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Removal of Pb and Zn from industrial effluent using humic acid

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Abstract

The present work was conducted to remove Pb and Zn from industrial effluents by coagulating the ions with humic acids. Seven types of effluents were collected from textile, tannery and pharmaceutical industries. Two commercially available humic acids one in a liquid state and another one in a semi-solid state, humic acid extracted from peat were used to remove Pb and Zn from industrial effluents as well as synthetic waste water. Optical property, carbon concentration and coagulation threshold of humic acids were studied. Same carbon concentration (1×10^{-5} g L^{-1}) of all the sources was maintained at neutral pH. The values of water soluble Pb and Zn in effluents were 0.000 - 0.0711 μg/mL and 0.002 - 0.024 μg/mL, respectively. Results indicated that liquid humic acid having E4: E6 ratio of 1.2 removed 100% Pb and Zn only from pharmaceutical effluent whereas humic acid extracted from peat having E4: E6 ratio of 3.18 completely (100%) removed these metals from pharmaceutical and tannery effluents. Semi-solid humic acid having the lowest E4: E6 ratio of 1.07 did not form coagulation with the metals. The performance of humic acid extracted from peat was better than that of commercially available humic acids.

Keywords : Industrial effluents; Lead; Zinc; Humic acids

Introduction

Heavy metals such as lead, zinc and so on are extensively used in several industries including textile, tannery, pharmaceuticals, mining, metallurgical, electronic, and metal finishing and thereby their pollution occurs directly by effluent outfalls from industries, refineries, and waste treatment plants and indirectly by the contaminants that enter the water supply from soils and/or ground water systems and from the atmosphere via rain water (Vijayaraghavan and Yun, 2008).

Conventional techniques have been employed for the treatment of lead, zinc and other metal bearing industrial effluents, which usually include precipitation, coagulation, adsorption, ion exchange, membrane filtration, electrochemical technologies (Xia and Liyuan, 2002) and bio-sorption (Malik, 2004). These techniques are expensive, not environment friendly and usually dependent on the concentration of the waste which are ineffective in diluted solutions, difficult to use on a large scale (Xia and Liyuan, 2002). So, the research on special coagulant became a hot focus (Li *et al.,* 1984).

Some researchers have reported that organic materials are important determinant of trace metal adsorption because of their high surface area (Sigg, 1985). Cooper and Harris (1974) suggested that significant fractions of lead have been reported to be associated with organic material in natural aquatic environment.

Humic acids are ubiquitous in the environment and comprise the most abundant pool of non-living organic matter (Hedges and Oades, 1997). Their peculiar feature is polyfunctionality, which enables them to interact with metal ions (Perminova and Hatfield, 2005). Some studies have shown that humic acids are capable of forming stable complexes with heavy metals of polluted soil (Adekulne *et al*., 2007; Boruvka and Drabek, 2004). The oxygen containing groups (carboxylic and phenolic) and the hydrophobic nature of humic acid affect metal sorption and the humic acids bound more Pb (0.911 mmol/g) than Cd (0.237 mmol/g) (Adekulne *et al.,* 2007). Because of their ability to complex metal, different humic acids are selected for removal of Pb and Zn from industrial effluents. This work was carried out to evaluate the efficiency of humic acids of different properties to remove Pb and Zn from different sources of waste water.

Materials and methods

(a) Collection and analysis of humic acids

Three different sources of humic acids viz commercially available liquid and semi-solid humic acid and also humic

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acid extracted from peat were used for removal of Pb and Zn. Carbon content of humic acids was determined by Tyurin's method (1931, 1936); coagulation threshold was observed by the method cited by Kononova (1966). The optical density at 465 nm and 665 nm was determined by a Shimadzu Spectrophotometer UV-120-02. For removal of Pb and Zn, the pH and carbon concentration of the humic acids were adjusted at 7 and 1×10^{-5} g /L, respectively. Definite carbon concentration of humic acids was selected based on coagulation threshold of humic acid (Kononova, 1966).

(b) Removal Pb and Zn from synthetic waste water using humic acids

Different concentrations (20 μg/mL - 40 μg/mL) of individual Pb and Zn solution and their combination were mixed with humic acids into various tubes to remove these metals. The completion of coagulation was observed and the time required was recorded. After coagulation of pure metal solutions with humic acids, the highest (40 μg/mL) and lowest (20 μg/mL) concentrated individual and mixed metal solutions were selected. Then the selected metal solutions were filtered with Whatman No.42 and the remaining metals (Pb and Zn) were determined by Atomic Absorption Spectrophotometer.

(c) Analysis of industrial effluent and removal Pb and Zn from industrial effluent using humic acids

Seven effluents were collected from textile (Savar, Dhaka), tannery (Hazaribagh, Dhaka) and pharmaceutical (Tongi, Gazipur) industries. For the present study, spot sampling was

mixed in ratio of 1:1 into different tubes. Then the tubes were shaken well and the coagulation time was observed. After the complete coagulation, the solution was filtered and then the metals present in filtrate were determined by Atomic Absorption Spectrophotometer.

Results and discussion

(a) Analysis of humic acids

The optical parameter, E_4/E_6 ratio expresses molecular condensation. Scheffer (1954) has shown that the ratio of the extinction E at the wavelengths 465 nm and 665 nm (the so-called E_4/E_6 ratio) is independent of the concentration of carbon in solution and by reflecting the steepness of the spectrophotometric curve, is a characteristic of humic acid. Data on E_4/E_6 ratio of humic acids are presented in Fig. 1. The E_4/E_6 ratio values were close to each other in case of liquid and semisolid humic acids. The value was highest (3.18) in humic acid of peat origin followed by liquid (1.2) and the lowest value (1.07) was found with semi-solid humic acid. According to Chen *et al* (1977), the E_4/E_6 ratios are a parameter inversely related to the molecular dimension. Therefore it can be said from the E_4/E_6 ratios that the molecular weight of different humic acids is in the following order

Semi-solid Humic Acid > Liquid Humic Acid > Humic Acid Extracted from Peat

On the other hand, Kononova (1966) has found that a value ≥ 5.0 indicates a reduced hydrophobic structure while that ≤5.0 suggests an increased hydrophobic structure. So, the
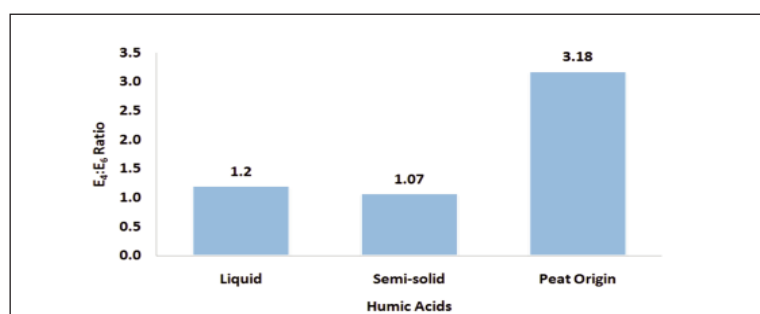

Fig. 1. E_4/E_6 ratio of humic acids.

done. Approximately 2 litre of different effluents was collected in plastic bottles. Total Pb and Zn were extracted by digesting the water sample with nitric acid (HNO_3). Total and water soluble Pb and Zn were measured from digested and raw water sample by Atomic Absorption Spectrophotometer (Model No. AA 240-Varian). To treat effluents, humic acids and different types of effluents were

values of E_4/E_6 ratio obtained from the study indicated that the molecules were increased hydrophobic.

Requirement of time as well as $CaCl_2$ concentrations for coagulation of humic acids were investigated by Kononova (1966). Data presented in Table I show the coagulation threshold values obtained with humic acids of different ori-

gin. The coagulation of liquid humic acid was rapid (1 hour was required for 3 meq CaCl$_2$/6 ml) due to its larger molecular size whereas slow coagulation (4 hours was required for 100 meq CaCl$_2$/6 ml) found with humic acid of peat origin because of its smaller molecular size. Humic acids were used for removal of Pb and Zn from synthetic waste water as well as seven collected effluents.

it was found in Table III that Zn removal from the highest concentration of Zn (40 µg/mL) ranged from 47% to 82% and the time duration for this removal varied between 1 and 7 days. Commercially available semi-solid humic acid removed highest amount of Zn and then liquid humic acid. After 7 days, it was observed that peat originated humic acid

Table I. Coagulation threshold of humic acids.

Humic Acid	Time required for coagulation (hour)	CaCl$_2$ concentration requirement for coagulation (meq/6 ml)
Liquid	1	3
Semisolid	6	6
Peat Origin	4	100

(b) Removal Pb and Zn from synthetic waste water using humic acids

Lead and zinc solution of different concentrations were treated with different humic acids to observe their coagulation capacity. Removal efficiency (%) and the time required for removal of Pb and Zn from individual solution by humic acids are shown in Table II and Table III, respectively. Data presented in Table II and III indicated that Pb and Zn were removed from the solution by applied humic acids. It was found that Pb removal from the highest concentration (40 µg/mL) ranged from 85% to 95% after 2 hours and lowest concentration (20 µg/mL) ranged from 82% to 94% after 7 days by the application of all humic acids. Humic acid, extracted from peat removed maximum amount of Pb followed by liquid humic acid and then semi-solid humic acid. Humic acids of different origins showed considerable variation in amount removed and time of Pb removal. Similarly,

did not precipitate Zn from the known concentration of solution. Liquid humic acid removed 70% Zn from 20 µg/mL of Zn solution after 2 days. Humic acids obtained at liquid and semi-solid states showed considerable variation in amounts and time of Zn removal.

Humic acids were added to the mixed pure solution of two different heavy metals (Pb and Zn) and their coagulation capacities were observed. Mixing effects were found to influence coagulation of metal ion. Removal efficiency (%) and the time required for removal of Pb and Zn from mixed solution by humic acids are shown in Table IV and Table V, respectively. Data presented in Table IV revealed that lead removal efficiency of the humic acids varied considerably due to application of different sources of humic acids. Humic acids of all the sources removed Pb from the highest concentrated mixed solution and values ranged between 75% and 96% whereas the removal range was 85% to 95% in case of

Table II. Percent value and time required for removal of Pb from pure solution by humic acids.

Humic Acid	Removal of Pb from 40 µg Pb/mL		Removal of Pb from 20 µg Pb/mL	
	%	Hours	%	Days
Liquid	90	2	87	1
Semi-solid	85	2	82	7
Peat Origin	95	2	94	7

Table III. Percent value and time required for removal of Zn from pure solution by humic acids.

Humic Acid	Removal of Zn from 40 µg Zn/mL		Removal of Zn from 20 µg Zn/mL	
	%	Days	%	Days
Liquid	47	1	70	2
Semi-solid	82	7	0.00	7
Peat Origin	0.00	7	0.00	7

pure individual Pb solution (Table II). The performance was better at the lowest concentration with liquid humic acid (99% Pb was removed from 20 µg/mL of mixed solution). Data presented in Table V indicated that Zn removal value from the highest concentration of mixed solution ranged from 75% to 86% from all sources of humic acids although only liquid and semi-solid humic acid precipitated Zn from pure Zn solution (Table III). At the lowest concentration, no humic acid participated in coagulation except liquid humic acid which removed 83% Zn within 2 days.

100% Pb from all effluents except effluent - 2 (textile origin) where the removal value of Pb was 1.1%. Semi-solid humic acid did not participate in Pb removal from all effluents. Like Pb, Water soluble Zn content in effluents varied from 0.002 to 0.024 µg/mL (Table VI). Table VIII represents percent value and time required for Zn removal from effluents by humic acids. Data presented in Table VIII indicated that Zn was removed from the solution by applied humic acids. Liquid humic acid removed Zn from effluent - 4 of textile origin and effluent - 5 of pharmaceutical origin and the

Table IV. Percent value and time required for removal of Pb from mixed solution by humic acids.

Humic Acid	Removal of Pb from 40 µg mixed metals/mL		Removal of Pb from 20 µg mixed metals/mL	
	%	Days	%	Days
Liquid	96	1	99	2
Semi-solid	96	5	0.00	7
Peat Origin	75	7	0.00	7

Table V. Percent value and time required for removal of Zn from mixed solution by humic acids.

| Humic Acid	Removal of Zn from 40 µg mixed metals/mL		Removal of Zn from 20 µg mixed metals/mL	
	%	Days	%	Days
Liquid	85	1	83	2
Semi-solid	86	5	0.00	7
Peat Origin	75	7	0.00	7

(c) Analysis of industrial effluent and removal Pb and Zn from industrial effluent using humic acids

Among the seven collected samples, effluents 1 to 4 were of textile origin, effluent 5 was collected from pharmaceutical, and effluents 6 and 7 were obtained from tannery industries. Data represented in Table VI show the total content and water soluble fraction of Pb and Zn present in effluents. Values of water soluble Pb and Zn concentration in this experiment were well below the acceptable limit of irrigation water standard of DoE (1997).

Water soluble Pb in effluents varied from 0.014 to 0.071 µg/mL (Table VI). Effluent - 3 of textile origin did not contain any water soluble Pb. Table VII represents percent value and time required for Pb removal from effluents by humic acids. Data presented in Table VII indicated that Pb was removed from the effluents by applied humic acids. It was found that liquid humic acid removed maximum (100%) and minimum (15.5%) amounts of Pb from effluent - 5 of pharmaceutical origin and effluent - 4 of textile origin, respectively. Humic acid extracted from peat successfully removed

removal percent values were 12.3 and 100, respectively. Humic acid from peat origin completely removed 100% Zn from all effluents except effluent - 1 and effluent - 4 of textile origin. Peat originated humic acid removed 25.6% and 32.6% Zn from effluent - 1 and effluent - 4 which was collected from textile industries. Semi-solid humic acid did not remove Zn from the seven collected effluents.

From our studies of metal ions complexation with humic acids, it was found in the following trend

$$Pb(II) > Zn(II)$$
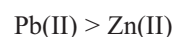
Of the two divalent metal ions examined, Pb has a high ionic strength and a great affinity to form Pb-HA(Humic Acid) complex than Zn (Plaza *et al.,* 2006). Pb(II) (the only non-transition metal ion) was found to form more stable complex with the oxygen carrying donor groups of humic acid (Millward, 1995; Baker and Khalili, 2007). The above trend is also consistent with the study of Rashid (1985).

Different treatment technologies are employed for removal of heavy metals. Though chemical precipitation is a widely

Table VI. Water soluble and total content of Pb and Zn in effluents.

Effluent	Water Soluble Pb (µg/mL)	Total content of Pb (µg/mL)	Water Soluble Zn (µg/mL)	Total content of Zn (µg/mL)
1	0.032	0.039	0.014	0.320
2	0.071	0.076	0.002	0.047
3	0.000	0.021	0.006	0.066
4	0.014	0.022	0.024	0.045
5	0.027	0.027	0.002	0.150
6	0.020	0.064	0.003	0.083
7	0.060	0.067	0.005	0.253

Table VII. Percent value and time required for removal of Pb from effluents by humic acids.

Humic Acid	Effluent-1		Effluent-2		Effluent-4		Effluent-5		Effluent-6		Effluent-7	
	%	Days	%	Days	%	Days	%	Days	%	Days	%	Days
Liquid	NC[1]	1	NC[1]	2	15.5	10	100	1	NC[1]	2	NC[1]	3
Semi-solid	NC[1]	10	NC[1]	10	NC[1]	10	NC[1]	10	NC[1]	10	NC[1]	10
Peat Origin	100	1	1.1	2	100	2	100	1	100	2	100	3

[1]Not coagulated

Table VIII. Percent value and time required for removal of Zn from effluents by humic acids

Humic Acid	Effluent-1		Effluent-2		Effluent-3		Effluent-4		Effluent-5		Effluent-6		Effluent-7	
	%	Days	%	Days	%	Days	%	Days	%	Days	%	Days	%	Days
Liquid	NC[1]	1	NC[1]	2	NC[1]	3	12.3	10	100	1	NC[1]	2	NC[1]	3
Semi-solid	NC[1]	10	NC[1]	10	NC[1]	3	NC[1]	10	NC[1]	10	NC[1]	10	NC[1]	10
Peat Origin	25.6	1	100	2	100	3	32.6	2	100	1	100	2	100	3

[1]Not coagulated

used method, it produces large amounts of concentrated toxic sludge wastes, which create disposal problems. There are concentration limits of 100 mg/L up to which the precipitation method is economical (Ceribasi and Yetis, 2001). On the other hand, humic acid was effective to remove Pb and Zn from their low concentration of solutions. It produced low amounts of sludge and the removal percent was highest (100) for most of the effluents. Ionic strength and pH of the medium is an important factor for metal complexation (Liu and Gonzalez, 2000). For removal of heavy metals, pH plays a significant role as charge development of humic acids depends on pH. Hydrophobic nature of humic acid also affects metal sorption (Adekunle *et al.,* 2007). The uptake of metal into the exchangeable fraction may be explained in terms of dehydration of the cation and the relaxation of the humic acid layer (Baker and Khalili, 2007). Variation of sorption capacity of metal ions with humic acids also occurred when the solution of metal was pure or mixed. However, mixing effects of these metals increased coagulation capacity of humic acids with metals in effluents as well as mixed metal solutions. As seven selected effluents had different pH values and ionic strength differed for each metal, specific metal removal varied for all the effluents. Due to the presence of relevant anions and particulate concentration (turbidity), the performance of humic acids was quite well for removing the trace metals in effluents. The performance of humic acid from peat origin in forming metal-organic complex was better than that of other sources of humic acid. The behavior of humic acids was peculiar because of their unknown structure and due to the presence of different functional groups. It is important to note that all the humic acids were not equally effective for removal of all the studied metals. However, to ensure optimum and systematic application, an expanded knowledge base is needed concerning interactions between humic acids and metals.

Conclusion

The present study indicated that humic acid has effects on the removal of Pb and Zn. The effects were controversial depending on the types of humic acids. On the basis of the study it should be noted that liquid humic acid completely removed Pb and Zn from pharmaceutical effluent (effluent - 5), semi-solid humic acid removed variable amounts of Pb and Zn only from synthetic waste water and humic acid extracted from peat was successfully removed all Pb and Zn from pharmaceutical (effluent - 5) and tennary (effluent - 6 and effluent - 7) effluents. Therefore, the performance of peat originated humic acid for removal of Pb and Zn in effluents was better than that of commercially available humic acids. Compared to effluents, humic acids effectively removed these metals from their high concentrated synthetic waste water. Thus it can be stated that effluents can be treated with humic acids even with elevated concentrations.

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