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Research Article

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Kinetic and thermodynamic studies of adsorption Pb (II) Ion on the micelles on anionic and nonionic surfactant

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ABSTRACT

Adsorption lead (II) ion onto three different surfactant, anionic as a Sodium dodecyl sulfate (SDS), cationic Cetayl trimethyl ammonium bromide(CTAB) and nonionic Triton X-100. under different experimental conditions were studied. From aqueous solutions and has been investigated through batch mode adsorption experimental. And have been studied adsorption at different PH (4-9) determine by using HANNA,PH-Meter(Instrument, Portugal. Electronic Balance Sartorius, W. Germany). and effect temperature change from (293 to 328) $\overset{o}{K}$*. Kinetic study shown this adsorption followed pseudo first order. The experimental isotherm data were analyzed by using two isotherm models the Langmuir and Freundlich equations. Our results provide that the adsorption process was spontaneous and exothermic under natural conditions. All the data were carried out by (UV- Visible Spectrophotometer(Libra Biochrom S60, England) after and before add surfactants.*

Keywords: lead, surfactant, Adsorption, Batch adsorption, kinetic, Isotherm

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INTRODUCTION

The chemical pollution of water is found inorganic or organic compound in environmental aquatic the common pollution of water du to organic compound such as fats, proteins, carbohydrate and other and the source of toxic inorganic usually coming from industrial water such as fertilizers ,DDT, coke stoves and etc. and free inorganic compounds are free such as pb, Ni, Hg, Cu, Zn, As, U and other [1-2]. One of the ways of water purification to be unfit for human consumption is on the adsorption Activated carbon or any material that could be used as a surface adsorbed his hand. The reason for this is very effective sorbent They are susceptible to penetration and so may very large areas available for absorption or Chemical reaction[3]. Main objective of the treatment of drinking water is to obtain a pure water fit for human consumption is subject to the International Standards and economic meaningful ways[4]. One of the methods used in water purification is the adsorption on the surface of activated carbon or any surface of his ability to adsorption[3]. Adsorption phenomenon attracted of attention during the last decades of the twentieth century, the world had to Langmuir is one of the first researchers in the field studied the adsorption of gas adsorption on solid surfaces(metal) [5].

Lead found in natural about 13 mg/kg it is the most abundant compared with other heavy elements[6]. Lead is present in the contaminated air and drinking water in the air is the result of emissions from automotive due to use tetraethyl in gasoline[7]. It was pointed out that the fate and transfer inorganic toxic in the environment mostly controlled by adsorption process[8]. Lead is a real threat to human health and particular pregnant women who work in the field of industry, where one of the reasons leading to the fetuses are aborted, category and more vulnerable to lead poisoning are lead miners, painters and plumbers[9]. The toxicity of lead is widely, inorganic lead cause a metabolic poison and inhibitor of the enzyme (such as most metals). Organic lead more poison like LEL(Tetra ethyl Lead) or TML (Tetra Methyl Lead) than inorganic lead[10]. In this study to treat aquatic pollution by lead(II) by using liquid surfactant. Surfactants are Widespread used in the industry, in domestic products such as detergents and for personal care, as well as in foods and for technology applications[11].

Surfaces consist of two parts of a component of a series of tail hydrocarbons hydrophobic and polar heads a hydrophilic [12]. Surfaces in aqueous solutions be monomer, but at the critical micelle concentration tends linked consisting micelle[13].

Adsorption kinetics on the speed of the withdrawal of adsorbent particles from the solution and stock at adsorbent after overcoming all inter-molecular forces and implied that hinder the process. Adsorption kinetics of great importance, it determines the period of time during which the adsorption process occurs and reach equilibrium after which stop adsorption process adsorption in the solution[15].

The aim of this study is to find out the possibility of adsorption ion lead duo from aqueous solutions on the micelles selected, and study the best conditions that can increase the amount of adsorption of lead-contaminated environment.

EXPERIMENTAL SECTION

2.1.Materials: in this experiment using $Pb(N0_3)_2$99% sodium hydroxide99% and Hydrochloride 97% supplied by sigma-aldrich, surfactant, Cetyl trimethyl ammonium bromide(CTAB) 99% supplied CDH Sodium dodecyl sulfate. 99.9% supplied Fluka and TritonX-100. 99.9% supplied Thomas B.

2.2 Preparation of Adsorbate: The reagent used was lead nitrate salt ($Pb(NO_3)_2$) without any purification directly from the company processes, and dissolve by deionized water 3.6821g of $Pb(NO_3)_2$ to obtain stock solution at concentration1000ppm, it was put in volumetric flaks 1000ml, and preparation stander solution from. Isotherm adsorption by taking (30)ml of different concentrations ion solution put in the 8 volumetric flax (100)ml and added (20)ml of CMC for each surface and placed in a water bath provider Shaker in (298)$\overset{o}{K}$ and speed (150)rpm. Subsequently measurement by uv -visible spectrophotometer to determine the quantity adsorption by surfactants Q_e mg/g. by calculated from equation

$q_e =[\overset{o}{C} -C_e]V/M$…………[1]

Where : Where, Ce and C^{o} are the ion concentrations (mg/l) at initial and any time concentration respectively, V the volume of the ion solution, and M the mass of adsorbent used.

2.3. Determine the Critical Micelle Concentration: It was appointed CMC for solution SDS, TritonX-100 and CTAB by dissolving 2.88g, 6.o2g and 0.364 of SDS, TritonX-100 and CTAB respectively by distilled water in the volumetric100ml to prepare the solution concentration of 0.1M of SDS and TritonX-100 and 0.01M for CTAB, from this solutions was prepare diluted solutions by used dilution law at concentration ranges between ($1x10^{-2}$-$9x10^{-2}$) M CMC of SDS, Triton X-100 and CTAB respectively.

2.4. Determine equilibrium time: To determine the best equilibrium time between surfactants and Pb(II) carried out by taking 20 ml of the surface and the addition of a 30 ml of the ion solution in volumetric flax 50 ml and placed in a water bath shaker provide, pulled samples at different time periods. Best tim of SDS, TX-100 and CTAB (25,20 and 35) respectively.

RESULTS AND DISCUSSION

Polar solvents such as water, amphiphilic surfactant monomers a compilation of to form a micelle such a way that their hydrocarbon tails crowd in the core of the micelle, and the polar head outer to face polar solvent locate at the micelle-water[15]. Adsorption isotherm tests for aqueous solutions containing Lead(II) carried out at the concentrations (10-80)ppm at pH(4–11) were performed at(298)$\overset{o}{K}$ at all three surfactants(SDS, TX-100 and CTAB). Data wee showing beast result quantity adsorption on SDS surface and at PH4 this is result of increase the intensity of the positive charge on the positive ion and thus increase forces of attraction between the anion surface. But on cationic surface (CTAB) the adsorption was lease than SDS and TX-100 as result of replication forces between negative charge on surface and ion. Adsorption onto surface depending on m

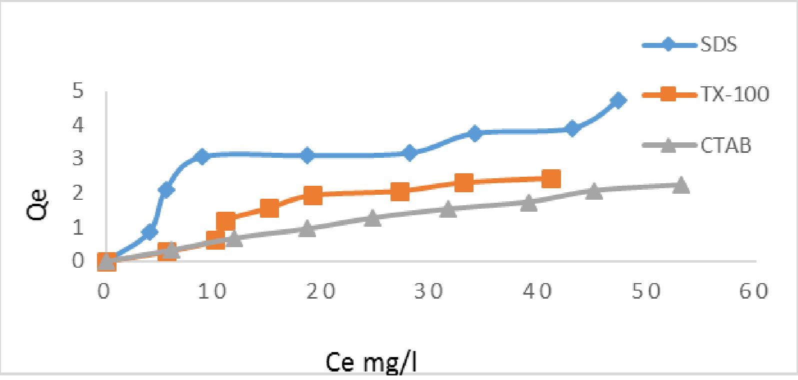

Fig. 1. Adsorption isotherm Pb^{+2} onto three surfactants (SDS, TX-100 and CTAB) neutral PH solution temperature 298K̊

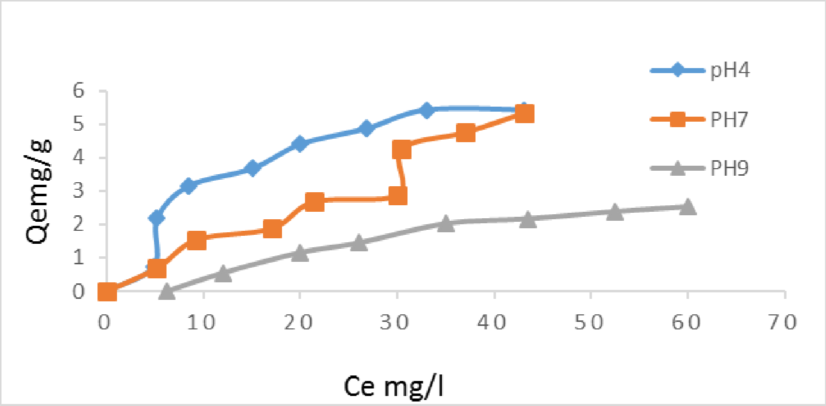

Fig. 2. Adsorption isotherm Pb^{+2} onto SDS surfactant at PH (4, 7 and 9) with solution temperature 298K̊

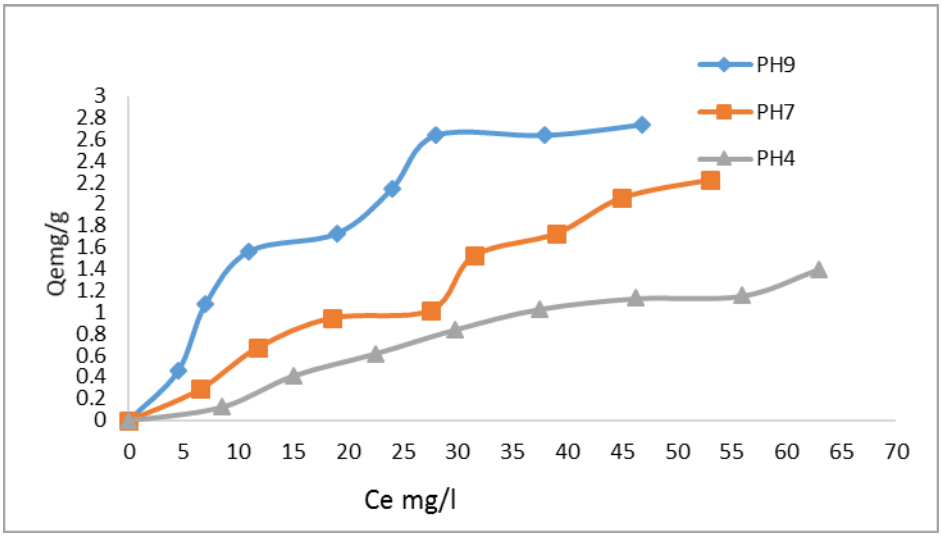

Fig. 3. Adsorption isotherm Pb^{+2} onto CTAB surfactant at PH (4, 7 and 9) with solution temperature 298K̊

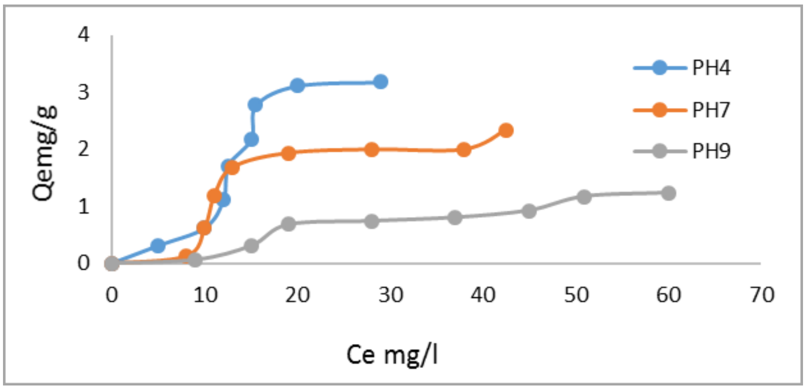

Fig. 4. Adsorption isotherm Pb^{+2} onto TX-100 surfactant at PH (4, 7 and 9) with solution temperature 298$\overset{o}{K}$

Effective the temperature on adsorption isotherm:

Many factor effective on CMC such as temperature, hydrocarbon chain length and the presence of salts and organic compensators; the amphiphiles have different CMC value according change condition[16-17]. At temperatures of 35 $\overset{o}{K}$ to 55 $\overset{o}{K}$ was used CMC slightly higher than the user when at 293 $\overset{o}{K}$ and 298 $\overset{o}{K}$, that shown in fig.(5,6 and 7). The experimental results indicate that the adsorption of the ion on the three surfaces (SDS, TX-100 an CTAB) least increase the temperature and this is accordance with the thermodynamic properties of adsorption, adsorption exothermic process and that this result is accordance with the Gibbs equation that mining the quantity of adsorption decrease with increase temperatures[18] and can be explain why this happens by two main reasons are first The increase in temperature increases the tendency of molecules to escape from the overlapping area and then reduce the quantity of adsorption[19]. And other the temperature affects the ionization of the adsorbent If increased solubility high temperature, it will lead to a decrease of adsorption[20]. All batch experimental data were applicable onto the isotherm models which well-known Freundlich and Langmuir shown at fig 8 and 9. At Langmuir model was depended on the idea that the maximum adsorption occurs at monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is fixed and there is no mobile of adsorbate molecules in the surface. The Langmuir isotherm is given by.

$$qe = \frac{q_m K_L C_e}{1+K_L C_e} \quad \ldots\ldots\ldots\ldots(2)$$

q_m and K_L are Langmuir constant determined from experimental data by linear regression by plotting (C_e/q_e) versus (C_e) that shown at fig. 8.

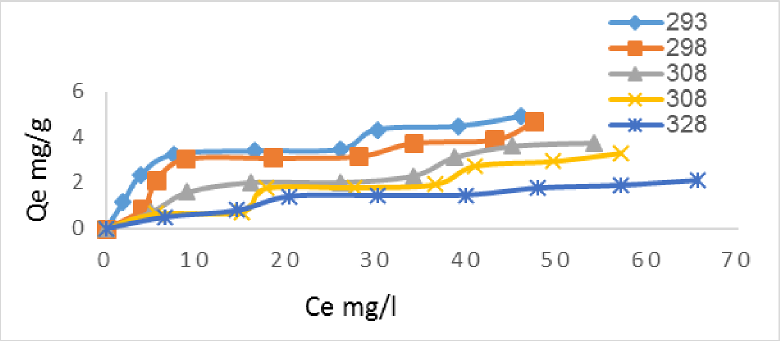

Fig. 5. Adsorption isotherm Pb^{+2} onto SDS surfactant at neutral PH with solution temperature (293, 298, 308, 318 and 328)

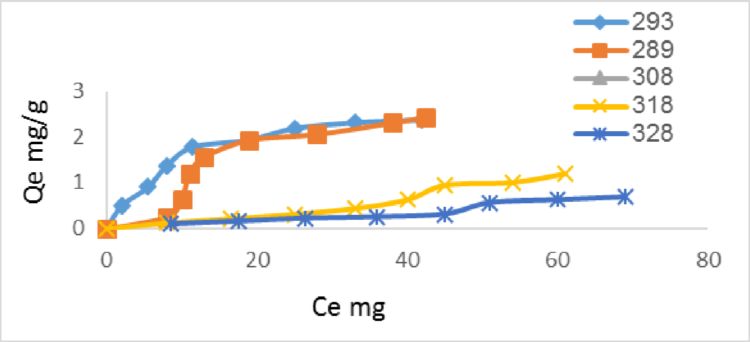

Fig. 6. Adsorption isotherm Pb^{+2} ontoTX-100 surfactant at neutral PH with solution temperature (293, 298, 308, 318 and 328

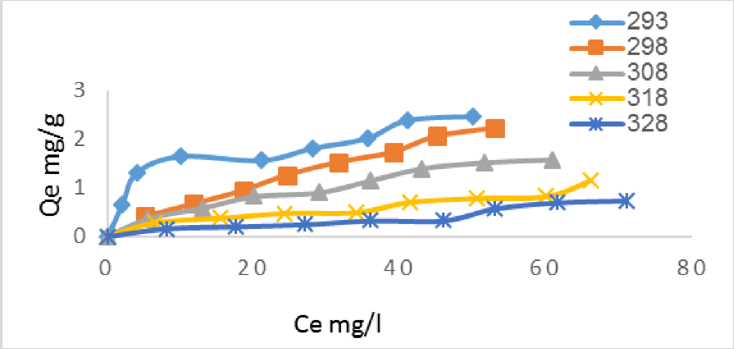

Fig. 7. Adsorption isotherm Pb^{+2} onto CTAB surfactant at neutral PH with solution temperature (293, 298, 308, 318 and 328)

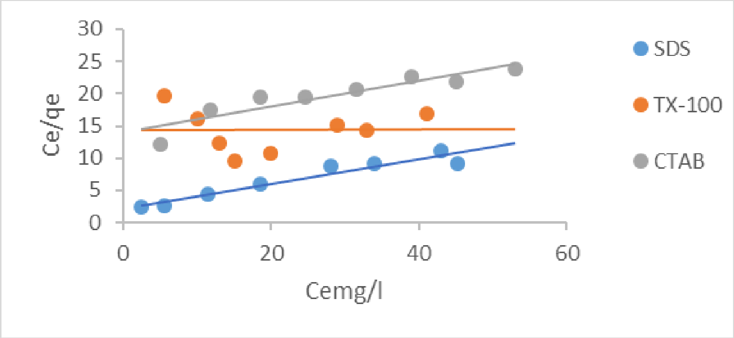

Fig. 8. Linearized Langmuir isotherm models for Pb^{+2} adsorption by the (SDS, TX-100 and CTAB) adsorbent at 298 K, adsorbent dosage, (10-80) mg/L

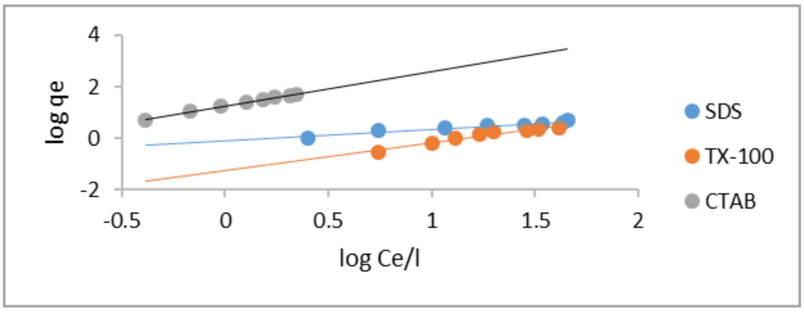

Fig. 9. Linearized Frendlich isotherm models for Pb^{+2} adsorption by the (SDS, TX-100 and CTAB) adsorbent at 298 K

Table 1. Parameters of Langmuir and Freundlich adsorption isotherm models for Pb^{+2} on to (SDS, TX-100and CTAB) adsorbent at 298K$^{\circ}$

Surfactants	Frandluch			Langmuir		
	K_f	n	R^2	K_L	q_m	R^2
Sodium dodecyl sulfate	-0.362	13.36898	0.933	-1.9491	5.21	0.922
Triton X-100	0.06	0.741	0.932	-8.988	9.0.5	0.178
Cetyl trimetheyl Ammonium Bromide	0.1	0.793	0.992	13.78	5	0.832

Thermodynamic study

Thermodynamic apply only when the adsorption isotherm equilibrium This means that any point can be accessed from either direction by adsorption or desorption at pressure and temperature constant[21]**.**

Thermodynamic parameter value obtain from plot between ($\log X_m$) and inverse temperature (1/T) by using Van 't Hoff plot the date view at table 2 and depending on (Clausius –Clapeyron) [22].

logXm = -ΔH/2.2303RT………….(3)

and obtain free energy (ΔG) from

ΔG= -RT ln Qe/Ce…..................(4)

From the gibbs eqution having ΔS entropy

ΔG=ΔH-TΔS……….(5) [23]

The positive value for the Gibbs free energy for Lead adsorption shows that the adsorption process is non-spontaneous and the degree of spontaneity of the reaction decreases with increasing temperature. Results showed that the adsorption processes on the three surfaces decreases with increasing temperature and the above-mentioned reasons. Positive charge of entropy ΔS that mean a redistribution process of energy between the adsorbate and the adsorbent. Adsorption is thus probably occur non spontaneously at normal and higher temperatures because ΔH< 0 and ΔS < 0

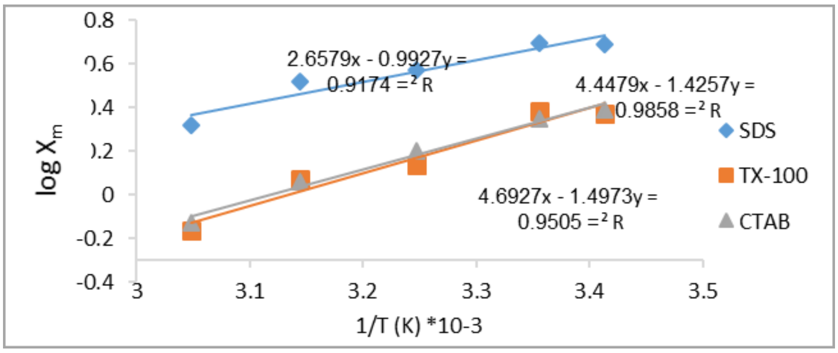

Fig.10 Van't Hoff schem

Table 2. Values of thermodynamic data for Adsorption of Pb^{+2} onto (SDS, TX-100 and CTAB) at 298K and 80mg/L from aqueous solutions

Surfactant	ΔH	ΔG	ΔS
Sodium dodoacyl sulfate	-3.986	2.372	-2.372
TritonX-100	-2.13	3.04	-3.048
Cytayl trimethyl ammonuim bromide	-3.053	3.412531	-3.402

Adsorption kinetics

The kinetic models which has been working out in this study are the pseudo-firstorder and pseudo-second-order equations which were used to determine the model that best described the adsorption of Pb(II) kinetics study was carried out at 60 mg/L and 298^{o}K onto SDS, TX-100 and CTAB. Pseudo-first-order model is given as:

ln (qe−qt) = ln qe − K_1t…..(6)

where qe and qt are the quantity of Pb^{+2} adsorbed (mg/g) at equilibrium and at time t (min) respectively, K_1 is the rate constant of pseudo-first-order adsorption (min−1), Pseudo-second-order equilibrium adsorption is given by:

$$\frac{t}{qt} = \frac{1}{K2\ qe2} + \frac{t}{qt} \ldots\ldots\ldots\ldots\ldots (7)$$

where k_2 (g/mg min) is the second-order adsorption rate constant. According to the values of R^2 will be high wherever followed is kinetic .we can see that the degree of fit R^2 for the pseudo-First-order kinetic model is large than R^2 of pseudo- second- order. From these figures, the values of K_1 and q_e were determined from the slope and intercept plots respectively.

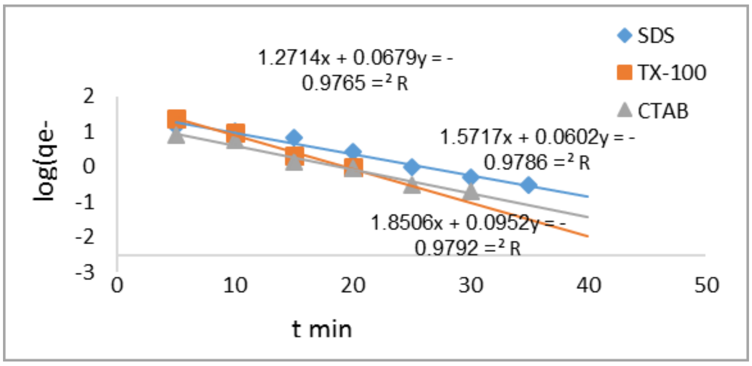

Fig.11. Pseudo-first order for Pb^{+2} onto (SDS, TX-100 and CTAB)

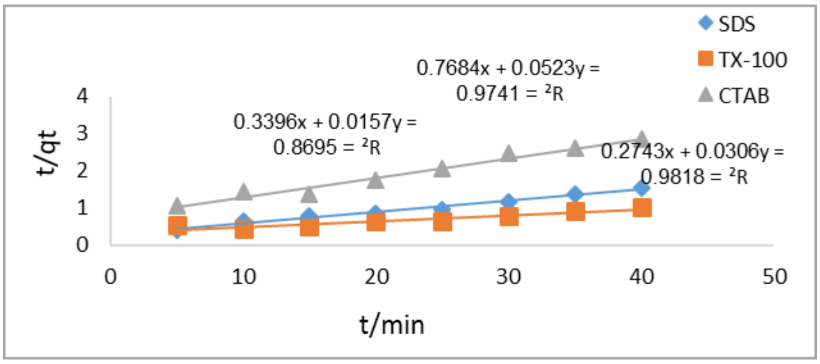

Fig.12. pesudo -second order for Pb^{+2} onto (SDS, TX-100 and CTAB)

CONCLUSION

The surfactants can using to treatment the aquatic contamination by lead (II) the adsorption process decrease with increase temperature and the type adsorption was physical adsorption , non spontaneous process this can be observed through the free energy value . The best quintity adsorption shown on SDS surface at PH4 and TX-100 PH4 than CTAB at PH9.

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