Impact of Remediation of Cu(II) and Zn(II) in aquatic environment using single and mixed surfactants

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Abstract : The removal of Cu(II) and Zn(II) from water and wastewater sample is of paramount significance because of its lethal repercussion when present high concentration. In the present study single and mixed surfactants were applied to remove Cu(II) and Zn(II) and analyse its accessory and synergitic effect in ionic –nonionicbinary systems.   The effect of pH was profound and removal percentage triggered around pH 4 to 6.Langmuir, Freundlich and Dubinin Radhushkevik Kaganer (DKR) Isotherms were studied. Adsorption equilibrium of the metal ion reveals that data were well fitted to both Langmuir and Freundlich Isotherms. Maximum monolayer capacity q_{max} obtained from Langmuir model was found to beappreciably high for Cu(II) and Zn(II) and was evaluated as 5 mg.g^{-1}and 5.88 mg.g^{-1} whenSDBS(Sodium dodecyl benzene sulphonate) was modified with Triton X-100 and Tween 80 respectively in a ratio of 4:1 was found to show removal efficiency of 98.66% and 98.58% respectively for Cu(II) and Zn(II). CTAB (Cetyltrimethyl ammonium bromide)both individually and in adjunct with Triton X-100 and Tween-80 showed a retarded response in the removal of both metals.Negative enthalpy and Gibbs free energy indicated exothermic and spontaneous process. Maximum activation energy was noted for Cu(II) and Zn(II) with SDBS+Triton X-100 and SDBS+Tween 80. Psuedo second order and intraparticle diffusion model were subjected to analyse the adsorption kinetics. Psuedo second order was asynchronous with experimental data.Noticeable boundary layer thickness was found to be appreciably high. It was identified that mixed surfactants of SDBS comparatively at a lower dosage were efficient adsorbent than unmodified SDBS ,CTAB and mixed surfactants of CTAB.

Keywords : Adsorption, Copper and Zinc , ionic and mixed surfactants, Adsorption Isotherms, Kinetics.

1. Introduction

Clean water is 3% of total water on earth, out of which only 1% is available for human consumption. There is always a great demand for clean water since major portion of the water has been locked in glaciers and snow[1]. Rapid industrialization urbanization and several anthropogenic activities have led to the reckless release of pollutants in the marine ecosystem [2].Among all the noxious pollutants heavy metals are matter of utmost apprehension as they are released in massive amount through industrial effluents. Non biodegradable and bioaccumulating in nature, heavy metals are toxic for both flora and fauna.Because of being highly noxious, the Agency for Toxic Substances and Disease Registry, of the U.S. Department of Health and Human Services, has designated these chemicalsas priority pollutants [3]. DespiteCopper is essential forhuman health, animal metabolism and the activity of many microorganisms, the excessive ingestion of copper, however,brings about

serious toxicological concerns, such as vomiting,cramps, convulsions or even death[4].Major sources of copper discharge are from industries such asmetal cleaning and plating, paper board, printed circuit board,wood pulp, fertilizer, paints and pigments[5,6].

Zinc is a trace metal. However, too much zinc have known to cause detrimental effects onhuman health.Zinc if taken in high dosage causes eminent health problems, such as stomach cramps,skin irritations, vomiting, nausea and anemia[7] . In the quest of removing heavy metal from water and wastewater ,several methods such as precipitation, ion exchange, electrochemical process, and adsorption are employed [8]. Adsorption is comparatively a feasible, cost-effective method and requires no sophisticated instruments. Several materials like Seaweed[9] mushroom harvest residues[10] ,pine bark, pine needles and leaves[11] ,modified chitosan, cassava, and loofah sponge[10], and saw dust[12] have been used as potential adsorbents in research studies. However, biomass is required in large doses and requires other inputs which in turn poses negative impact on environment.

Surfactants are amphipathic molecules containing two parts namely hydrophilic head(water-loving) and hydrophobic tail (water- hating). At low concentration, surfactants can lower surface tension of the system by adsorbing onto the interfaces and altering the interfacial free energies of those interfaces. At high enough surfactant concentration, surfactant molecules can spontaneously self-aggregate into a variety of structures, which are called micelles.Micelle formation takes place at a concentration termed as Critical micelle concentration(CMC). Surfactants are used as emulsifier in food and cosmetic industries as well as in most of cleaning products such as detergents or soaps [13].In the recent past decades, surfactants have been extended in environmental area for mainly toxic metal treatment purposes [14].Also interfacial and micellar properties of mixed surfactant systems have attracted significant attention in the area of surface science and solution chemistry in recent past [15]..Sodium dodecyl benzene sulphonate (SDBS) was used as an anionic surfactant and Cetyltrimethyl ammonium bromide as cationic surfactant. Non-ionic surfactants are biodegradable and have relatively lower cmc. The present study includes, the incorporation of non-ionic surfactants, 4-octylphenol polyethoxylate (Triton X-100) andPolyoxyethylene (20) sorbitanmonooleate(Tween 80) on SDBS and CTAB to study the combined impact on remediation of Cu(II) and Zn(II) in aquatic environment.

2. Material and methods

2.1 Chemicals and reagents

All reagents were of analytical reagent grade and were used as supplied. Stock solutions of Cu(II) and Zn(II) were prepared by direct dissolution of proper amounts of their nitrates salts. All the solutions were further diluted as per the requirement. Sodium dodecyl benzene sulphonate (SDBS), Cetyltrimethyl ammonium bromide (CTAB), Triton X-100, Tween 80, sodium hydroxide, hydrochloric acid and Sodium chloride were obtained from Merck. pH of the solutions were maintained by using 0.1M NaOH and 0.1M HCl.

2.2. Optimization of metal ion adsorption

Optimization studies were carried out in the batch mode. 50 ml aqueous solution of metal ion (10 mgL^{-1}) were taken in 250 ml Erlenmeyer flask. 1 gL^{-1} and 1: 4 ratio of single surfactant and mixed surfactant respectively were added to the batch. 1M solution of NaCl was mixed to the solution. The pH of the solution was adjusted to the desired value and was stirred for 300 minutes at an agitation speed of 160 rpm[16]. After the metal ion adsorption , surfactants were separated by using 10kDa MWCOpolyether sulphonemembrane filter. The residual metal ion adsorption was further analysed by Perkin Elmer Aanalyst 400 Atomic Absorption Spectrophotometer. The following equation was applied to calculate the metal ion removal efficiency in the treatment experiments:

Removal efficiency (%)$= \frac{c_o - c_e}{c_o} \times 100$ (1)

Where C_0 andC_e are initial and residual concentration of the metal ion in the solution (mgL^{-1}), respectively.

The amount of Cu(II) and Zn(II) adsorbed at equilibrium, q_e (mg/g), which represents the metal uptake and it was evaluated by the following equation:

$$q_e = \frac{Ci - Ce}{m} . V \text{(2)}$$

The adsorption experiment was carried out individually for each metal ion separately. The data for adsorption experiment were replicated three times and the average results were reported.

3. Results and Discussion

3.1. Effect of pH

pHhas been identified as the most important variable affecting metal adsorption onto adsorbent, because the surface charge density of the adsorbent and the metallic species depend on the pH and also partly because hydrogen ions themselves are strongly competing with adsorbate[17]. The Cu(II) removal was registered highest 98.25% with SDBS+Triton X-100 followed by SDBS showing 97.8% adsorption at pH 4. The Adsorption performance of all the adsorbents are stated in **Fig. 1**. As expected, the adsorption of metals decrease with decreasing pH because the SO_3^- group present as a hydrophilic head of SDBS are more protonated and, hence, they are less available to retain the investigated metal. The Cu^{2+} ions in aqueous environment may undergo hydration , hydrolysis or polymerization . Lower pH results in the protonation of the adsorbent surface which results in extensive repulsion of Cu^{2+} ions[18]. Zn(II) are present in the cationic form in aqueous solution , heretofore exhibited a highest removal efficacy with SDBS+Tween 80 of 97.8% and 97.3% with SDBS respectively as shown in **Fig. 2**.
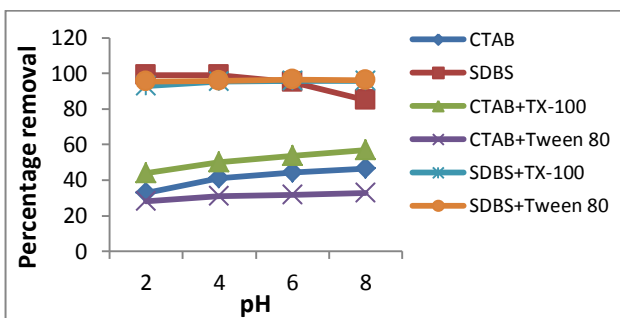

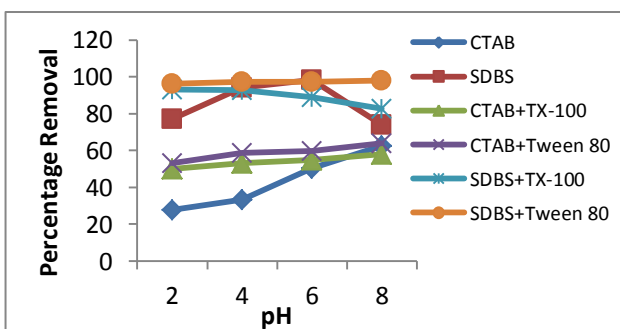**Figure 1. Effect of pH on the removal percentage of Cu(II).**

Figure 2. Effect of pH on the removal percentage of Zn(II).

3.2.Effect of initial metal ion concentration

Adsorption of metals by any adsorbent is highly dependent on the initial concentration of metal ion. It is a process parameter that is directly related to binding of adsorption sites. It was found that the maximum removal percentage for Cu(II) and Zn(II) 98.15% and 97.27% was with SDBS+Triton X-100 and SDBS+Tween 80 respectively. It was observed that percentage removal and adsorption capacity both decreased with the increase of initial metal ion concentration from 20 to 50 mg /L. The effect of initial metal ion concentration on the adsorption efficiency of the studied adsorbents is shown in **Fig. 3 & 4.**The ratio of number of moles of metal ions to the surface area of adsorbent is large at optimum concentration (20 mg/L), so adsorption takes place without any interruption. It means that the adsorption is highly dependent on the initial concentration of

heavy metals. This is because at lower concentration, the ratio of the initial number of metal ions to the available surface area is low, subsequently, the fractional adsorption becomes independent of the initial concentration [19].
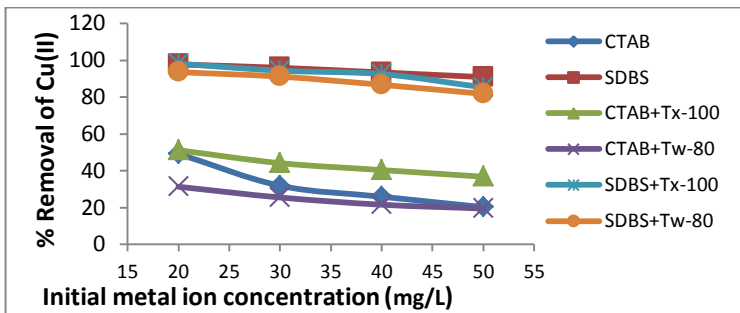

Figure 3. Effect of initial metal ion concentration on the removal percentage of Cu(II)
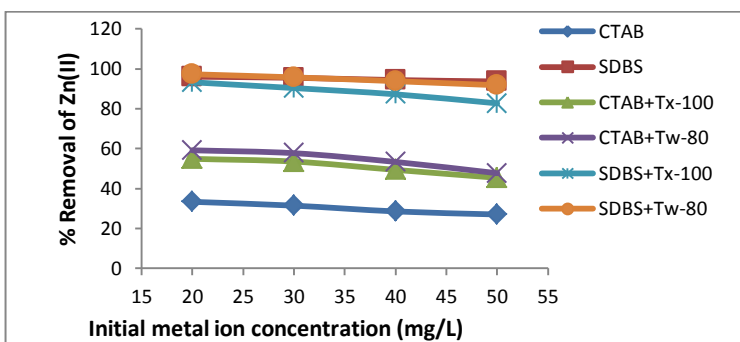

Figure 4. Effect of initial metal ion concentration on the removal percentage of Zn(II)

3.3. Effect of non-ionic surfactants in mixed surfactant systems

Impact of varying adsorbent dosage on the removal of metal ion is a subject of high interest . Our study found that on increasing the adsorbent dosage from 0.25g/L to 2g/L there was a marked change in removal percentage. The decrease in removal of metal ion can be due to relinquishment of micelles at lower dosage of surfactants.But as the concentration was increased in order to decrease the total energy of the system, the monomers assembled to form micelle. Molar ratio of mixed surfactant were also varied to analyse their individual behavioural changes. **Fig.5&6** shows an expected increase of adsorption efficiency with 4:1 ionic : non-ionic surfactant ratio.
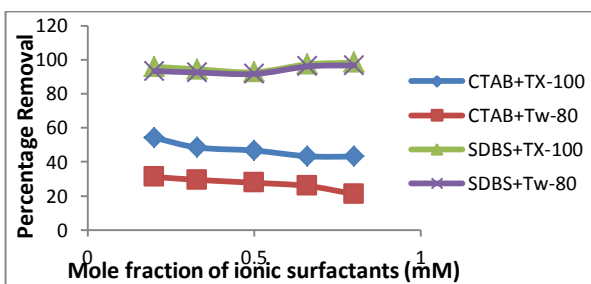

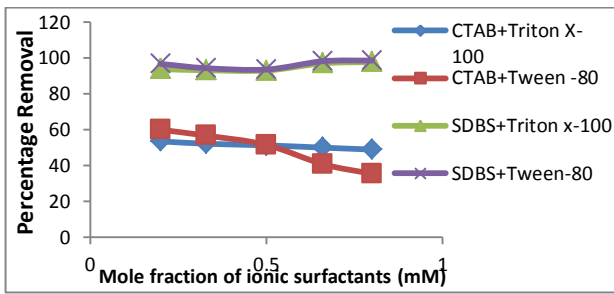**Figure 5.Effect of non-ionic surfactants in mixed surfactant systems on the removal percentage of Cu(II)**

Figure 6.Effect of non-ionic surfactants in mixed surfactant systems on the removal percentage of Cu(II)

However, , the percentage removal with respect to varying molar ratios of Cu-SDBS+Triton X-100 is greater than Zn-SDBS+Tween 80.

3.4. Adsorption Isotherms

The equilibrium study was carried out using three adsorption Isotherms namely, Langmuir, Freundlich and D adsorption isotherms.Isotherm parameters for the Langmuir, Freundlich and DKR models for single and mixedsurfactants are given in **Table 2.** Two commonly used empirical adsorption models, Freundlich and Langmuir which correspond to heterogeneous and homogeneous adsorbent surfaces respectively, were employed in this study.The linearised form of Langmuir, Freundlich and DKR adsorption isotherm are given in equation 3, 4 and 5 respectively.

$C_{eq}/q = 1/q_{max}.b + C_{eq}/q_{max}$ (3)

$logq_e = log K_F + 1/nlogC_e$ (4)

$lnq_e = lnq_D - \beta e^2$ (5)

where$q_e(mg\ g^{-1})$ is the amount of adsorbates adsorbed per gram of adsorbents at equilibrium; $C_e\ (mg\ L^{-1})$ is the equilibrium concentration of adsorbates in the solution;

K_F, is a Freundlich isotherm constant for the system and the slope 1/n, ranging between 0 and 1, indicative of the degree of nonlinearity between solution concentration and adsorption; $q_m(mg\ g^{-1})$ is the maximum monolayer adsorption capacity and b (L mg^{-1}) is the constant related to the free energy of adsorption.

The mean free energy From DKR isotherm is obtained from equation(6)

$E = 1/\sqrt{2\beta}$ (6)

If E_{DR} value is between 8 and 16 kJ/mol, the biosorption process is by chemical ion-exchange and if $E_{DR}< 8$ kJ/mol, the sorption process is of a physical nature[20]..In our study all EDR values(**Table 1**)are less than 8 kJ/mol except for 8.45 kJ/mol for SDBS +Triton X-100 with Cu(II) .The correlation coefficient $R^2 \geq 0.99$ inLangmuir isothermfor both heavymetals with specified adsorbent types.This infers that the data fit well in the Langmuir model. The high value of correlation coefficient indicated a good agreement between the parameters.The parameters evaluated from the each model are tabulated in **Table 1**for Cu^{2+}and in **Table 2**and Zn^{2+}. The value of correlation coefficients showed that the data fit Langmuir equation best.

Table 1.Langmuir ,Freundlich and DKR model parameters for the Copper ion adsorption onto single and mixed surfactant systems

Metal ion	Isotherm model							
	Langmuir			Freundlich			DKR	
Cu(II)	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	n	K_F (L mg^{-1})	R^2	E_{DR} (kJ/mol)	

CTAB	0.65	0.24	0.9954	3.83	1.58	0.9809	0.77
SDBS	5.37	1.05	0.9908	4.83	3.45	0.9515	3.16
CTAB+Tx-100	2.90	0.05	0.9909	1.98	3.09	0.9987	0.31
CTAB+Tw-80	1.36	0.05	0.9919	2.47	4.60	0.9970	2.35
SDBS+Tx-100	5.00	0.82	0.9985	2.77	2.24	0.9350	8.45
SDBS+Tw-80	5.07	0.43	0.9987	2.53	1.76	0.9836	3.22

Table 2.Langmuir ,Freundlich and DKR model parameters for the Zinc ion adsorption onto single and mixed surfactant systems

Zn(II) with different Surfactantsyste	Isotherm model						
	Langmuir			Freundlich			DKR
	q_{max} (mg g^{-1})	K_L (L mg^{-1})	R^2	n	K_F (L mg^{-1})	R^2	E_{DR} (kJ/mol)
CTAB	3.19	0.01	0.9907	1.44	2.77	0.9954	0.14
SDBS	6.49	0.68	0.9917	1.80	12.64	0.9905	1.42
CTAB+Tx-100	4.71	0.03	0.9931	1.53	3.69	0.9898	0.21
CTAB+Tw-80	4.32	0.04	0.9695	1.66	2.84	0.9617	0.23
SDBS+Tx-100	5.40	0.36	0.998	2.30	1.67	0.9926	1.10
SDBS+Tw-80	5.88	0.80	0.9915	2.35	2.54	0.9988	1.97

3.5. Thermodynamic study

The study of free energy, enthalpy and entropy are important thermodynamic parameters for better understanding the entire adsorption process.

Table 3.Thermodynamic parameters for Cu(II) and Zn(II) sorption

Metal ion	Surfactants	ΔG^0 kJ/mol at 30°C	$\Delta H°$ kJ/mol	$\Delta S°$ kJ/mol	E_{Act} kJ/mol
Cu(II)	CTAB	0.94	22.71	-0.07	-22.93
	SDBS	-9.93	-70.00	0.19	31.16
	CTAB+Tx-100	-0.17	-15.73	0.05	16.39
	CTAB+Tw-80	0.85	-17.76	0.06	14.97
	SDBS+Tx-100	-8.01	-39.61	0.10	70.56
	SDBS+Tw-80	-7.54	-31.62	0.07	25.58
Zn(II)	CTAB	1.642	22.49	-0.06	-21.61
	SDBS	-9.255	-57.88	0.16	21.59
	CTAB+Tx-100	-0.257	-13.84	0.04	14.03
	CTAB+Tw-80	-0.984	-20.38	0.06	11.45
	SDBS+Tx-100	-7.457	-49.24	0.13	43.25
	SDBS+Tw-80	-8.564	-62.13	0.17	49.53

For calculating thermodynamic parameters, following equations were followed:

$$K_c = \frac{c_{Ae}}{c_e} \qquad (7)$$

$$\Delta G^0 = -RT \, lnK_c \quad (8)$$

whereC_e is the equilibrium concentration in solution in mg/L and C_{Ae} is the equilibrium concentration on the sorbent in mg/ L and $K_c$isthe equilibrium constant. All the thermodynamic parameters and Activation energy E_{Act} calculated using vanthoff plots are mentioned in the **Table 3**. Negative enthalpy has been noted in all the cases except CTAB. This suggests that all the surfactants were effective in removal of Cu(II) and Zn(II) except

CTAB. The ineffective adsorptive efficiency of CTAB is due to cation–cation repulsion between the cationic head of CTAB and divalent metal cations.In addition to that, the positive value of entropy($\Delta S°$) revealed that the degreesof free active sites increased at the interface and demonstrate an increase in randomness during the adsorption[21]. In general, the sorption process is classified to be film-diffusion controlled when Ea is below 16 kJ mol−1 , particle-diffusion controlled when E_a is 12–50 kJ mol^{-1}, and chemical-reaction controlled when E_{Act} is greater than 40 kJ mol^{-1}[20]. The Activation energy for Cu(II) and Zn(II) adsorptionshow 70.56 kJ/mol with SDBS+Triton X-100 and 49.53 kJ/mol with SDBS+Tween-80 respectively, which suggests that sorption is chemical reaction controlled. Whereas all the other surfactant system with metal ion seemed to exhibit particle diffusion controlled. Almost all values of ΔG^0 ranges from -20 to 0 kJ/molwhich indicated that the interaction between metal ion and surfactant system was mainly via physical forces[22]. Adsorption thermodynamics thus indicate that the sorption for Zn(II) and Cu(II) are spontaneous and exothermic in nature.The mechanism relies mainly on attractive electrostatic interaction between metal ions and functional groups that contain different charges depend upon environmental solution**.**

3.6. Kinetic Study

The kinetics of sorption describes the solute uptake rate,which in turn governs the residence time of sorption reaction. It is one of the important characteristics in defining the efficiency of sorption. In order to clarify the adsorption kinetics of Zn (II) and Cu(II) ions onto single and mixed surfactants, pseudo second-order and Weber –Morris kinetic models were applied to the experimental data.
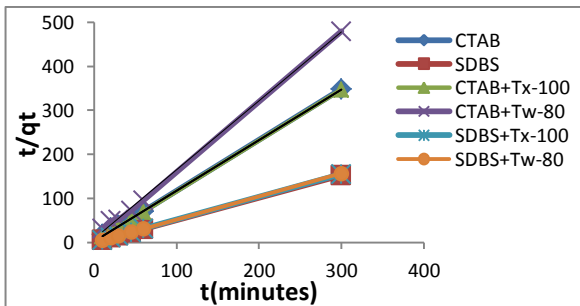

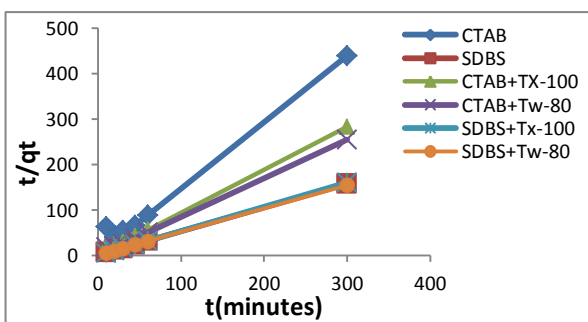**Figure 7.Psuedo second order plot for Cu(II) sorption**

Figure 8.Psuedo second order plot for Zn(II) sorption

3.6.2. Pseudo-second order model

The adsorption data were subjected into pseudo second order model according to the generic equation:

$$\frac{t}{q_t} = \frac{1}{V_0} + \frac{1}{q_e}t \qquad (9)$$

Where t is time q$_t$is metal uptake capacity at time t. A plot between t/q$_t$and t shown in **Fig. 7&8** exhibit unity values of correlation coefficients .This apparently indicates that reaction preferably proceed via pseudo-second order kinetics

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Table 4. Adsorption kinetics constant for Cu(II) sorption

Cu(II) with surfactant system	PsuedoSecondorder		WeberMorrismodel	
	K_2 (min-^{1})	q_e (mg.g^{-1})	K_{int}(min$^{0.5}$)	R^2
CTAB	0.25	0.87	0.08	0.987
SDBS	1.07	1.91	0.02	0.9077
CTAB+Tx-100	0.73	0.87	0.05	0.9953
CTAB+Tw-80	0.27	0.64	0.08	0.9942
SDBS+Tx-100	1.65	1.93	0.06	0.9925
SDBS+Tw-80	1.13	1.91	0.03	0.8636

Table 5. Adsorption kinetics constant for Zn(II) sorption

Zn(II) with surfactant system	Psuedo Secondorder		WeberMorrismodel	
	K_2 (min-^{1})	q_e (mg.g^{-1})	K_{int}(min$^{0.5}$)	R^2
CTAB	0.17	0.72	0.11	0.9588
SDBS	0.42	1.91	0.10	0.9742
CTAB+Tx-100	0.19	1.08	0.16	0.9207
CTAB+Tw-80	0.24	1.19	0.17	0.7460
SDBS+Tx-100	0.70	1.87	0.07	0.9894
SDBS+Tw-80	12.27	1.94	0.007	0.9906

3.6.3. Weber-Morris model

Adsorption is considered to be a three step process. The first step involves transport of the adsorbate molecules from the aqueous phase to the film surrounding the adsorbent. In the second step diffusion of the solute molecules from the film to the adsorbent surface takes place. Finally, in the third step the adsorbate molecules diffuse into the pore interiors. The equation for intraparticle model is:

$$q_t = k_{int}t^{1/2} \quad (10)$$

Where K_{int} is the intaraparticle diffusion rate constant. A plot between $q_t$and $t^{0.5}$ is shown in **Fig.9 and 10** for Cu(II) and Zn(II) respectively. From the plot ,slope and intercept value **(Table 4& 5)** of K_{int}intraparticle diffusion rate constant and boundary layer thickness I was obtained respectively.
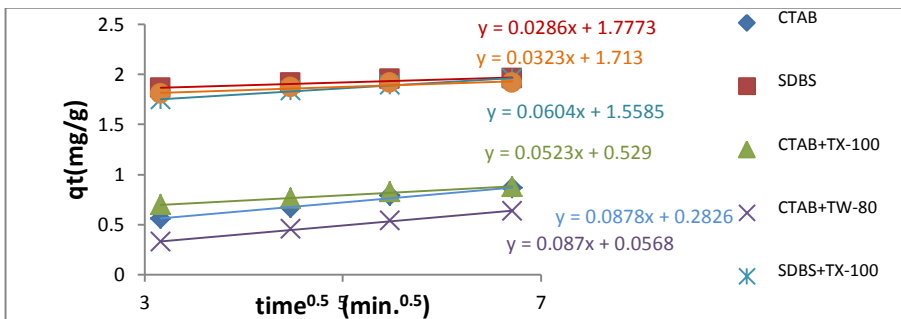

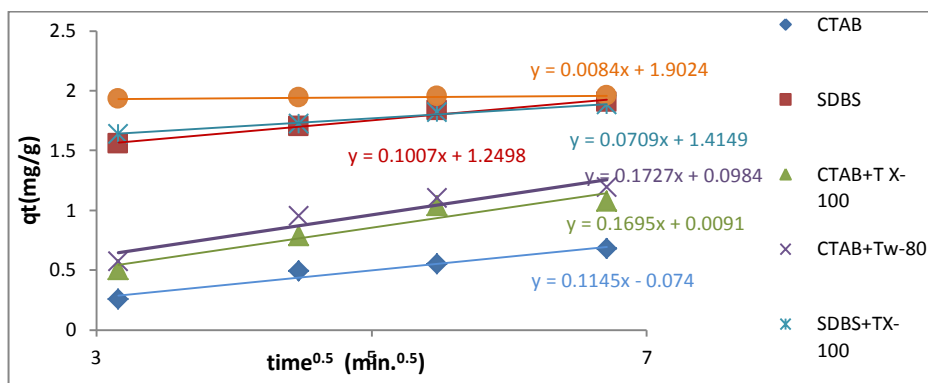**Figure 9. Intra-particle diffusion plot for sorption of Cu(II)**

Figure 10. Intra-particle diffusion plot for sorption of Zn(II)

According to this model , if the q_t vs $t^{0.5}$ plot is linear and exactly passes through the origin , it indicates that the intraparticle diffusion step is the only rate controlling step[23]. The intercept I, also called as boundary layer thickness was found to be appreciably high in the case of mixed surfactants in comparison to their individual contributions and henceit can be suggested that larger the intercept, the greater the boundary layer effect. This evidently shows occurrence of more than one rate controlling step.

4. Conclusion

In this work ,removal of Cu(II) and Zn(II) was studied using four surfactants namely SDBS, CTAB, Triton X-100 and Tween 80 in single surfactantand mixed surfactant systems. It was found that Langmuir data fitted well , which suggests the reaction to be showing monolayer coverage and homogeneous in nature. The energy calculated fromDKR isotherm and negative value of enthalpy indicates occurrence of physisorption and exothermic reaction for single surfactant systems. Whereas very high negative values of enthalpy for SDBS+TritonX-100-Cu(II) and SDBS+Tween80–Zn(II) system infersinteraction through chemical bond formation. Adsorption kinetics revealed that the reaction showed second order rate and the intraparticle diffusion step was not the only rate controlling step. Use of mixed surfactants not only enhance the adsorption efficiency but also lowers the cmc which facilitates removal of metal ion at a lower concentration of surfactants. However, thiscan be recommended as a feasible method for the removal of toxic hazardous materials and recovery of precious metals along with the surfactants from industrial effluents.

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