Detection of Heavy Metal Ions from Water using Conventional Chelating Agents (Citric Acid And EDTA) in and around Murtizapur Region

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Abstract

Heavy metals are toxic to human and also cause water and soil pollution. Contamination of freshwater resources continues due to domestic effluents, industrial discharges and use of chemicals in agriculture. The objectives of this study were: to Laboratory experiments were carried out to examine the effects of chelating agents on heavymetal extraction from water sample in and around Murtizapur region. One of the most helpful elements in chelation therapy is an ingredient called EDTA (ethylenediaminetertraacetic acid). EDTA is a naturally safe chemical – less toxic to the system than aspirin – that passes through the body, taking toxins and heavy metals out with it as a green chemistry.Ethylenediamine tetra acetate (EDTA), citric acid (CA) was tested in different concentrations each: 0.01,0.05, 0.1 mg/l, respectively.Solubilisation of heavy metals arsenic, cadmium,pb,Cu and Zn was observed for EDTA and citric acid. It was observed that solubilized metal levels were positively related to the chelating agent concentration.

Keywords - heavy metal, chelating agent, EDTA.

Introduction-

An excess level of heavy metals are exposed into environment, for example by industrial waste and fertilizers causes serious concern in nature as they are non- biodegradable and accumulate at high levels. Heavy metal pollution is a global problem, although severity and levels of pollution differ from place to place (1).The common heavy metals like Cd, Pb,Cu Co, and Zn etc. are phytotoxic at both low concentration as well as very high concentration are detected in waste water. If these metals are presented in sediments then thesereach the food chain through plants and aquatic animals (2).

In recent years there has been increasing need for estimating effect done by contamination of water.In this regard, there is growing interest in the use of Chelating agents like Ethylene diamine tetra acetate (EDTA), citric acid (CA) for detecting heavy metal ions, because of their sensitivity and selectivity (3).Solubilisation of heavy metals arsenic cadmium, cobalt, Cu and Zn was observed for EDTA and citric acid. It was observed that solubilized metal levels were positively related to the chelating agent concentration.The purpose of this study was optimization of Experimental conditions for selected heavy metals (Zn, Cu, Cd, As and Pb) extraction from wastewater sludge usingaqueous solutions of EDTA (ethylenediaminetetraacetic acid) and citric acid at differentconcentration.

2. Materials and Methods-

2.1. Samples, sampling techniques-

In and around Murtizapurregion areas where the monitoring of heavy metal contamination was ongoing for many years were choosen to collect different types of samples for my investigations.Where there is a pond is formed near the college area due to deeply dining and some bricks industries around their and an ongoing monitoring has been in place since 2011.

Surface samples were gathered at depths ranging from 4 to 12 inches. Equipment's used for collecting the samples were cleaned according to EPA "Standard Cleaning Procedures", prior to use for each sample a separate a plastic bottle of one liter was used. In order to preserve the water sample, the plastic bottle was sealed immediately after sampling. Representative samples were collected from areas corresponds to low, medium and high concentrations of metals contamination in fresh water.The samples were air-dried under laboratory condition (temperature about 25ºC)

2.2 Chemical -Analytical grade chemicals viz: acetic acid, ammonium acetate, citric acid, hydroxylamine hydrochloride and EDTA were obtained from quligenchem Ltd. and used without further purification.

The material was analyzed for water content, dry mass, pH, ignition residual and ignition losses as well as selected heavy metals (Zn, Cu, Cd, As, Pb) content. All analysis was carried out in triplicate and results given are mean values. Water content, dry mass, ignition residual, ignition losses and pH were measured according to standard methods (4-8). A total content of the analyzed heavy metals(Zn, Cu, Cd, As, Pb) in waste water sampleS1,S2,S3, and S4was determined and Content of heavy metals was detected by atomic absorption spectrometry (model -POEMS III USA, spectrometer).

2.3 Extraction procedure-Efficiency of EDTA and citric acid solutions for selected heavy metals removal was determined using single step washing tests. Extraction of waste water sample in 25ml for S1, S2, S3, and S4 was carried out with 50 ml EDTA solution at concentration (Deionized water), 0.010,0.050, 0.100 M and citric acid solution with concentration (Deionized water), 0.010,0.050, 0.100 M. Samples were shaken for 6 hours, thenthe extracts were filtered through a filter paper and finally extracts were analyzed for heavy metals content by atomic absorption spectrophotometry.To study the quantitative elutionof metal ions were performed by adding 10g resin cation exchange resin Purolite C100 ina 100 ml solution waspassed through the column at a rate of 1 ml/min, resinbed (1.4 x 12.9 cm). The resin was washed with 50ml, of water and then the M (II) was eluted with 200ml of different eluents. The latter include 0.01 MEDTA and citric acid at different pH's. In eachcase the elation rate was 1 ml/min and the eluantingagent was collected in 10 ml. The elution constant, E,for each eluting agent is calculated, from therelation (10).

$$E = d.A/V \text{ ----------} \quad (1)$$

Where V is the volume of eluent, which is required to displace M(II) under essentially equilibrium conditions through a distance d cm in a column of cross sectional area A cm^2, the free column volume .

Results and Discussion-

1) Stability Metal ion complex formation-

The presence of chelating agent such as Ethylenediaminetetraacetic acid, EDTA in solution Considerably changes the metal ion sorption ability. In the reaction between EDTA and metal ion, donor atoms of EDTA molecule shield metal ion as a substitute for six water molecules. It means the transition from aqua complex to EDTA metal complex. The shape of metal complex with EDTA becomes octahedral ($sp3d^2$ hybrid orbit) since six donor atoms shield one metal ion. An asterisk attached oxygen and nitrogen (O. and N.) means a donor atom with unshared electron pair, which can coordinate a metal ion. Each complex has different valency against pH because hydrogen of aqua ion ($–OH_2$) or carboxylate ion (–COOH) is removed as pH increases.Thus, EDTA reacts with metal ions, and forms a metal EDTA complex compound as the equation below (10).

$$M^{2+} + EDTA \leftrightarrow M\text{-}EDTA \text{-------(2)}$$

2) Quantitative elution of zinc ions.

Single step extraction procedures indicated different behavior of metals in solutionsof EDTA and citric acid. Wide variations in metal removal efficiency were depending onboth the considered metal and the agent used for extraction.

The amount of Zn in wastewaterSample was the highest among investigated metals and concentrations obtained in particular extractants were the highest . As concentration of EDTA increased, the concentration of Zn in eluateincreased reaching the highest value 248.20 mg/dm^3in 0.050 M EDTA. Relationshipbetween zinc concentration changes and EDTA concentration is almost linearand the further increase of Zn content is stopped only by limited solubility of EDTAin water. Thus optimal concentration of EDTA for removal of zinc from the studiedwastewater Sample was determined at the level of 0.050 M. Efficiency of 0.050 M EDTAfor zinc extraction (calculated assuming Zn concentration in eluate and total metal contentwastewater Sample) was equal to 72%.

Similarly Zn concentration in eluate versus concentration of citricwas similar as EDTA concentration. For citric acid solutions from 0.010 Mup to0.100M the relationship is nearly linear and the concentration of zinc changesfrom 0.010M to 310.0 mg/dm^3. For higher concentration of citric acid, the processof metal extraction reached equilibrium and the concentration of zinc was equal340.0 and 380.0 mg/dm3 in 0.050 and 0.10 M citric acid, respectively. Optimalconcentration of citric acid for zinc extraction was 0.100 M, and related efficiency ofcitric acid was 94%.

3) Quantitative elution of Cu, Cd, As and Pbions–

1) Similarly to the behavior described for zinc, the lowest values of concentration were obtained in water sample (80, 85, 30, and 60 mg/dm^3 for Cu, Cd, As andPbrespectively) for 0.010M EDTA concentration.Calculated efficiencies for optimal concentration of0.010M EDTA solution were 54, 34, 12 and 22% for Cu, Cd, As and Pb, respectively.
2) Similarly to the behavior described for zinc, the highest values of concentration were obtained in water sample (210, 180, 90, and 120 mg/dm3 for Cu, Cd,As and Pb respectively) for 0.050M EDTA concentration. Calculated efficiencies for optimal concentration of 0.050M EDTA solution were 70, 68, 48and 62% for Cu, Cd, As and Pb, respectively
3) But thebehavior were different for 0.100M EDTA concentration were obtained in water sample (200, 170, 95, and 120 mg/dm^3 for Cu, Cd, As and Pbconcentration respectively). Calculated efficiencies for optimal concentration of 0.100M EDTA solution were 68, 65, 42 and 74% for Cu, Cd, As and Pb, respectively.
4) Similarly to the behavior described for zinc, the lowest values of concentration were obtained in water sample (60, 55, 20, and 40 mg/dm^3 for Cu, Cd, As and Pb respectively) for 0.010Mcitric acid concentration. Calculated efficiencies for optimal concentration of 0.010M citric acid solution were 52, 33, 11 and 24% for Cu, Cd, As and Pb, respectively.
5) Similarly to the behavior described for zinc, the lowest values of concentration were obtained in water sample (320, 215,60, and 98 mg/dm3 for Cu, Cd, As and Pb respectively) for 0.050M citric acid concentration. Calculated efficiencies for optimal concentration of 0.050M citric acid solution were 82, 70, 32 and 52% for Cu, Cd, As and Pb, respectively.
6) Similarly to the behavior described for zinc, the lowest values of concentration were obtained in water sample (380, 265, 80, and 120 mg/dm3 for Cu, Cd, As and Pb respectively) for 0.100M citric acid concentration. Calculated efficiencies for optimal concentration of 0.100M citric acid solution were 88, 75, 38 and 68% for Cu, Cd, As and Pb, respectively

The studied wastewater sample was characterized at 5.2pH.The total content of heavy metals in wastewatersample was relatively high are given in Table 1,2 and 3. Theconcentration mg/dm^3 for zinc, copper, cadmium, arsenic and lead, respectively. The order of metal content in sampleS1, S2, S3, and S4 wereZn> Cu > Cd>Pb>As. Especially large concentration of zinc and copper, classified the analyzed sample S3, and S4 as potentially hazardous material.

Studied metals removals from wastewater sample werein the order: Zn >Cu > Cd >Pb>Asusing 0.0500 M EDTA. For the same concentration of citric acid theobtained order was: Zn > Cu >Cd >Pb> As. The highest efficiencies were observed for 0.1000 M citric acid and reached about 94% for Zn, 88% for Cu, 75% for Cd, 68% for Pb and 38% for As. The mobility of zinc, cadmium and copper was higher than the

mobility of lead and arsenic. Extraction efficiencies of various metals, presented in the literature, are different (10, 11) independently of an extractants type. EDTA and citric acid efficiencies for metals removal, determined previously.

Table (1). Values of Eluting for different metal ions in the presence of 0.01M EDTAand 0.01M citric acid at, 5.2pHthe concentration of metal at 25ºC ± 0.1ºC.

Waste water Sample	Ea mg/dm3									
	Zn (II)		Cu(II)		Cd(II)		As(II)		Pb(II)	
	EDTA	Citric	EDTA	Citric	EDTA	Citric	EDTA	Citric	EDTA	Citric
S1	212	302	78	58	82	52	32	26	44	32
S2	220	304	76	56	84	54	32	24	48	30
S3	210	306	78	59	83	56	36	24	55	32
S4	222	310	80	60	85	55	30	20	60	40

Table (2). Values of Eluting for different metal ions in the presence of 0.05M EDTA and 0.05M citric acid at 5.2 pH's, the concentration of metal at 25ºC ± 0.1ºC.

Waste water Sample	Ea									
	Zn (II)		Cu(II)		Cd(II)		As(II)		Pb(II)	
	EDTA	Citric	EDTA	Citric	EDTA	Citric	EDTA	Citric	EDTA	Citric
S1	228	332	206	312	162	208	88	56	112	92
S2	230	334	208	316	168	206	83	58	114	94
S3	234	336	204	314	172	211	84	54	116	96
S4	248	340	210	320	180	215	90	60	120	98

Table (3). Values of Eluting for different metal ions in the presence of 0.10M EDTA and 0.10M citric acid at 5.2 pH's, the concentration of metal at 25ºC ± 0.1ºC.

Waste water Sample	Ea									
	Zn (II)		Cu(II)		Cd(II)		As(II)		Pb(II)	
	EDTA	Citric	EDTA	Citric	EDTA	Citric	EDTA	Citric	EDTA	Citric
S1	230	374	186	342	162	264	91	71	112	111
S2	232	368	186	348	164	268	92	74	114	113
S3	228	372	184	344	168	263	94	76	116	114
S4	232	380	200	380	170	265	95	80	120	120

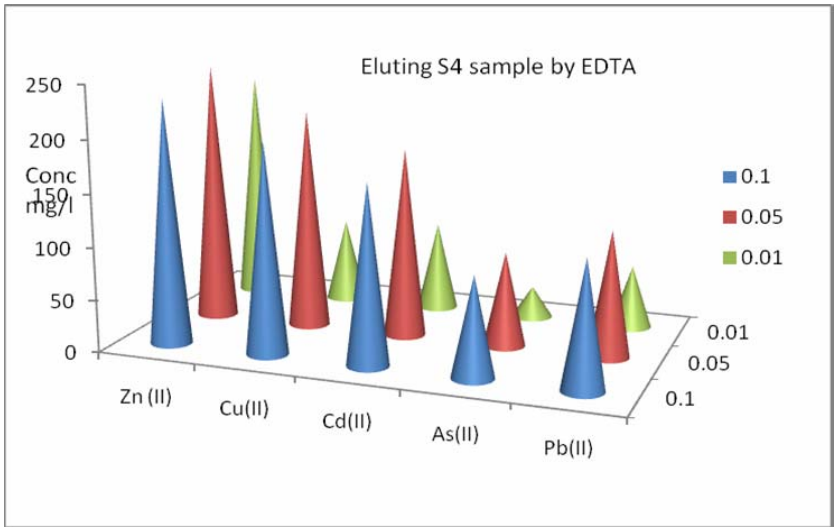

Fig-1 Eluting S4 sample by different Conc. Of 0.01, 05 and 0.1M EDTA

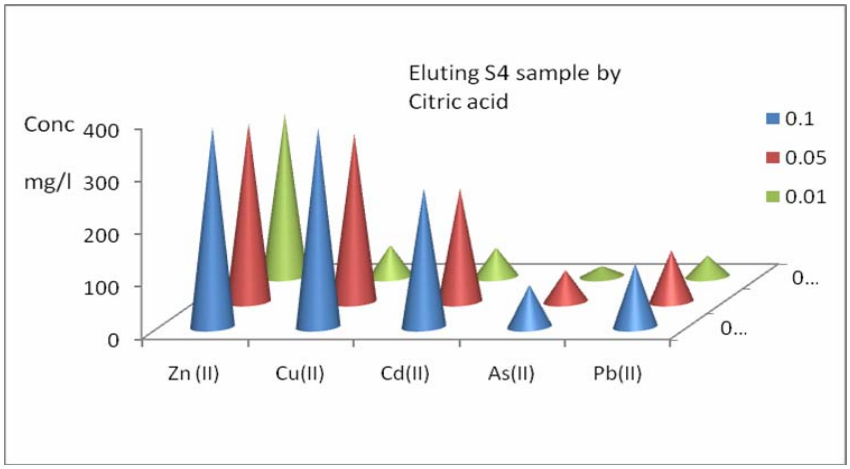

Fig-1 Eluting S4 sample by different Conc. of 0.01, 05 and 0.1M Citric acid.

Conclusions-

The studied waste water sample contained a relatively high concentration of zinc, copper and cadmium and could be environmentally hazardous. Both analyzed chelators: EDTA and citric acid were efficient for selected heavy metals removal from waste water sample . Removal of analyzed metals was dependent on the concentration of extracting agent and raised with increasing concentration of chelators. The results of Experimental tests performed at different chelators concentrations show that Citric acids was more effective with respect to EDTA in removing zinc and copper but EDTAwas more effective for cadmium, arsenic and lead removal from the waste water sample.

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