of silicates, silica gel, zeolite and silica (Kalapathy et al., 2002). RH silica has fine particle size and high reactivity and has been used in the production of activated silica, sodium silicate, potassium silicate and solar grade silicon (Krishnarao et al., 1998).

The main methods used for arsenic removal from contaminated water sources are coagulation/direct filtration, ion exchange, adsorption on iron oxides or on activated alumina,

iron-oxide coated sand and reverse osmosis (Kartinen and Martin, 1995). These methods usually require a preliminary oxidation step, for the transformation of  $As(III)$  to  $As(V)$ , in order to achieve efficient arsenic removal (Jekel 1994; and Viraraghavan *et al.*, 1999).  $As(III)$  oxidation is usually performed by the addition of chemical reagents, such as, potassium permanganate, hydrogen peroxide or ozone (Molnar *et al.*, 1994; and Kim and Nriagu, 2000).

Different methods can be used for removing lead including filtration, chemical precipitation, coagulation, solvent extraction, electrolysis, ion exchange, membrane process and adsorption. Ion exchange and adsorption are the most common and effective processes for this purpose (Patterson, 1985).

The major techniques for removal of fluoride ion include precipitation and coagulation, as well as adsorption and ion exchange. The viability of the last method is dependent completely on the development of adsorptive materials. In contrast to the materials widely used for anion removal activated alumina (Bellack, 1971), inorganic ion exchangers are considered the most prospective because of their chemical stability and possible ability to control surface chemistry (DeMarco *et al.*, 2003; and Wasay *et al.*, 1996).

Polyinorganic coagulants and conventional coagulants such as aluminum sulphate, aluminum chloride, ferrous sulphate ... etc. are widely used in water and wastewater treatment. When activated silica is added to water, it produces a stable solution that has a negative surface charge. The activated silica can unite with the positively charged aluminum or with iron flocs, resulting in a larger and denser floc that settles faster and enhances enmeshment. Many researchers used adsorbent materials for removal of some pollutants (Aboabboud *et al.*, 2013; Okasha *et al.*, 2012; Abo-El-Enein *et al.*, 2011; Okasha and Ibrahim, 2010; Al-Meshragi *et al.*, 2009; Abo-El-Enein *et al.*, 2009; Kaur *et al.*, 2008; Yuan *et al.*, 2006; Bin Jusoh *et al.*, 2005; Munter *et al.*, 2005; and Reddad *et al.*, 2002). So, this study concerns with the comparison of a novel polyinorganic coagulants in removal of pollutants from wastewater.

## 2. Materials and Methods

All chemicals used are of commercial grade except sodium hydroxide is an analytical grade (Analar) product. Deionized water was used to make all solutions.

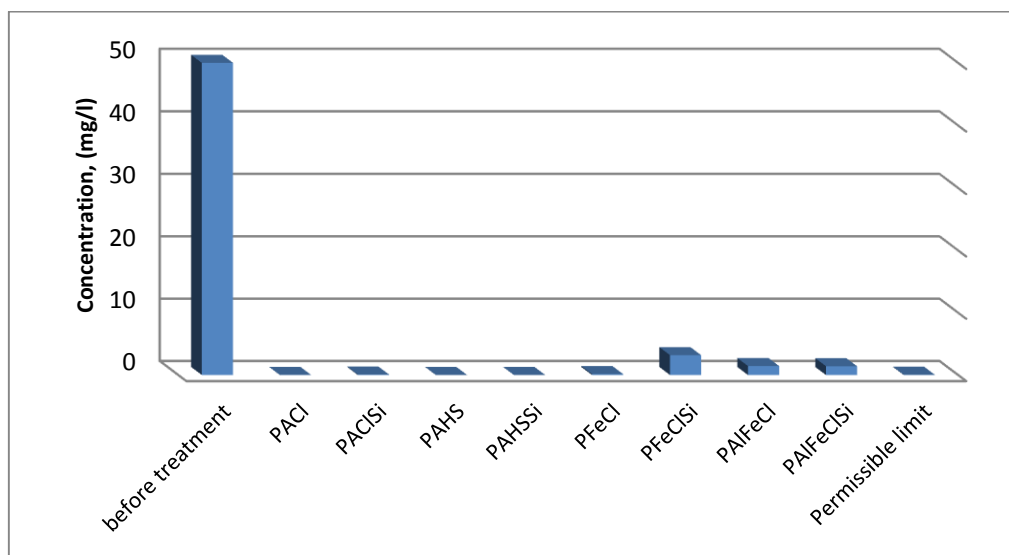
Eight samples of novel polyinorganic coagulants were prepared, and characterized namely, poly aluminum chloride (PACl) polyaluminum chloride silicate (PAClSi), polyaluminum hydroxy sulphate (PAHS), polyaluminum hydroxy sulphate silicate (PAHSSi), polyferric chloride (PFeCl), polyferric chloridesilicate (PFeClSi), polyaluminum ferric chloride (PAIFeCl), and polyaluminum ferric chloride silicate (PAIFeClSi). These coagulants were prepared and characterized as conducted by (Abo-El-Enein *et al.*, 2011; Ahmed, 2009; Kaur *et al.*, 2008; Yuan *et al.*, 2006; Bin Jusoh *et al.*, 2005; Munter *et al.*, 2005; and Reddad *et al.*, 2002). The samples of novel polyinorganic coagulants, were used to remove some pollutants

from wastewater such as lead, arsenic and fluoride from representative samples of wastewater. To obtain the water quality for reuse in agricultural drip irrigation systems, wherein, the treatment depends on precipitation, coagulation and adsorption techniques by polyinorganic coagulants (PIC). Each sample was mixed with 5-10 ppm of (PIC) and agitated for 1-minute rapid mixing (300 rpm), followed by slow mixing for five minutes and (30 rpm) and 20 minutes standing time. The concentrations of pollutants were measured in ore samples and in the filtrate using atomic absorption spectrophotometer (AAS) and analyses according to standard methods (FEW, APHA, 2005).

### 3. Results and Discussion

The data presented in Table (1) represented the variations of physicochemical properties of wastewater before and after treatment using eight samples of polyinorganic coagulants.

Figure (1) represents the variation of lead concentration of wastewater before and after treatment by using eight polyinorganic coagulants, results indicate to the removals percentages of lead are 99.97, 99.84, 99.978, 99.98, 99.7, 93.63, 97.12, and 97.18% using PACl, PAClSi, PAHS, PAHSSi, PFeCl, PFeClSi, PAIFeCl, and PAIFeClSi respectively. The maximum removal reached to 99.98% with PAHSSi. The maximum permissible limits are 0.05 mg/l according to WHO (Kaur et al., 2008).

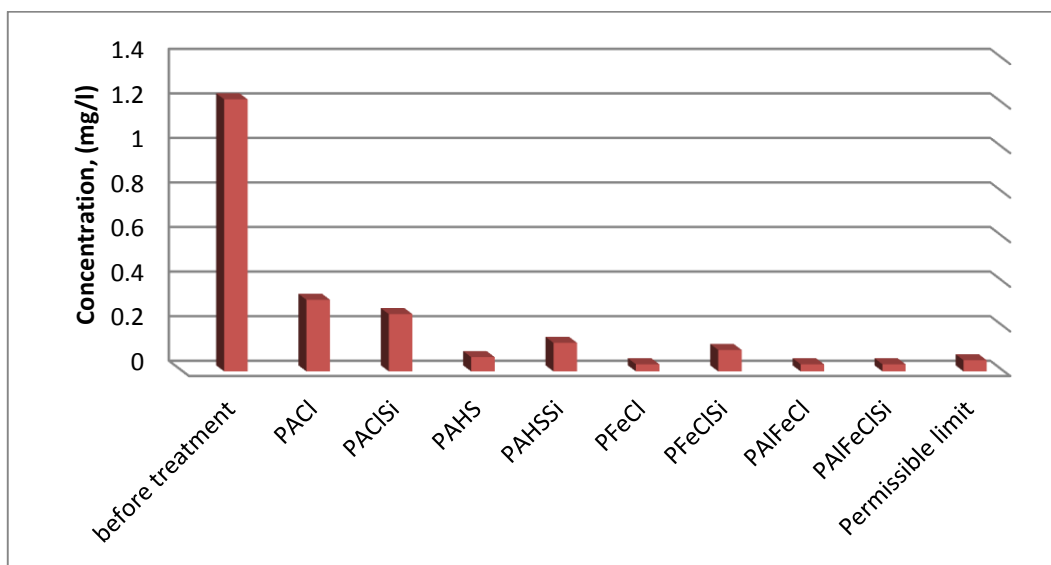


**Figure 1.** Variations of  $Pb^{2+}$  concentrations before and after treatment with different types of polyinorganic coagulants

**Table 1.** The variations of  $F^-$ ,  $As^{3+}$  and  $Pb^{2+}$  sample in the studied area before and after treatment with different types of polyinorganic coagulants.

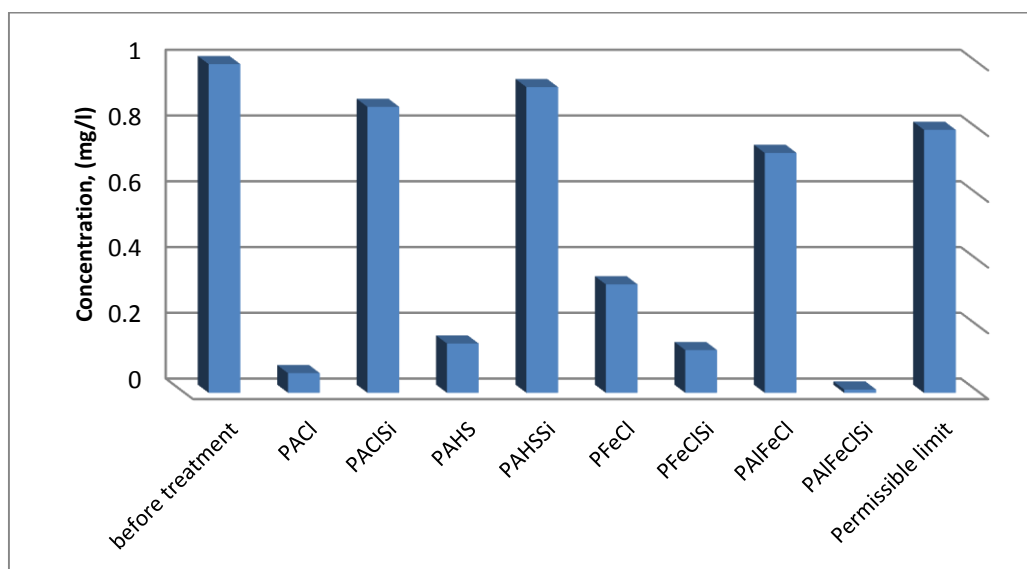
| Parameters           | Before treatment | After treatment |        |       |        |       |         |         |           | Permissible limit |
|----------------------|------------------|-----------------|--------|-------|--------|-------|---------|---------|-----------|-------------------|
|                      |                  | PACl            | PAClSi | PAHS  | PAHSSi | PFeCl | PFeClSi | PAIFeCl | PAIFeClSi |                   |
| Color, (Hazen U)     | 13               | 9               | 8      | 4     | 7      | 5     | 5       | 5       | 6         | 20                |
| TDS, (mg/l)          | 559              | 755             | 780    | 747   | 705    | 735   | 822     | 775     | 682       | 1200              |
| Turbidity, (NTU)     | 8.7              | 2.3             | 1.9    | 3.9   | 1.8    | 1.7   | 1.2     | 1.1     | 1.4       | 5                 |
| EC, ( $\mu$ mhos/cm) | 887              | 1174            | 1204   | 1189  | 1130   | 1137  | 1278    | 1207    | 1089      | 1200              |
| PH                   | 7.45             | 8.31            | 8.33   | 7.53  | 7.58   | 8.33  | 7.67    | 8.21    | 8.07      | 6.5-9.2           |
| $CO_3^{2-}$ , (mg/l) | 0                | 45              | 45     | 0     | 0      | 45    | 10      | 45      | 10        | -                 |
| $HCO_3^-$ , (mg/l)   | 250              | 295             | 302    | 318   | 295    | 302   | 272     | 300     | 272       | -                 |
| $Cl^-$ , (mg/l)      | 65               | 110             | 118    | 67    | 67     | 93    | 115     | 114     | 115       | 500               |
| $SO_4^{2-}$ , (mg/l) | 84               | 122             | 124    | 179   | 168    | 122   | 92      | 122     | 92        | 400               |
| $Ca^{2+}$ , (mg/l)   | 86               | 79              | 80     | 82    | 80     | 84    | 54      | 81      | 54        | 200               |
| $Mg^{2+}$ , (mg/l)   | 28.1             | 28.2            | 28.8   | 32.4  | 28.8   | 30    | 26.6    | 28.2    | 27.6      | 150               |
| $Na^+$ , (mg/l)      | 48               | 124             | 128    | 120   | 113    | 115   | 135     | 142     | 135       | 200               |
| $K^+$ , (mg/l)       | 4                | 3               | 3      | 3     | 3      | 3     | 3       | 3       | 3         | 10                |
| $Al^{2+}$ , (mg/l)   | 0.113            | 0.18            | 0.607  | 0.309 | 0.256  | 0.075 | 0.057   | 0.132   | 0.076     | 0.2               |
| $Pb^{2+}$ , (mg/l)   | 50.0             | 0.017           | 0.078  | 0.011 | 0.01   | 0.15  | 3.186   | 1.438   | 1.411     | 0.05              |
| $As^{3+}$ , (mg/l)   | 1.221            | 0.321           | 0.257  | 0.064 | 0.128  | 0.032 | 0.096   | 0.032   | 0.032     | 0.05              |
| $F^-$ , (mg/l)       | 1                | 0.06            | 0.87   | 0.15  | 0.93   | 0.33  | 0.13    | 0.73    | 0.01      | 0.8               |

Figure (2) presents the variations of concentration of arsenic of wastewater before and after treatment using eight samples of polyinorganic coagulants. It was found that, the removal percentages of arsenic are 73, 79, 95, 90, 97, 92, 97, and 97% using PACl, PAClSi, PAHS, PAHSSi, PFeCl, PFeClSi, PAIFeCl, and PAIFeClSi respectively. The maximum removal reached to 97% with PFeCl, PAIFeCl, and PAIFeClSi. The maximum permissible limits are 0.05 mg/l according to WHO (DeMarco *et al.*, 2003).



**Figure 2.** Variations of  $As^{3+}$  concentrations before and after treatment with different types of polyinorganic coagulants.

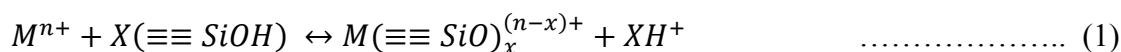
Variation of fluoride concentration of wastewater before and after treatment using eight polyinorganic coagulants is presented in Figure (3). It was found the removal percentages of fluoride are 94, 13, 85, 17, 67, 87, 27, and 99% using PACl, PAClSi, PAHS, PAHSSi, PFeCl, PFeClSi, PAIFeCl, and PAIFeClSi respectively. The maximum removal reached to 99% with PAIFeClSi. The maximum permissible limit is 0.8 mg/l according to WHO therefore the fluoride concentrations of studied area after treatment are within normal limits (Ahmed, 2009).



**Figure 3.** Variations of  $F^-$  concentrations before and after treatment with different types of polyinorganic coagulants.

The results shown through Figures (1-3) indicate to that PAIFeCl and PAIFeClSi are the superior polyinorganic coagulant copolymer. This is due to of  $Si^{4+}$ ,  $Al^{3+}$  and  $Fe^{3+}$  as copolymers (Yuan *et al.*, 2006). As for the total dissolved solids it increased due to the formation new spiked ions as shown in Table (1). Also, no variations of pH occurred and all the values after treatment are within permissible limits according to Egyptian law 44/2000. In all cases the residual aluminum was less than the permissible limits (0.2 mg/l). Concentration of sulphate and chloride ions increased by using polyinorganic coagulants, whereas the concentration of sodium increased due to the use of sodium carbonate to raise pH value. Also show that the total dissolved solids and the electrical conductivity increased due to the spiking of new materials in solution, whereas no considerable variation was observed in the concentration of calcium, magnesium and potassium.

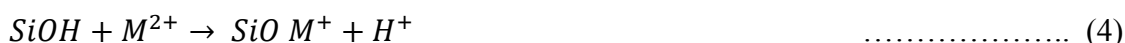
The proposed mechanism for the ion-exchange reaction on the silica surface is accomplished through the substitution of protons of the surface silanol groups by the metal ions from solution, as follows:



Most particles in water, mineral and organic, have electrically charged surfaces, and the sign of the charge is usually negative, in activated silica case, two important processes for producing this charge are considered in the following;

First, surface groups on the solid may react with water and accept or donate protons. For an oxide surface such as silica, the surface site might be indicated by the symbol  $SiOH$  and the surface site ionization reactions take place.

Second, surface groups can react in water with solutes other than protons. Again, using the  $SiOH$  surface groups of silica.



where, M= Fe, Mn, As, and Pb.



where,  $Mo^{2-} = 2F^-, 2NO_3^-,$  and  $HPO_4^{2-}$ .

These reactions of surface complex formation reactions involve specific chemical reactions between chemical groups on the solid surface (e.g., silanol groups) and adsorbable solutes (e.g., lead and nitrate ions). Surface charge is again related to solution chemistry. Where  $M^{n+}$  = metal ion with  $n+$  charge,  $(\equiv SiOH)$  = silanol group on the  $SiO_2$  surface and  $xH^+$  = number of protons released. The cation-exchange mechanism is expected with the four metal ions as the sorbent contains large amounts of silica. Also, since electrostatic attraction was possible



negatively charged adsorbent surface and positively charged metal ion species, it seems that some electrostatic forces were involved in the adsorption process (Namasivayam and Ranganathan, 1995).

#### 4. Conclusion

All coagulants under investigation were gave the removal percentages of lead below permissible limits, except for PFeCl, PFeClSi, PAIFeCl, and PAIFeClSi. All coagulants under investigation were gave the removal percentages of arsenic above permissible limits except PFeCl, PAIFeCl, and PAIFeClSi. While for the coagulants investigated gave the removal percentages of fluoride below permissible limits except PACSi and PAHSSi. The usage of inorganic polymers is suggestive as replacement technology of chemical oxidation of lead, arsenic and fluoride in one side. Polyaluminum Ferric Chloride Silicate (PAIFeClSi) is suggestive as favorable coagulants in different treatment technology. The developed rice husk coagulants are considered as a better replacement technology for ground and sewage wastewater treatment due to low cost and good efficiency in this application.

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