# Removal of Pb (II) Ion and Safranin Dye from Aqueous Solution by Sheep Wool

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**ABSTRACT:** *The ability of sheep wool to remove Pb(II) ions and safranin dye from aqueous solutions through the adsorption process was investigated at room temperature. The metal ions concentration was determined by flame atomic absorption spectrophotometer method. The influence of pH, contact time, amount of adsorbent, temperature and initial metal ions concentration were examined by the batch method. The experimental data were analyzed using the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm equations. The correlation coefficients were determined by analyzing each isotherm. The results indicate that the experimental data show better correlation with the Freundlich isotherm for Pb(II) ion and Langmuir isotherm for safranin dye than other isotherms. Thermodynamic parameters such as Gibbs free energy enthalpy and entropy have also been evaluated and it has been found that the sorption process was feasible, spontaneous and exothermic. The maximum amounts of Pb(II) and safranin dye adsorbed ($q_m$), that show in order of 12.787 mg/g for Pb(II) and 4.6533 mg/g for safranin of sheep wool. The morphological analysis of the sheep wool was performed by the Scanning Electron Microscopy (SEM).*

**KEYWORDS:** *Sheep wool; Isotherms; Kinetics; Thermodynamics; Removal.*

## INTRODUCTION

Lead is one of the potentially toxic heavy metals when adsorbed into the body. For the last few decades the pollution of water resources due to indiscriminate disposal of lead metals has been creating a worldwide threat. Lead is not biodegradable and can accumulate in living tissues, thus becoming concentrated throughout the food chain and can be readily absorbed into the human body. The presence of lead in drinking water even at low concentration levels may cause diseases such as anemia, encephalopathy, hepatitis, and nephritic syndrome. Lead is released into the environment in several ways, including lead-acid batteries, pulp, and paper, petrochemicals, refineries, printing, pigments, photographic materials, explosive manufacturing, ceramic, glass, paint, oil, metal, phosphate fertilizer, electronic goods, wood production and also combustion of fossil fuel, forest fires, mining activity, automobile emissions, sewage wastewater and sea spray [1-2]. The discharge of toxic heavy metal ions into the environment is a serious pollution problem affecting water quality. Major sources of water pollution with heavy metals are plating plants, mining, metal finishing, welding, and alloys manufacturing. Several methods have been applied during many years for the elimination of these metal ions present in the industrial wastewater. The traditional methods commonly used for removal of heavy metal ions

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from aqueous solutions include ion-exchange [3-5], solvent extraction, chemical precipitation, nano-filtration, reverse osmosis, and adsorption. Adsorption is an alternative technique for heavy metal removal. The activated carbon is the most widely used adsorbent material. The use of activated carbon is expensive for the regeneration required. Losses during the application processes could make it even more expensive. Many researchers have been investigating new adsorbent materials as an alternative to activated carbon, such as seaweeds, marine algae, clays, activated sludge biomass, perlite and maple sawdust for the removal of heavy metal ions from wastewater. The heavy metal ions are not only toxic to living organisms in water but also cause harmful effects to land animals including humans through food chain transfers. In living organisms, heavy metal ions can particularly bind to nucleic acids, proteins, and small metabolites. The contaminated organic cells are altered or missed their biological functions with losing the homeostatic control of essential metals, resulting in fatal health problems [6, 7]. Therefore, it is necessary to eliminate such hazardous heavy metal ion in wastewater before discharging it into the ecosystem. Several techniques, such as ion exchange, chemical precipitation, membrane processes, electro-dialysis and adsorption have been developed for the removal of heavy metals from aqueous media. Among these purification methods, the adsorption process using adequate adsorbents is considered as one of the most efficient and economical techniques in the viewpoint of simple design and facile handling. Numerous efforts have been contributed to the development of effective adsorbents like activated carbon, chitosan, zeolite, polymer, functionalized silica and clay [8-10]. Besides, there is also a huge interest to adsorption on metallic and coated surfaces in the field of petroleum science. Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a molecular or atomic film (the adsorbate). It is different from *absorption*, in which a substance diffuses into a liquid or solid to form a solution. The term *sorption* encompasses both processes, while *desorption* is the reverse process. Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, synthetic resins, and water purification. Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption [11, 12].

Wool is a reactive material because of its main functional groups, including peptide bonds, side chains of amino acid residues and disulfide crosslinks [13]. Wool is known to bind a wide range of metal ions, such as mercury, copper, aluminum, nickel, zinc, cobalt, chromium, silver and gold [14]. There have been many reports where native wool fibres, chemically-modified wool fibres and regenerated wool protein [15] have been used to remove metal ions from industrial effluent and/or recover precious metal ions from solution.

## EXPERIMENTAL SECTION

### *Equipment and apparatus*

The adjustment̓s of pH were made with digital pH-meter using HCl (0.1 mol/L) and NaOH (0.1 mol/L).

Incubator**,** The incubator device is equipped by a shaker that gives an ability to the device that can be regulated from 20 to 200 cycles in a minute. And the temperature range of this device is between -5 to +60 degrees of Celsius.

### *Preparation of adsorbent*

The adsorption process is one of the best possible choices for the transfer of heavy metals from aqueous solutions Sheep wool is biological adsorption due to the negative charges on the outer layer, this charges will have the ability to attract positive ions .As it was carefully examined (discarded waste sheep wool). We can use it for removing heavy ions from the solution and therefore reduced the environmental problems. Collected sheep wool was rinsed with proper detergents and distilled water and then dried, crushed so that their sizes were in the order of millimeters, which will be used for the adsorption process

***Preparation of aqueous solution***

A stock solution of Pb(II) ion was prepared with their respective salts by carefully weighing out 1.6 g of $Pb(NO_3)_2$. And also the 1 gram of safranin dye was weighing. And they were both dissolved in a 1000 mL volumetric flask and diluted with distilled water to the mark, which gave of concentration of 1000 mg/L. Successive dilutions were made, first, by preparing a concentration of 100 mg/L from the 1000 mg/L stock solution, by pipetting 10 mL of the solution into a 100 mL volumetric flask and making up to the mark with distilled water. Successive dilution of the 100 ppm was used to prepare different concentrations.

***Adsorption Experiments***

To determine the effect of physicochemical parameters such as pH, Adsorbent dose, contact time and initial metal ion concentration of the solution. The adsorption experiments were performed by the batch equilibrium method. The initial pH of solutions was adjusted by 0.1 M NaOH or 0.1 M HCl. All experiments were performed at room temperature and kept for stirring for a given period.

Thereafter the mixture was centrifuged and the initial and final metal and dye ions concentrations were determined by flame atomic absorption spectrophotometer and UV visible spectrophotometer device. The removal of metal ion and the amount of metal ion adsorbed on human hair ($q_e$) was calculated by Eqs. (1) and (2), respectively:

$$\mathrm{Removal}(\%) = 100\frac{(C_0 - C_{eq})}{C_0} \tag{1}$$

$$q_e = \frac{(C_0 - C_{eq})V}{m} \tag{2}$$

Where $C_0$ and $C_{eq}$ are the initial and final (equilibrium) concentrations of the Pb (II) and safranine ions in solution (M), $V$ the solution volume (l) and the $m$ is the mass of human hair (g).

## RESULTS AND DISCUSSION

***Characterization of the adsorbent***

Characterization of the adsorbent was investigated by Scanning Electron Microscopy (SEM) investigations. Scanning Electron Microscopy (SEM) of material used was carried out in a Vpleo1455. To see the surfaces of sheep wool after and before modified by treating with $HNO_3$. Fig. 1 shows SEM images of wool. In this form the cuticle layer, which is composed of flaky cells, is visible. Fig. (1.a) shows the SEM images of the wool that has been washed with distilled water, while the appearance of wool has not changed. Fig. (1.b) shows the surface of the wool and rinsed with 0.1 M acid and Fig. (1.c) the apparent image of the wool was washed with 1 M acid, the loss, and fragmentation scales on the cuticle layer is displayed.

***Effect of pH***

The effect of pH of a solution is an important controlling factor in the adsorption experiment. To study the effect of pH on adsorption, experiments were carried out in the pH range 2–9 for Pb(II) and 2–8 for safranin dye. The amount of metal and dye ions removed by the substrate at low pH of 1, 2, and 3 were low compared to pH of 6 and 7. This may be due to an increase in competition between the hydrogen ion and the metal and dye ions, because at this pH value, the concentration of hydrogen ion is high. Concerning the (Fig. 2a- b), for safranin dye and Pb(II) in order of pH=7 and pH=6 as the optimal pH chosen, and was used continuously in the experiments.

***Effect of adsorbent dose***

The Figs. (3.a) and (3.b) show that the amount of Pb(II) and safranin ions removed as dosing mass was increased. The increase in metal and dye uptake with an increase in the dose of adsorbent from 0.01 – 0.06g for Pb(II) and 0.025 – 0.25g for safranin were due to the increase in surface area and several active sites for the adsorption. The result shows that the adsorbent of metal and dye ions increased in order from 57 to 88% and 63 to 82% for Pb(II) and safranin respectively. Further increase in adsorbent dose, it did not cause any significant increase in % removal of metal and dye ions. This was due to the concentration of metal ions reached an equilibrium status between the solid and solution phase. With increasing in the amount of adsorbent, the number of available positions is increasing which leads to an increase the number of adsorbate ions. Therefore the amount of 0.15 g and 0.03 g for safranin and Pb(II) was chosen as the optimal amount.

***Effect of contact time***

With increasing the time of contact of ions and adsorbent the number of encounters will increase and

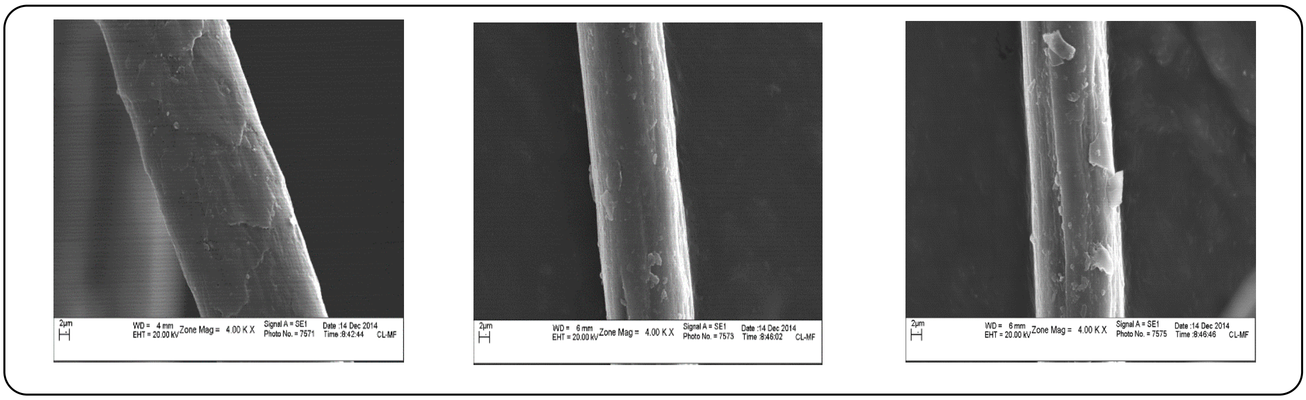

*Fig. 1: SEM micrograph of surfaces of sheep wool after washed with distilled water (a) with 0.1 M acid (b) with 1 M acid (c)*

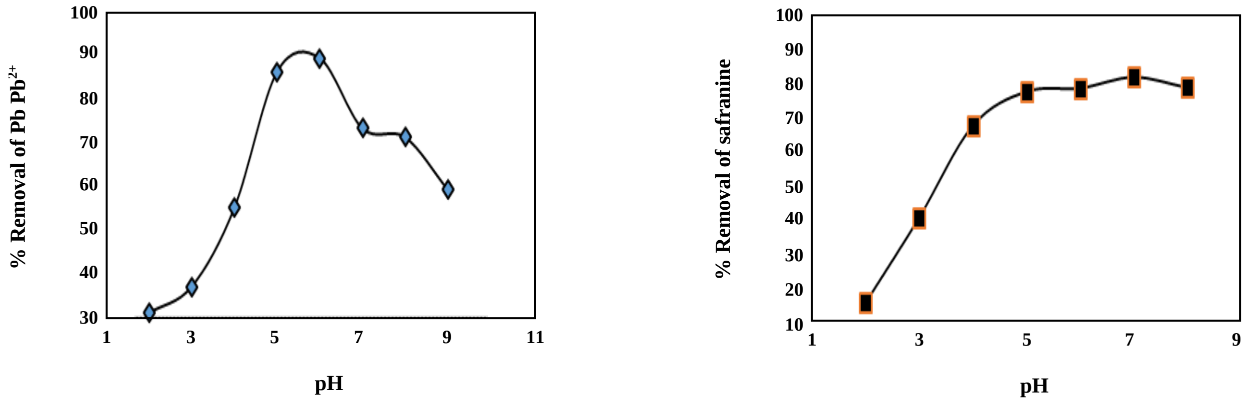


*Fig. 2: (a) Effect of pH on adsorption of Pb (II) on sheep wool. (b) Effect of pH on adsorption of safranine on sheep wool.*

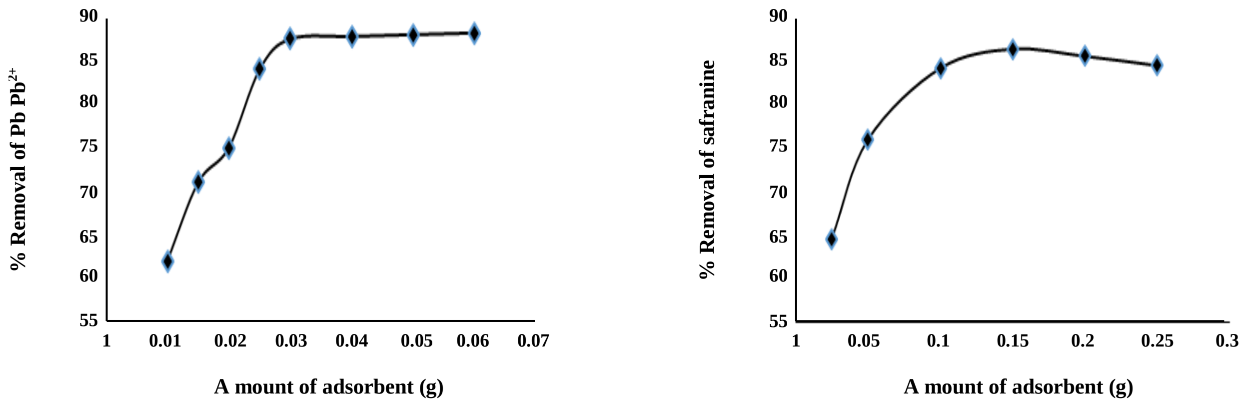


*Fig. 3: (a) Effect of adsorbent dose on adsorption of Pb (II) on sheep wool. (b) Effect of adsorbent dose on adsorption of safranine on sheep wool.*

then almost moved to the constant amount. So, the time-lapse cannot affect on the adsorbent efficiency. So that the equilibrium happened between the adsorbent and solution after the optimal time and the contact between the adsorbent and adsorbate after the balancing time does not have any effect on the amount of adsorption. Concerning the (Fig. 4a- b), 15 minutes is for safranin dye and 40 minutes is for the Pb(II) as the optimal time.

### *Effect of initial metal ion concentration*

In the ions solution the adsorption capacity is increased by increasing the ion concentration.

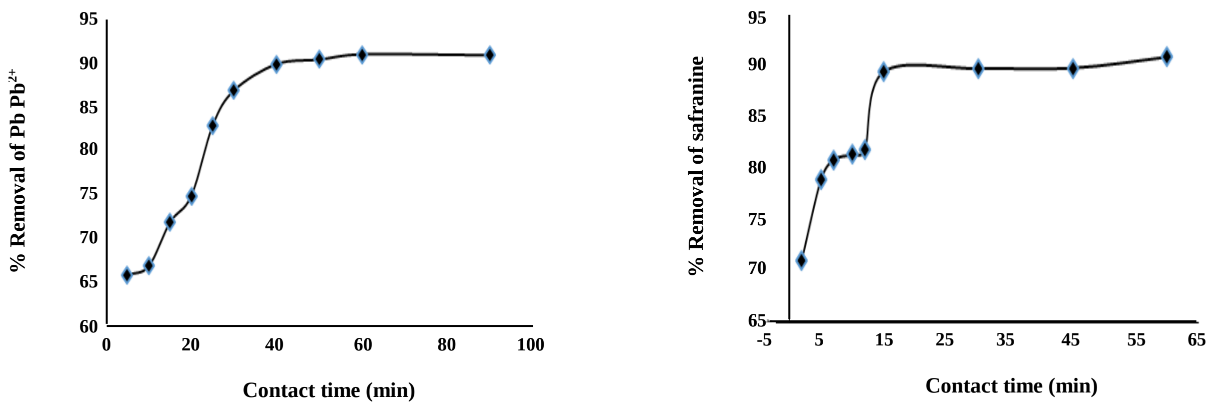


***Fig. 4:** (a) Effect of contact time on adsorption of Pb (II) on sheep wool. (b) Effect of contact time on adsorption of safranine on sheep wool.*

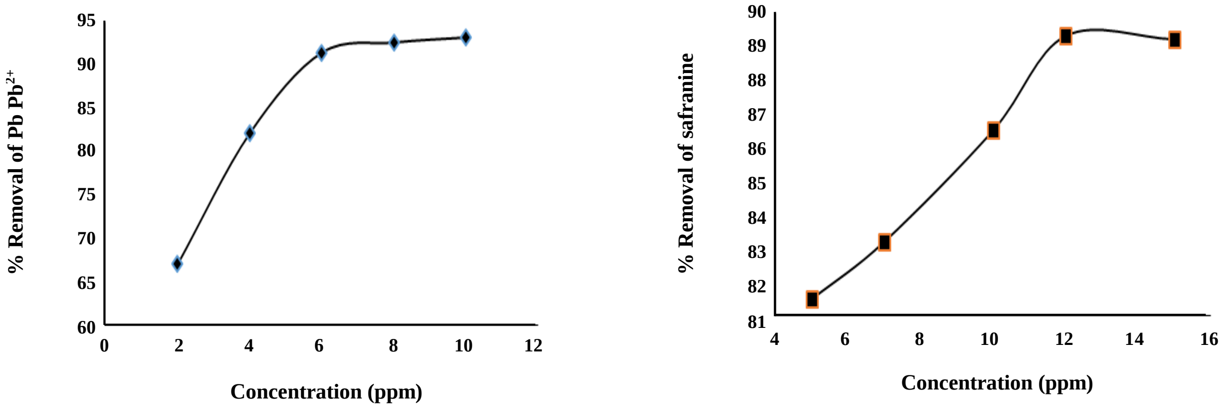


***Fig. 5:** (a) Effect of Initial metal ion concentration on adsorption of Pb (II) on sheep wool. (b) Effect of Initial metal ion concentration on adsorption of safranine on sheep wool.*

Therefore increasing the ion concentrations, leads to the enhancement of the collision between the ions and the adsorbent, which accelerates the adsorption process. The effect of different concentration of Pb(II) and safranin on the adsorption has been investigated at 295 K for Pb(II) and 298 K for safranin, Pb(II) and safranin adsorption capacities of sheep wool were given as a function of initial concentration in (Fig. 5a- b). Concerning the figures, 8 ppm of concentration was obtained for Pb (II) as Fig. (5.a) and 12 ppm was obtained for safranin as the Fig. (5.b).

If the same ion concentration in the solution is the higher sorbent active sites of metal ions surrounded by a larger and more efficient adsorption process are done. Therefore, concerning the (Fig. 6a- b), the adsorption capacity ($q_e$) increases with an increasing initial concentration of metal and dye ions [15].

Maximum adsorption capacity, $q_m$, for complete monolayer coverage is 12.787 mg/g for Pb(II) and 4.6533 mg/g for safranin. Comparison of $q_m$ of the present study with a few other adsorbents used in the past, revealed that the adsorption capacity of sheep wool is very high. (Table 1) $R^2$ (correlation coefficient) values approaching one, clearly suggest that Langmuir isotherm holds good to explain adsorption of Pb(II) and safranin hold good on sheep wool. Freundlich isotherm for both ions is shown in (Fig.8a –b) and the corresponding parameters are given in Table 1. n is the measure of adsorption intensity of cations on sheep wool. For Pb(II), 1/n is equal to 0. 4170 whereas it is 0.5656 for safranin. $K_F$ (ultimate adsorption capacity), as calculated from Freundlich isotherm is 10.3585 for Pb(II) and 1.6861 for safranin. $R^2$ values given in Table 1, indicate that isotherm holds good for Pb (II).

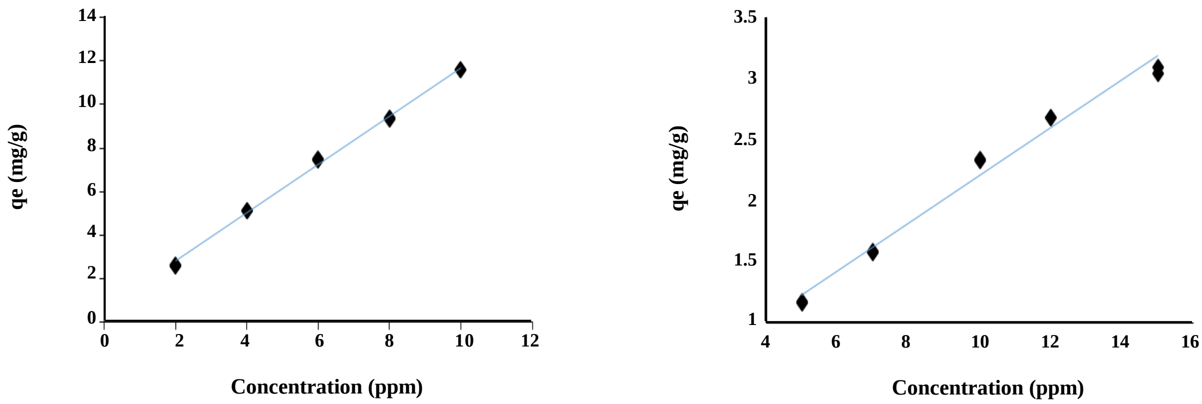


*Fig. 6: (a) the amount of $q_e$ at the different concentrations of Pb (II) solution. (b) The amount of $q_e$ at different concentration of safranine solution.*

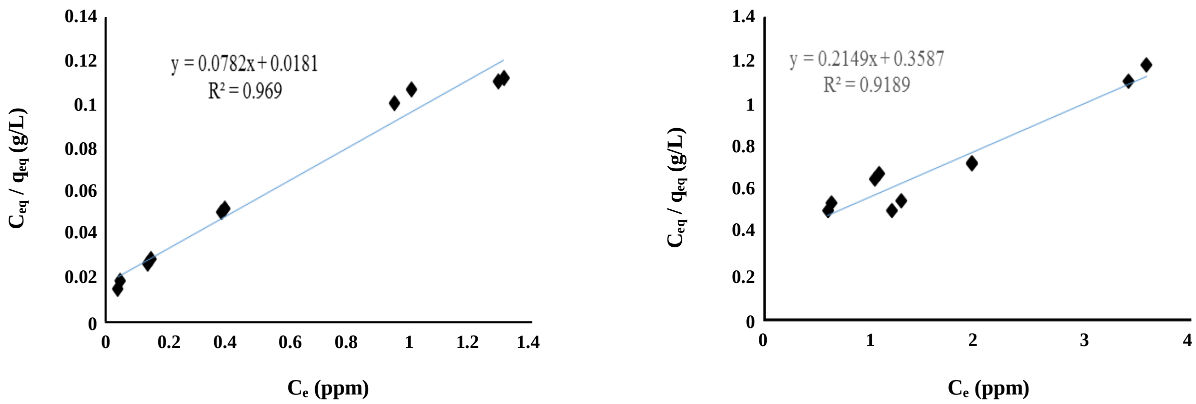


*Fig. 7: (a) Langmuir adsorption isotherm for Pb (II) at 295 K. (b) Langmuir adsorption isotherm for safranine at 298 K.*

***Adsorption Isotherm***

The purpose of this section to find the model that is known to be able to describe the experimental data obtained in vitro.

These models can be useful and practical information about the capacity of the metals are adsorbed by various structures. The adsorption curve of the relationship between the amount of sample adsorbed by the adsorbent and the amount of binding remaining in solution is described. Data can be obtained using the information about the mechanisms of adsorption and surface properties and the affinity of the adsorbent to adsorb achieved. To understand the interaction between the adsorbent and the adsorption isotherms of adsorption capacities, especially for the removal of heavy metals is widely applied. The different adsorption curves plotted in mind - capturing the correlation coefficient of the equation, they can adsorb and understand the data capture process such as the constant adsorption phase of the capacity for the adsorption of the analysis measured. The model of adsorption isotherms for the interaction of metal and dye ions with the adsorbent is used [16]. $R^2$ coefficient indicates the amount of the desired temperature is consistent with the experimental data [17].

Langmuir isotherm for Pb(II) and safranin is shown in Fig.7a- b and the related parameters of the isotherm are given in Table 1.

Temkin isotherm for Pb(II) and safranin is shown in Fig.9a- b and the related parameters are given in Table 1. $B_1$, related to the heat of sorption, is 2.4952 and 1.1346 J/mol, for Pb(II) and safranin, respectively.

***Effect of temperature and thermodynamic parameters***

The effect of temperature on the adsorption of Pb(II) and safranin on sheep wool was investigated at 273, 283, 293, 303, 313, 323 and 333 K. It was observed that

***Table 1: Langmuir, Freundlich and Temkin adsorption isotherms constants***

| | Langmuir Isotherm | | | Freundlich Isotherm | | | Temkin Isotherm | | |
|---|---|---|---|---|---|---|---|---|---|
| | $q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $K_F$ (mg/g) | 1/n | $R^2$ | $b_t$ (kJ/mol) | $K_T$ (L/mg) | $R^2$ |
| **Pb (II)** | 12.787 | 4.320 | 0.969 | 10.358 | 0.417 | 0.974 | 0.983 | 57.338 | 0.972 |
| **Safranine dye** | 4.653 | 0.947 | 0.919 | 1.686 | 0.565 | 0.873 | 2.183 | 4.811 | 0.912 |

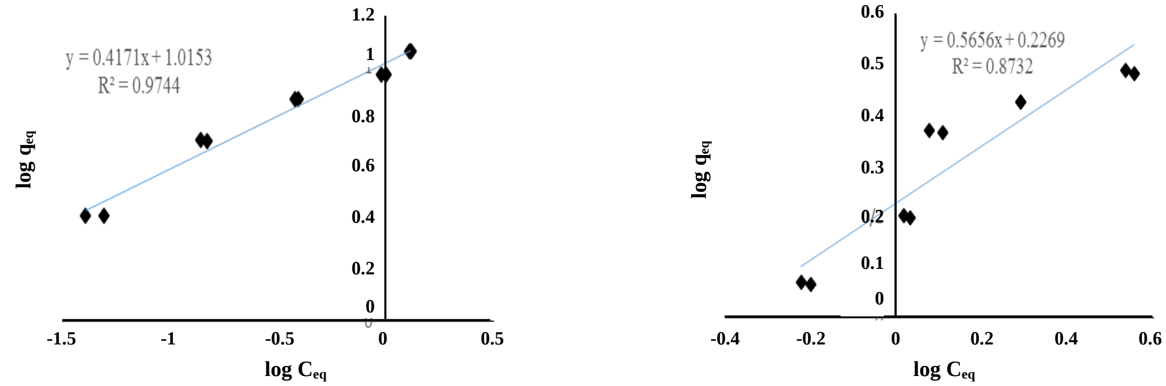


***Fig. 8: (a) Freundlich adsorption isotherm for Pb (II) at 295 K. (b) Freundlich adsorption isotherm for safranine at 298 K.***

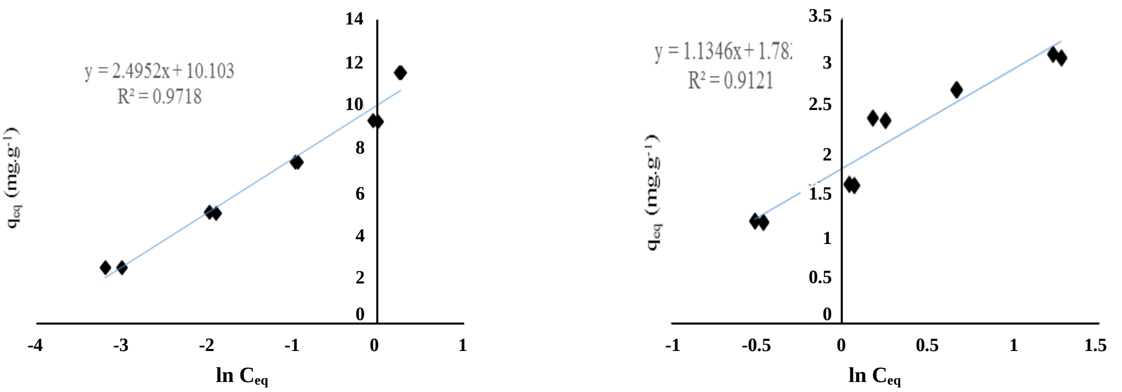


***Fig. 9: (a) Temkin adsorption isotherm for Pb (II) at 29 K. (b) Temkin adsorption isotherm for safranine at 298 K.***

on increasing the temperature percentage removal of ions increased. This showed that the adsorption process was endothermic.

Thermodynamic parameters such as a change in standard Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated using the following equations:

$$K_C = \frac{C_{ad,eq}}{C_{eq}} \tag{3}$$

Where $C_{ad,eq}$, and $C_{eq}$ is the concentration of ions on the adsorbent and residual concentration at equilibrium respectively.

$$\Delta G^\circ = -RT \ln K_c \tag{4}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

$$\ln K_C = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{6}$$

ΔH°, ΔS° and ΔG° are changed in standard enthalpy (kJ/mol), entropy (J (mol K)$^{-1}$) and free energy (kJ/mol), respectively. R is the universal gas constant (8.314 J/mol.K) and T is the temperature (K).

***Table 2: Thermodynamic parameters for adsorption Pb (II) and safranine on sheep wool.***

| | ΔH (kJ/mol) | ΔS° (kJ/mol) | ΔG° (kJ/ mol) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 273 K | 283 K | 293 K | 303 K | 313 K | 323 K | 333 K |
| Pb (II) | - 39.789 | -0.111 | -9.203 | -8.354 | -7.193 | -5.737 | -5.050 | -4.277 | -3.452 |
| Safranine | -7.095 | $-6.8 \times 10^{-3}$ | -5.224 | -5.148 | -5.077 | -5.007 | -4.939 | -4.871 | -4.396 |

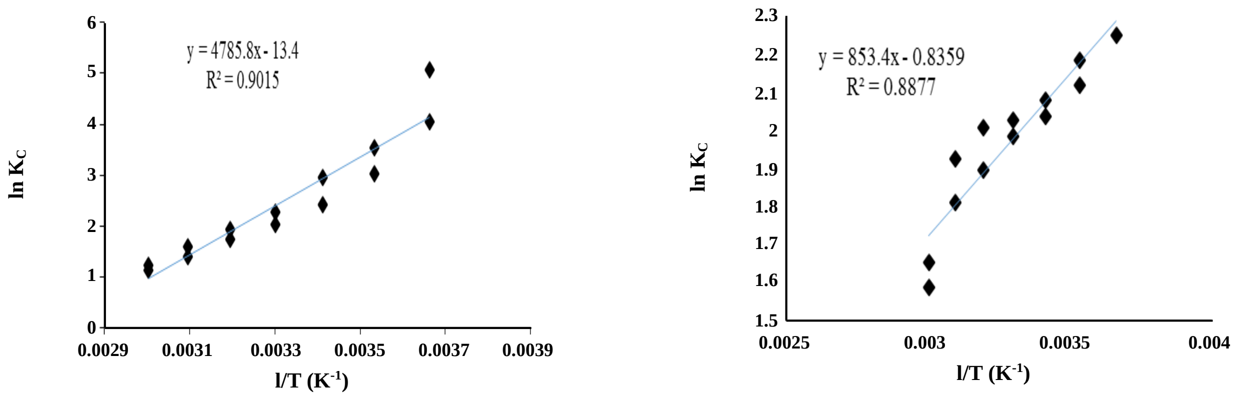


***Fig. 10: (a) .ln $K_c$ vs. 1/ T plot for Pb (II). (b) ln $K_c$ vs. 1/ T plot for safranine dye.***

The values of ΔH° and ΔS° were obtained from the slopes and intercepts of the Van't Hoff plots of ln $K_c$ vs. 1/T, respectively, thereafter ΔG° values were determined from Eq. (5). The values of thermodynamic parameters are presented in Table 2. The results showed that the ΔG° values are negative and decreased in their absolute values with temperature [18].

This result suggested that a low temperature is favored for the adsorption of adsorbing on sheep wool. The values of heat of adsorption, ΔH° is negative for metal and dye ions, indicated that the adsorption process on sheep wool was exothermic. The negative value of ΔS° shows the decreasing randomness at the solid/liquid interface during the adsorption.

## CONCLUSIONS

The present work aims to investigate the ability of crushed particles of sheep wool to remove Pb(II) and safranin ions from aqueous solution. The results indicate that the Freundlich isotherm for Pb(II) ion and the Langmuir isotherm for safranin dye showed a better correlation with the experimental data than the other isotherms. The maximum adsorption capacity for Pb(II) and safranin ions were 12.787 and 4.653 mg per g of adsorbent. The thermodynamic parameters such as standard enthalpy change (ΔH°), standard entropy change (ΔS°) and standard free energy change (ΔG°) were also evaluated. These parameters indicated that the adsorption of Pb(II) and safranin ions were exothermic processes, absorption process was associated by decreasing the entropy.

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