

Removal of Arsenic, Lead and Fluoride from Waste Water using Novel Poly Inorganic Coagulants

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Summary: The present study is a highlight to remove some dangerous pollutants such as arsenic, lead and fluoride in waste water. The treatment using novel poly inorganic coagulants. The eight novel poly inorganic coagulants were prepared, and characterized namely, poly aluminum chloride (PACl), poly aluminum chloride silicate (PAClSi), poly aluminum hydroxysulphate (PAHS), poly aluminum hydroxy sulphatesilicate (PAHSSi), poly ferric chloride (PFeCl), poly ferric chloridesilicate (PFeClSi), poly aluminum ferric chloride (PAIFeCl), and poly aluminum ferric chloride silicate (PAIFeClSi). It was found that; the maximum percentages removal of F, As and Pb ions from waste water reached 99, 97 and 98%, using PAIFeClSi, PAIFeClSi and PFeClSi, respectively. Therefore, poly inorganic coagulants impregnated with silica and considered as a good coagulant for waste water treatment due to the low cost and good efficiency in this application. Also, it will solve the problem of water shortage and to sustain non-conventional water resources.

Introduction

Heavy metals are dangerous for living organisms because of their stability, toxicity and tendency to accumulate in the environment.⁽¹⁾ The industrial wastewater is considered to be the main source of heavy metal impurities. Their purification prior to discharge into a recipient is, therefore, necessary. Iron and aluminum co-precipitation/adsorption are well-accepted processes 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⁽¹⁾.

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⁽²⁾. There are several methods for the extraction of silica from biomass.⁽³⁻⁶⁾ thermal treatment is a reasonable method for natural silica extraction. Sodium silicate, the precursor for silica production, is currently manufactured by smelting quartz sand with sodium carbonate at 1300°C.⁽⁷⁾ 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.⁽⁸⁾ 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.⁽⁹⁾ These methods usually require

a preliminary oxidation step, for the transformation of As(III) to As(V), in order to achieve efficient arsenic removal.^(10,11) As(III) oxidation is usually performed by the addition of chemical reagents, such as, potassium permanganate, hydrogen peroxide or ozone.^(12,13)

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.⁽¹⁴⁾ 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,⁽¹⁵⁾ inorganic ion exchangers are considered the most prospective because of their chemical stability and possible ability to control surface chemistry.^(16, 17)

Poly inorganic coagulants and conventional coagulants such as aluminum sulphate, aluminum chloride, ferrous sulphate ...etc is widely used in water and waste water treatment.⁽¹⁸⁻²⁴⁾

This study concerns with the comparison of a novel poly inorganic coagulants for the removal of arsenic, lead and fluoride from spiked waste water.

Experimental

Five samples of rice husk ash (RHA), three samples of sodium and eight samples of poly inorganic coagulants were prepared and characterized as conducted by.⁽¹⁹⁻²⁵⁾ The samples of novel poly inorganic coagulants, were used to remove lead, arsenic and fluoride from representative samples of waste water. To produce water quality for re-use in agricultural drip irrigation systems, where in the treatment depends on precipitation, co-agulation and adsorption techniques by poly inorganic coagulants (PIC). Each sample was mixed with 5-10 mg/L 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 As, Pb and F were measured in acidified ore samples and in the filtrate. pH-meter calibration using buffer 4, 7 and 10. Use of AAS at wavelength; 383.3, 193.7 and 211.245 nm, respectively according to (APHA, 2005)⁽²⁶⁾.

Results and Discussion

The results were recorded in Table (1) and represented in Fig. (1). The physico-chemical properties of waste water before and after treatment of lead using eight samples of poly inorganic coagulants. It was found that, the removal percentages of lead are 99, 99, 99, 99.9, 99, 94, 97 and 97% using PACl, PAClSi, PAHS, PAHSSi, PFeCl.P, FeClSi, PAIFeCl and PAIFeClSi, respectively. The maximum removal reached 98% with PAHSSi. The maximum permissible limits 0.05 mg/L according to WHO.

Table (1): Physico-chemical variations and F(I) , As(III) and Pb(II) concentrations in spiked waste water before and after treatment with different types of polyinorganic coagulants.

Co-agulants Parameters	before treatment	after treatment								Permissible limit
		PACl	PAClSi	PAHS	PAHSSi	PFeCl.P	FeClSi	PAIFeCl	PAIFeClSi	
color	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 μ 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 ⁻ 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	1
As(III) 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

Fig. (1): Variations of Pb²⁺ levels (mg/L) before and after treatment with different types of poly inorganic coagulants.

Also, Table (1) and Fig.(2) represented that the physico-chemical properties of waste water before and after treatment of arsenic using eight samples of poly inorganic 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 97% with PFeClSi,PAIFeCl and PAIFeClSi. The maximum permissible limits 0.05 mg/L according to WHO.

Fig. (2): Variations of F¹⁻ levels (mg/L) before and after treatment with different types of poly inorganic coagulants.

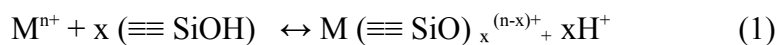
In case of fluoride, Table (1) and Fig. (3) indicated that the physico-chemical properties of waste water before and after treatment of fluoride using eight samples of poly inorganic coagulants. It was found that, the removal percentages of fluoride: 94, 13, 85, 17, 67, 87, 27 and 99% using PACl, PAClSi, PAHS, PAHSSi, PFeCl.PFeClSi, PAIFeCl, and PAIFeClSi respectively. The maximum removal reached 99% with PAIFeClSi. The maximum permissible limit is 0.8 according to WHO therefore, the fluoride concentrations of studied area after treatment are within normal limits.

Fig. (3): Variations of As(III) levels (mg/L) before and after treatment with different types of poly inorganic coagulants.

PAIFeCl and PAIFeClSi is the superior poly in-organic coagulant copolymer may be attributed to the co-polymers of Si (IV), Al (III) and Fe (III).⁽²³⁾. The total dissolved solids, it increased due to the formation of new spiked ions. No variations of pH occurred and all the values after treatment are within the 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 was increased by using poly inorganic coagulants, whereas the concentration of sodium increased due to the use of sodium carbonate to raise pH value. Table (1) shows 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

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 discussion:

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, $\text{MO}^{2-} = 2\text{F}^{1-}, 2\text{NO}_3^{1-}, \text{and } \text{HPO}_4^{2-}$

These surface complex formation reactions involve specific chemical reactions between chemical groups on the solid surface (e.g., silanol groups) and absorbable solutes (e.g., lead and nitrate ions). Surface charge is again related to solution chemistry where M^{n+} = metal ion with n+ charge, $(\equiv \text{SiOH})$ = silanol group on the SiO_2 surface and $x\text{H}^+$ = number of protons released. The cation-exchange mechanism is expected with the four metal ions as the sorbent contains large amounts of silica. The 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. ⁽²⁷⁾

From above mentioned results we can concluded that all coagulants under investigation were succeed the removal of fluoride below the permissible limits except PACSi and PAHSSi. Also, all coagulants under investigation were succeeding the removal of lead below permissible limits, except for PFeClSi. In addition to, the coagulants under investigation were removal of arsenic but above permissible limits except for PFeCl, PAIFeCl and PAIFeClSi. The usage of inorganic polymers is

suggestive as replacement technology of chemical oxidation of lead, arsenic and fluoride in one side. Poly aluminum 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 waste water treatment due to low cost and good efficiency in this application.

References

1. SenGupta Arup, K., Environmental Separation of Heavy Metals. New York, Washington. (2002)
2. Protor A., Shultz J., Kalapathy U., Bioresource Technology, 73: 257-264,(2000).
3. Garza C., and Riveros H., J. Crys. Grow. 75:126-131, (1986).
4. Yalcin N., and Sevic V., Ceram. Inter., 27: 219-224., (2001).
5. Holtza D., Kuhn I., and Della V. P., Mat. Lett., 57:818-821,(2002).
6. Kumar J., Krishnarao R. V., and Subramanyam T., J. Euro.Cem. Soc., 21: 99-104, (2001).
7. Foletto E., Gratieri, and Hadlich L., Mat. Res., 9, 3 335-338,(2006).
8. Krishnarao, R. V., Kumar T. J., Mahajan Y. R., J. Eur. Ceram. Soc., 181: 47-152, (1998).
9. Kartinen, E.O., and Martin, C.J., "An overview of arsenic removal Processes", Desalination, 103, 79–88 (1995).
10. Jekel, M.R., "Removal of arsenic in drinking water treatment", New York, Wiley-Int., 119–130 (1994).
11. Viraraghavan, T., Subramanian, K.S., and Aruldoss, J.A., Wat. Sci. Technology, 40 (2), 69–76 (1999).
12. Molnar, L., Vircikova, E., and Lech, P., Hydrometallurgy, 35, 1–9, (1994).
13. Kim, M.J., J. Sci. total envir., 247, 71–79, (2000).
14. Patterson, J.W., "Industrial Waste Water Treatment Technology, Science Publishers", New York (1997).
15. Bellack, E., and Am., J., Journal of the American Water Works Association, 63, 454,(1971).
16. DeMarco, J.M., SenGupta, A.K., and Greenleaf, J.E., Water Research, 37, 164 (2003).
17. Wasay, S.A., Tokunaga, A., and Park, S.W., Separation Science. Technology, 31, 1501-1514, (1996).
18. Salah A. Abo-El-Enein, Mamdouh A. Eissa, Abdel hakim A. Diafullah, Magdy A. Rizk, Fathy M. Mohamed, J. Haz. Mat., 172: 574–579, (2009).
19. Salah A. Abo-El-Enein, Mamdouh A. Eissa, Abdel hakim A. Diafullah, Magdy A. Rizk, Fathy M. Mohamed, J of Haza. Mat., 172:574–57, (2011).
20. Jusoh A. B., Cheng W.H., Low W.M., Nora A., and Megat M. J., desalination, 182:347-353,(2005).
21. Kaur, S., Walia, T., and Mahajan R.K., Eng. Sci., 7: 83-90,(2008).
22. Munter R., Ojaste H., and Sutt J., J. of Env. Engi., 131:1014–1020,(2005).
23. Yu-li Y., Yue-zhang, and Si-zhen L., J. Zhejiang Univ. Science A., 340 :34 -47, (2006) .
24. Zacaria R., Envir. Sci. Tech., 36: 2073 – 2067 (2002).
25. Fathy. M. Mohamed, Treatment of some water pollutants using novel sorbent materials. P.h.D. Thesis, Faculty. Science. Ain Shams University., (2009).

26. APHA, AWWA, WEF, Standard methods, 19th ed. Washington, DC, (2005).
27. Namasivayam, C., and Ranganathan, K., Wat. Res., 29:1737 – 1744, (1995).