



## Effective removal of heavy metal ions from a binary mixture by adsorption on activated coconut shell carbon using complexing agent

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### ABSTRACT

Simultaneous removal of Cu(II) – Zn(II) ions in the presence and absence of complexing agent was studied by batch adsorption techniques. The activated carbon used in the study was Coconut Shell Carbon (CSC) and the complexing agent, disodium salt of Ethylene Diammine Tetra Acetic acid (EDTA). Characterisation of the treated and untreated CSC was carried out using Infrared spectroscopy (IR), Thermogravimetry (TG) and Atomic Absorption Spectroscopy (AAS). The metal ion concentration in the adsorption study was determined complexometrically and confirmed by AAS. Experiments had been performed to study the effect of initial concentration of the metal ions / metal-EDTA, pH of the solution, contact time and dose rate of the CSC. The optimum conditions for the maximum removal of metal-EDTA complexes were determined. It was observed that EDTA assisted the removal of metal ions to an extent of 23% higher in the case of Cu(II) and 28% in Zn(II) ion and also observed that less amount of CSC was required for the combined removal of the metal ions than what was required for the removal of individual metal ions at the same concentrations. The equilibrium data obtained had been fitted to Langmuir and Freundlich isotherms. The adsorption capacity of the CSC was found to decrease in the following order:  $Cu(EDTA)^{2-} > Zn(EDTA)^{2-} > Cu(II) > Zn(II)$ . The kinetics of adsorption obeyed first-order rate equation.

**Keywords:** Batch adsorption techniques, Coconut Shell Carbon(CSC), ethylene diammine tetra acetic acid (EDTA), Infrared spectroscopy (IR), Thermogravimetry (TG).

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### INTRODUCTION

Science and technology, industrialisation and population growth are main causes for environmental pollution. It is unavoidable crisis when the country leads towards economical growth. So, it is not possible to make the country completely free from environmental pollution but can be controllable using science and technology. The impact of heavy metal toxicity is one of the main problems in water pollution and they have to be necessarily removed from industrial effluents in order to control the toxic effect of the heavy metal-containing water[1,2].

Among the various processes available for the removal of heavy metals, adsorption technique[3] is the most effective and low cost technique. Elaborate reports are available in literature about the removal of the heavy metal ions by adsorption over various types of activated carbons[4-8]. Only a few reports are available on the studies of the removal of binary[9-11] metal ions using various adsorbents. EDTA has been widely applied in various industries as strong complexing agent for most metals. The presence of EDTA enhances the percentage removal of metal ions and is well documented[12-14]. But, the studies on the EDTA assisted removal of the binary metal ions from aqueous solution by adsorption technique are very scarce and less information have been provided in literature. The present study is an attempt to arrive at conducive parameters for 100% removal of the Cu(II) and Zn(II) ions

from a binary mixture in the presence of EDTA by batch adsorption technique on activated coconut shell carbon (CSC) and to compare the efficiency of the adsorbent in the removal of metal ions in the absence of the EDTA.

## EXPERIMENTAL SECTION

The materials used for the present study were: copper(II) sulphate (S.D. fine, A.R.), zinc(II) oxide (S.D. fine, A.R.) and EDTA (Qualigens, L.R.) Nitric acid treated CSC of particle size ranging between 75 and 90 mesh was used as adsorbent. The mock effluent samples containing copper(II) and zinc(II) ions were prepared by dissolving appropriate metal ion salts in de-ionised water. The other necessary reagents, like bismuth(III) nitrate, xylenol orange, fast sulphon black F indicators were prepared following the procedure given elsewhere[15]. The physical and chemical parameters of the CSC were determined using thermogravimetric analysis (TGA), infrared spectroscopy (IR) and atomic absorption spectroscopy (AAS) techniques.

### Preparation of treated CSC

Coconut shell carbon was commercially available in granular and powdered form and procured from M/S V.V.D. coconut oil company, Tuticorin, India. The particles obtained by sieving, carbon with 75-90 mesh sieves, was used in the present study. The adsorbent was activated by digesting 500g of the carbon in one liter of 1:1 nitric acid solution for 120 minutes at 80°C and kept aside for overnight. The supernatant solution was decanted. The carbon was washed with boiling de-ionized water several times to remove acid and the metal ions present in it. The washings were tested with pH paper for the removal of acid. One washing was continued until the washings gave blue colour with Eriochrome black T (EBT) indicator, ensuring the absence of the metal ions. The treated CSC was dried in air oven for about five hour. Then it was stored in wide mouth air-tight container and used for adsorption studies.

### Thermogravimetric Analysis

The adsorbent (CSC) was characterised for its moisture content, volatile matter, carbon content and ash content by subjecting the sample to a dynamic heating rate of 10°C min<sup>-1</sup> from room temperature to 900°C in oxygen atmosphere on universal V 2.5 HTA instrument. The surface area and pore volume of the adsorbent were determined using the procedure given by pan *et al.*,[15].

### Infra - red Spectroscopy

IR spectrum of the treated CSC was recorded on ABB Bomen MB 104 Mid –IR using KBr pellet technique.

### Atomic Absorption Spectroscopy

Atomic absorption spectrometer –spectra AA 100/200 – Varian –Australia was used to estimate the concentration of various metal ions present in the solution which was prepared by dissolving the ash of both treated and untreated CSC in 10 mL of 1:1 hydrochloric acid. Appropriate hollow cathode lamps were used.

### Adsorption Studies

Batch technique was adopted to study the simultaneous removal of the metal ions in the presence and absence of EDTA. The concentrations of the metal ions / metal-EDTA complexes present in the equilibrated binary mixture solution were determined complexometrically. To test the reliability of the volumetric analysis at low concentrations, the equilibrated solutions obtained in the optimum conditions for the maximum removal of the metal ions were subjected to AAS estimation.

### Determination of Concentration of Metal–EDTA Complexes

The total concentration of the metal–EDTA complexes present in the filtrate was determined based on the following principle. An aliquot of the filtrate was treated with known quantity of excess Bi(III) solution which abstracts EDTA from metal–EDTA complexes present in the solution. From the concentration of uncomplexed Bi(III) ion, the total concentration of the metal-EDTA complexes was determined. Another aliquot of the filtrate was heated with thiourea in acidic medium to release EDTA selectively from Cu-EDTA. The amount of released EDTA was determined from which individual concentration of metal-EDTA complexes was determined.

### Determination of Concentration of Metal ions

The total concentration of the metal ions present in the filtrate was determined complexometrically using back titration technique[16]. The individual concentration of the metal ions was determined by masking Cu(II) selectively using thiourea in acidic medium. In all the estimations, xylenol orange was used as indicator.

## RESULTS AND DISCUSSION

## Characterization of Adsorbent

The treated and untreated adsorbents are analysed by TG method for the moisture, carbon contents, surface area and pore volume, and by AAS method for the metal ions content. These parameters are given in Table 1. The TG and DTG (differential thermogravimetry) traces of the untreated and treated CSC are given in Figs. 1 and 2 respectively. Treated CSC is found to have higher moisture content, surface area and pore volume than untreated CSC which may be attributed to the increase in active site due to nitric acid treatment. The IR spectrum of the treated CSC, shown in Fig.3 contains absorption frequencies due to adsorbed water molecules and / or C-OH group ( $3448\text{ cm}^{-1}$ ) present in the CSC, C=O stretching vibration (around  $1630\text{ cm}^{-1}$ ),  $-\text{CH}_2-$  asymmetric stretching vibration ( $2926\text{ cm}^{-1}$ ) and due to various M-O stretching vibrations like Fe-O, Na-O, K-O, *etc.*, below  $680\text{ cm}^{-1}$ .

Table 1: Physical and Chemical Parameters of CSC

S. No.	Parameter	CSC	
		Untreated	Treated
1.	Particle size (mesh)	75 – 90	75 – 90
2.	Moisture (%)	7.9	19.9
3.	Volatile matter (%)	5.0	3.2
4.	Carbon content (%)	65.6	73.8
5.	Ash (%)	21.5	3.1
6.	Surface area ( $\text{m}^2\text{g}^{-1}$ )		
	Total	1140	1405
	Micro pore	765	901
	Mesopore	375	504
7.	Pore volume( $\text{cm}^3\text{g}^{-1}$ )		
	Total	0.488	0.545
	Micro pore	0.339	0.390
8.	Mesopore	0.149	0.205
	Metal ion content (ppm)		
	i Calcium(II)	168.40	NIL
	ii Magnesium(II)	102.80	NIL
	iii Mercury(II)	Nil	NIL
	iv Cadmium(II)	0.01	NIL
	v Copper(II)	1.32	0.002
	vi Nickel(II)	0.98	0.009
	vii Lead(II)	2.62	0.01
	viii Iron(II)	132.00	6.21
	ix Sodium(II)	321.80	20.37
	x Potassium(II)	602.30	42.6
	xi Arsenic(III)	Nil	Nil
	xii Zinc(II)	40.87	2.1
	xiii Manganese(III)	1.20	0.01

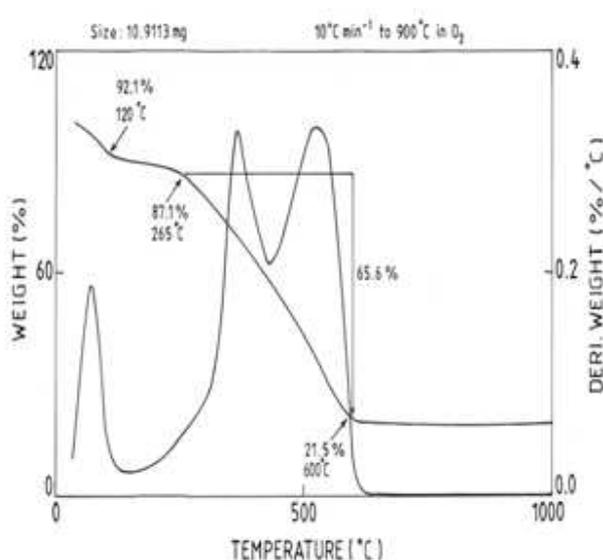


Fig-1 TG and DTG for Untreated CSC

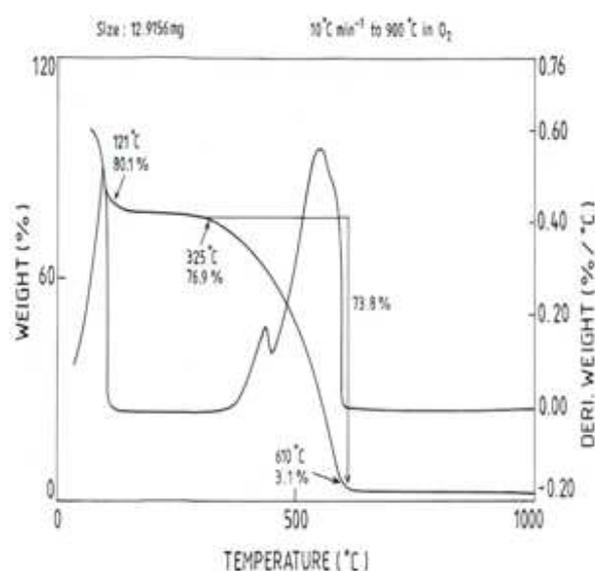


Fig-2 TG and DTG for treated CSC

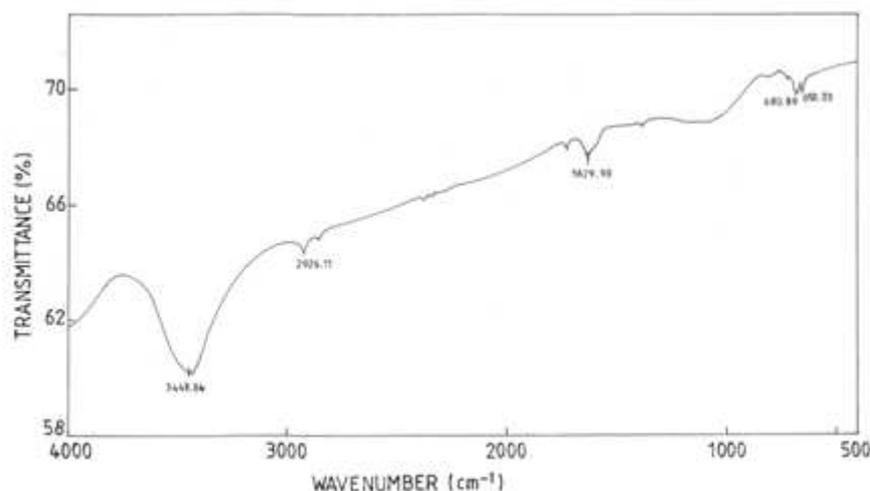


Fig-3 IR for Treated CSC

As evident from AAS study, the treated CSC contains very small concentration of certain metal ions (Fe, Na and K) and hence the bands due to Ca-O, Mg-O, Cu-O, Ni-O, *etc.* are absent in the IR spectrum of the treated CSC. This reveals that the presence of more active sites and rare existence of foreign materials in the treated CSC.

#### Effect of Initial concentration

The adsorption experiments were carried out at different initial concentrations of the Cu(II) and Zn(II) ions over the range: Cu(II) : 39.9 - 74.7 ppm, Zn(II) : 20 - 55.2 ppm in the presence of EDTA and absence of EDTA, by keeping the dose rate, contact time, pH, shaking speed and temperature to be constant of the metal ions for each binary system. It is observed that the percentage removal of the Cu-EDTA and Zn-EDTA complexes as well as the Cu(II) and Zn(II) ions are low at higher concentrations and gradually increases as the concentration decreases[17]. This is due to the fact that after the formation of mono ionic layer at lower concentration over the adsorbent surface, formation of additional layer is highly hindered at higher concentration due to the interaction between the ions on the surface Cu-EDTA and Zn-EDTA complex ions / Cu(II) and Zn(II) and in the solution. The optimum concentration of the metal ions for 100% removal in the presence of EDTA is found to be Cu(II): 44.8 ppm and Zn(II): 25.3 ppm. In the absence of EDTA, the percentage removal at the same optimum concentration is found to be 77 for Cu(II) and 72 for Zn(II) ions. It is observed that EDTA assists the removal of metal ions to an extent of 23% higher in the case of Cu(II) and 28% in Zn(II) ion.

To test the reliability of the volumetric results, the equilibrated solution obtained at the optimum concentrations of the metal ions (44.8 ppm for Cu(II) ion and 25.3 ppm for Zn(II) ion) are estimated using AAS technique. The analysis reports indicate the presence of 0.022 ppm of Cu(II) ion and 0.025 ppm of Zn(II) ion in the equilibrated solution against zero ppm as reported by volumetric analysis. Thus, the validity of the volumetric analysis in the estimation of the metal ions at low concentration is tested.

#### Adsorption isotherms

The adsorption data fit the Freundlich and Langmuir adsorption isotherms and their plots are shown in Figs. 4 and 5.

Freundlich isotherm

$$\log x/m = \log K + 1/n \log c_e$$

Langmuir isotherm

$$c_e/q = 1/Q_0b + c_e / Q_0$$

where K and 1/n are the measures of adsorption capacity and intensity of adsorption respectively; q the amount adsorbed per unit mass of adsorbent;  $c_e$ , the equilibrium concentration (ppm);  $Q_0$  and b, the Langmuir constants, which are the measures of monolayer (saturation) adsorption capacity (mg/g) and surface energy (L/mg) respectively. The various parameters obtained from the plots are given in Table 2. The adsorption capacity ( $Q_0$ ) of the CSC for the metal ions under study is in the order Cu-EDTA > Zn-EDTA > Cu(II) > Zn (II) ions. Low values of adsorption intensity (1/n) infer that the intra-particle diffusion of the metal-EDTA complex is less.

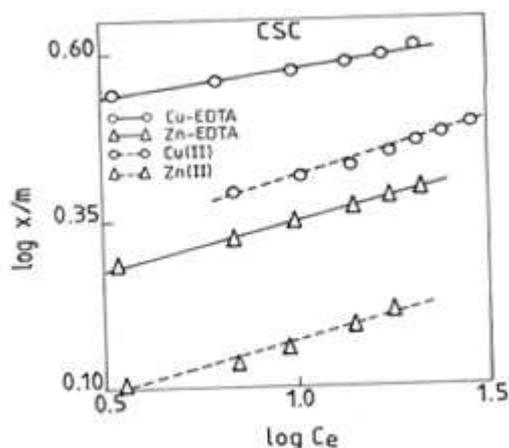


Fig- 4 Freundlich Isotherm

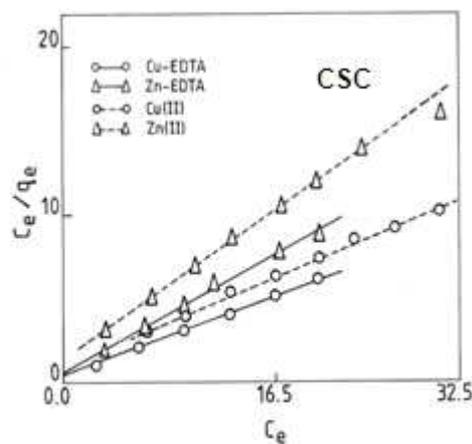


Fig- 5 Langmuir Isotherm

Table 2: Various Parameters Derived from Langmuir and Freundlich Isotherms

Metal system	Langmuir isotherm			Freundlich isotherm
	Q <sub>0</sub> mg/g	b L/mg	R <sub>L</sub> = 1/1+bc <sub>i</sub>	(1/n)
Cu-EDTA	4.4	0.11	0.16	0.08
Zn-EDTA	2.5	0.10	0.28	0.12
Cu (II)	2.1	2.38	0.01	0.14
Zn (II)	1.8	2.78	0.014	0.17

The calculated values of R<sub>L</sub> are found to be in the range 0 - 1, which indicate that the adsorption process is favourable[16].

#### Effect of Contact time

In the adsorption system, contact time plays a vital role, compared to the other process parameters affecting the kinetics of adsorption. Fig. 6 shows the percentage removal of Cu(II) and Zn(II) ions in the presence of EDTA and absence at various contact times ( 5 to 60 minutes) using 13.3 gL<sup>-1</sup> dose rate of CSC in the optimum concentration of Cu(II) and Zn(II) ions at constant pH. It is observed that the percentage removal of metal ions increased with the increase in contact time and reached a constant value after the optimum contact time[18- 20]. For the combined removal of the metal ions and their EDTA complexes at the optimum concentrations, the contact time required for the maximum removal is 40 min for Cu-EDTA, 50 min for Zn-EDTA, 50 min for Cu(II) and 60 min for Zn(II) ions.

#### Kinetics of Adsorption

The adsorption data are applied in the following first order kinetic equations[19,20].

$$\text{Natarajan -Khalaf equation} \quad \log (c_i / c_e) = (k / 2.303) t$$

$$\text{Lagergren equation} \quad \log (q_e - q_t) = \log q_e - (k / 2.303) t$$

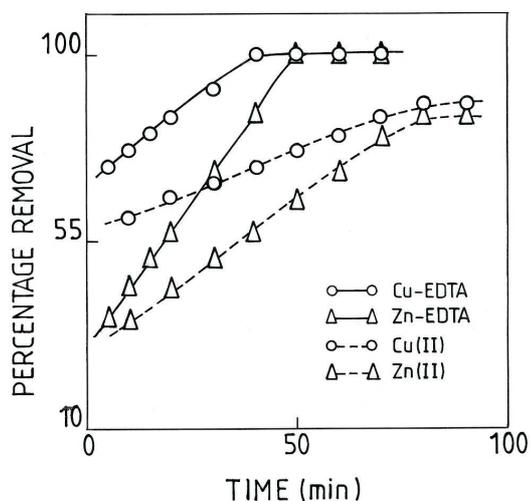
where c<sub>i</sub>, c<sub>e</sub> and c<sub>t</sub> are the concentrations of metal ions / metal-EDTA complexes (in ppm) at the initial, equilibrium and at time t, (in min), K, the first-order rate constant for adsorption (in min<sup>-1</sup>), q<sub>e</sub> and q<sub>t</sub>, the amount adsorbed at equilibrium and at time t (in min). The adsorption data are found to obey these equations exhibiting linear relationship. The liner plots due to a Lagergren equation only is shown in Fig.7. The calculated rate constants and correlation coefficients from the above equations are give in table .3. The r-values(correlation coefficient close to unity) indicate the applicability of these kinetic equations and the first order nature of adsorption of Cu(II), Zn(II), Cu-EDTA and Zn-EDTA ions on treated CSC. The values of rate constant (k) of adsorption over CSC are found to decrease in the order : Cu-EDTA > Zn-EDTA > Cu(II) > Zn(II).

The following reason may be attributed to the observed trend. CSC surface contains positively and negatively charged groups with former as the predominant. Therefore, the surface is said to be positively charged. The rate of adsorption depends on the ease of migration of the ions (which is inversely related to mass) in solution and charge over the ions. In the case of metal-EDTA complexes, the charge over the species is two negative charge and on the free metal ions, two positive charge. Columbic attractive force is favorable phenomenon, whereas mass is

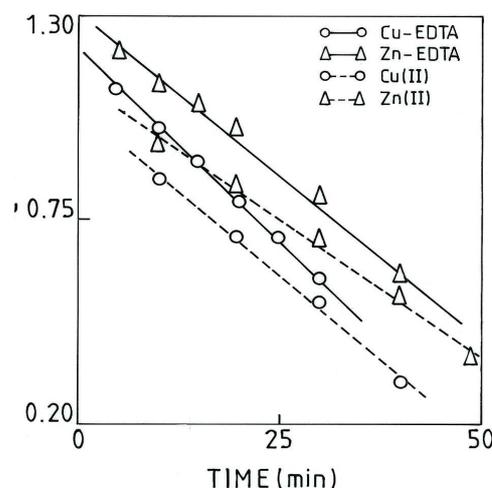
unfavorable for the adsorption in the case of metal-EDTA complexes. The situation is completely reversed in the case of free metal ions. The attractive force is found to play a dominant role in the adsorption study. Hence, the results.

**Table 3. Parameters derived from Natarajan-Khalaf and Lagergren Equations**

S.No	Kinetic Equations/Parameters	Cu(II)	Zn(II)	Cu-EDTA	Zn-EDTA
1.	Natarajan-Khalaf Equation				
	k ( $10^{-2} \text{min}^{-1}$ )	3.4	1.7	4.9	3.9
	r-value	0.981	0.972	0.988	0.987
2.	Lagergren Equation				
	k ( $10^{-5} \text{min}^{-1}$ )	5.2	4.6	6.5	5.5
	r-value	0.969	0.989	0.997	0.992



**Fig. 6 Effect of Contact Time**



**Fig. 7 Lagergren Plots**

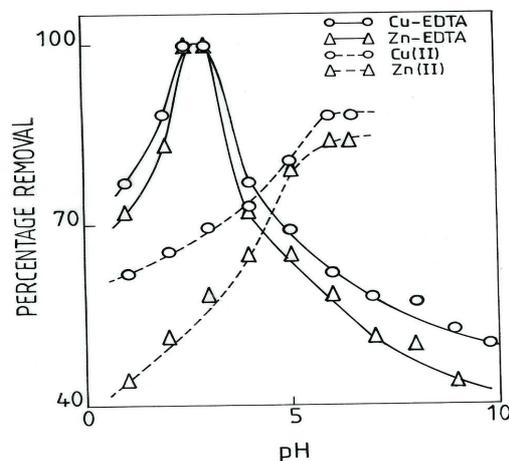
#### Effect of the Dose rate

The combined removal of metal ions / metal-EDTA complexes was studied with different dose rate of the CSC at optimum concentrations of the metal ions / metal-EDTA complexes in the mixture with fixed contact time and pH. The percentage removal of the metal-EDTA complexes as well as free metal ions is found to increase with the increase in amount of the adsorbent. This is due to the increase in number of active sites of adsorbent with increase in dose of the adsorbent [21,22]. The optimum dose rate for the maximum removal of both metal ions / metal-EDTA complexes present in the mixture is observed to be: Cu-EDTA – Zn-EDTA :  $13.3 \text{ gL}^{-1}$  and Cu(II) – Zn(II) ions:  $16 \text{ gL}^{-1}$ .

#### Effect of pH

The adsorptions of the metal ion mixtures as well as their EDTA complexes on to CSC were studied at different pH values, keeping the system at the optimum conditions of the initial concentration of the metal ions / metal-EDTA complexes, contact time and dose of the adsorbent. The plots of the percentage removal of the metal ions in the mixture with respect to change in pH are shown in Fig. 8. The optimum pH ranges observed are: for Cu(II) and Zn(II) ion mixture 6 - 6.5 and for Cu-EDTA and Zn-EDTA mixture 2.5 - 3.0. In the case of mixture of metal ions, at low pH the percentage removal is low and drastically increases with increasing pH [11,24-26]. It is due to the fact that with increasing pH, surface charge of the adsorbent becomes more negative and available for the adsorption of dipositively charged metal ions. In the case of metal-EDTA complexes, an enhancement of adsorption is observed in high acidic medium. In high acidic medium, the concentration of  $\text{H}^+$  ions is high and they get preferentially adsorbed on the surface of the adsorbents and the surface Charge of the adsorbents becomes positive and enhances the adsorption of negative charged metal-EDTA complexes. At very high acidic medium ( $\text{pH} < 2$ ), the stability of metal-EDTA complexes is low. At very low pH, the metal-EDTA species may undergo partial decomposition.

The solution may contain undecomposed metal-EDTA complex, free metal ions and free EDTA. Under this condition, the metal-EDTA complex and EDTA are preferentially undergoing adsorption, than the free metal ions. This accounts for the decrease in the percentage removal of metal-EDTA complexes at very low pH. At higher pH, the concentration of OH<sup>-</sup> ions is increased and they get preferentially adsorbed on the surface of the adsorbent and the surface charge of the adsorbent becomes negative which retards negatively charged metal-EDTA complex from adsorption.



**Fig. 8 Effect of P<sup>H</sup>**

### CONCLUSION

The EDTA proves to be a potent assistant in the efficient removal of the Cu(II) and Zn(II) ions mixture as their 1:1 metal-EDTA complex by adsorption on activated CSC. EDTA enhances the percentage removal of metal ions. The removal of the Cu-EDTA and Zn-EDTA complexes requires lesser time to reach the maximum efficiency than the removal of the Cu(II) and Zn(II) ions mixture. The optimum dose rate for maximum removal of Cu-EDTA and Zn-EDTA complexes is lower than the removal of Cu(II) and Zn(II) ions mixture. All the above occur at low pH. Therefore EDTA assistance may play an important role in the treatment of industrial effluents containing metal ions which are generally acidic in nature.

### Acknowledgement

The authors wish to thank the management and principal for their constant support and encouragement during the research work.

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