A new approach to modification of an agro-based raw material for Pb(II) adsorption

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Abstract−This paper describes a relatively new and effective modification with thiourea of an agro-based raw material, sorghum biomass for adsorption of Pb(II) ions. The modification was done under microwave irradiation. Changes in characteristics of modified material were determined by FT-IR and CHNS analysis. Effect of adsorbent dosage, contact time, solution pH and temperature on equilibrium process was extensively studied. Famous equilibrium models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich) in non-linear fashion were applied to evaluate the equilibrium data using different initial concentrations of Pb(II) ranging from 20 mg/L to 300 mg/L. The adsorption process followed the pseudo-second-order kinetics. This paper also discusses the thermodynamic parameters (free energy, enthalpy and entropy) and reveals that the adsorption process is spontaneous. An appreciable increase in adsorption capacity of the modified adsorbent was observed, depicting the advantages of thiourea modification of sorghum biomass under microwave ir-radiation.

Keywords: Modification, Thiourea, Non-linear Modeling, Microwave Irradiation, Reaction Kinetic, Thermodynamics

INTRODUCTION

Heavy metals fit into the most imperative group of water pollutants. Potential toxic effects related with heavy metals accumulation in the environment are well known. Researchers have studied the harmful effects of heavy metals on human health [1,2].

Heavy metals are currently used in various industrial processes, such as metallurgy, mining, painting, smelting, batteries, and alloys [3-5]. Heavy metal ions are present at high concentration in industrial effluents and are often deposited directly in the environment without any pretreatment. Due to high toxicity of heavy metal ions in the environment, there is an increasing demand to eliminate or at least to reduce the concentration of heavy metal ions in industrial effluents prior to release into the environment. A list of 13 toxic metals was made by USEPA in 1978 (antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc) [6]. Among these, lead is considered to be a long lasting pollution, thus posing a serious environmental threat [7]. The permissible concentration of lead in drinking water suggested by USEPA is 0.015 mg/L [8].

Ion exchange, chemical co-precipitation, reverse osmosis, membrane filtration and adsorption are the most frequently used techniques to remove lead from wastewater [9]. Adsorption is by far the most promising, and activated carbon is usually used for the purpose. However, its use is very expensive; therefore, substantial concern has been diverted to evaluate cost-effective adsorbents [10]. Literature reports the removal of lead by cost-effective biological materials such as rice straw [11], wheat straw [12], banana peels [13], bagasse [14], agricultural and forest waste [15], and treated onion skins [16]. Some inorganic clay material such as bentonite

has also been reported for heavy metals adsorption [17,18].

Various methods, both physical and chemical, have been developed to enhance the adsorption capacity, to have information about the binding sites and to incorporate known functional groups with the biological materials [19-23]. Chemical modification alters the surface chemistry of adsorbent by incorporation of new functional groups or by changing the already existing functional groups. These new functional groups act as complexing/chelating agents for metal ions [24]. Thus, the modified biological material offers greater adsorption capacity due to increase in number of binding sites for metal ions. A relatively new modification of biological materials has been reported under microware irradiation, which is beneficial because of easy handling and eco-friendly nature. Also, the method does not require any solvent for modification [25-32].

The present study explains an entirely new modification (thiourea modification) of sorghum biomass and its use as a low cost adsorbent for Pb(II) remediation. Sorghum biomass is a plentiful waste agro-material because it is the fifth major cereal crop grown in the world [33]. The effect of various process parameters like adsorbent dose, contact time, solution pH, and temperature for unmodified (UMS) and thiourea-modified sorghum (TMS) was studied. A non-linear approach has been adopted to study the adsorption equilibrium using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models in order to reveal the information about the adsorption of Pb(II) ions. Kinetic models and thermodynamic parameters were also used to explain the adsorption mechanism.

MATERIALS AND METHODS

1. Preparation of Adsorbent

Sorghum biomass was obtained from a local market in Lahore, Pakistan. Later, the mass was washed with distilled water and dried in a drying oven at 70 ℃ till it became moisture free. The dried biomass was ground to a fine powder using a laboratory grinder and

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was sieved in the particle size range of 60-80 mesh (ASTM). The ground/processed material was stored in airtight plastic containers. This material was designated as unmodified sorghum biomass (UMS).

The sorghum biomass was modified by blending the dried sorghum biomass and thiourea (Sigma-Aldrich) in a ratio of 1 : 2 by mass and was exposed to microwave radiation (2,450 MHz) for a 9 minutes using a microwave oven (Dawlance). The resulting mass was then boiled in distilled water for 25-30 min and filtered while hot. The excess of thiourea was removed by frequent washing of the residue with hot water. The resulting mass was dried in an oven at 70 °C to constant mass. This was designated as thiourea-modified sorghum (TMS) and used for further study.

2. Chemicals, Equipment and Apparatus

High purity chemicals and reagents, purchased from Sigma-Aldrich (Taufkirchen, Germany) were used during the study. Batch experiments were performed in 250 ml conical flasks on top of orbital shaker (VORTEX Model-OSM-747). 0.1 M HCl and 0.1 M NaOH were used with pH adjustment using a digital pH meter (Adwa, AD-130). Pb(II) ions concentration was determined by atomic absorption spectrophotometer (Perkin Elmer, Model-AAnalyst 100) at 283.3 nm. FTIR (Perkin Elmer Spectrum-RX1) was used to characterize the adsorbent materials. Elemental analysis was performed using an elemental analyzer (Vario EL III Elementar).

3. Batch Adsorption Studies

Batch adsorption studies were performed to check the effect of various process parameters--variation in contact time, solution pH, adsorbent dose and temperature--on Pb(II) adsorption using UMS and TMS for an initial concentration of 50 mg/L. The effect of a certain parameter was studied by varying it gradually, keeping all other parameters constant. After the batch adsorption study under certain conditions, solutions were subjected to atomic absorption spectrophotometer to determine the remaining Pb(II) ion concentration. The adsorbent dose was varied in a range of 0.1 g/50 mL to 1.2 g/50 mL for both UMS and TMS to check its effect. pH 1-9 was varied to examine the most favorable pH for Pb(II) adsorption.

The contact time of 5-45 min was studied for different initial Pb(II) ion concentrations: 25 mg/L, 50 mg/L, 100 mg/L and 200 mg/L. Effect of temperature was also studied for the temperature range 10-40 °C. For equilibrium modeling, initial Pb(II) ion concentration was varied in the range of 20-300 mg/L to perform the batch experiments under the most favorable conditions obtained from a preliminary study of process parameters.

RESULTS AND DISCUSSION

1. Characterization of Adsorbent

Ground, dried sorghum biomass (UMS) was subjected to solid phase FTIR analysis for its characterization in terms of functional groups (potential adsorption sites). The spectrum shows the presence of various functional groups which may be considered as possible binding sites. A broad peak observed at 3,338.78 cm^{-1} indicates the presence of hydroxyl group (-OH). A peak observed at 2,918.30 cm^{-1} shows the presence of alkyl group (-R). The spectrum also indicates the presence of carbonyl group (C=O) having a peak at 1,637.56 cm^{-1}, and other peaks at 1,514.12, 1,421.54, 1,246.02 and 1,157.29 cm^{-1} indicate asymmetric stretching frequency of carboxylate ion (O=C-O$^-$) [34]. Thus, the FTIR spectrum indicates that UMS is rich in oxygen-containing functional groups.

The thiourea-modified sorghum (TMS) was also subjected to solid phase FTIR analysis. A notable change in spectrum was observed as illustrated in Fig. 1. The peak at 1,649.17, 3,612.67 cm^{-1} indicates the presence of primary amines. Very sharp peaks at 2,380.16 cm^{-1} and 2,305.79 cm^{-1} affirm the presence the isothiocyanates group (-N-C=S); the peak at 1,033.65 cm^{-1} also confirms its presence [35]. Peaks at 1,516.05, 1,460.11 and 1,417.68 cm^{-1} indicate the presence of carboxylate ion (O=C-O$^-$).

Comparison of the FTIR spectrum data for UMS and TMS affirms the incorporation of thiourea in the sorghum biomass. Thus, TMS becomes enriched with nitrogen and sulfur content as compared to UMS. In other words, the functionality the TMS has been increased
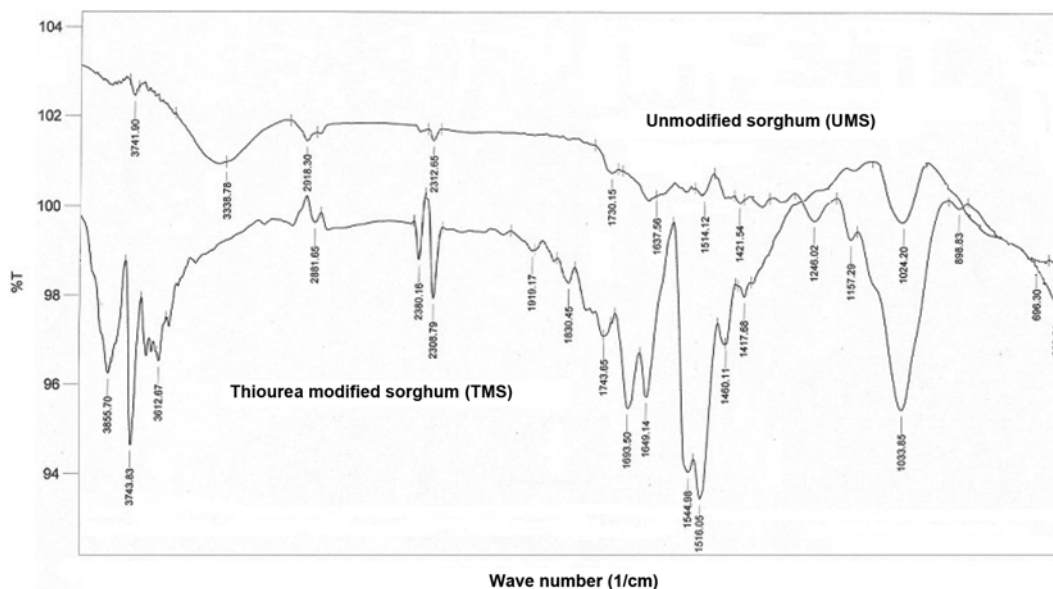

Fig. 1. FT-IR spectrum of UMS and TMS.

Table 1. Elemental analysis of modified (TMS) and unmodified (UMS) sorghum biomass

Elements	Unmodified sorghum (UMS)	Modified sorghum (TMS)
C (%)	44.51±0.50	44.29±0.30
H (%)	6.97±0.05	7.05±0.04
N (%)	0.86±0.05	9.37±0.05
S (%)	0.17±0.02	4.76±0.04

as compared to UMS, thus increasing more binding sites on surface of TMS for Pb(II) attachment.

$$\text{Sorghum} + N_2NCSNH_2 \xrightarrow[\text{09 mins}]{\text{Microwave Radiation}} \text{Sorghum-NHCSNH}_2$$
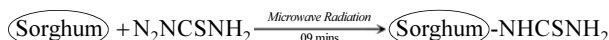
Both the adsorbents were also subjected to an elemental analyzer for the confirmation of this aspect. The data obtained from elemental analysis is in Table 1. The comparative data showed a significant increment of nitrogen and sulfur content in TMS, while carbon and hydrogen content remained almost similar on UMS and TMS. The obtained results thus reinforce the above conclusion that modification with thiourea increases the functionality in TMS in terms of nitrogen and sulfur bearing functional groups.

2. Effect of Adsorbent Dose

Experiments were conducted to check the effect of adsorbent dose on Pb(II) ion adsorption from its aqueous solution using an initial concentration of 50 mg/L of Pb(II), while the dose of UMS and TMS adsorbent varied in a range of 0.1-1.2 g/50 mL. Percentage adsorption efficiency and adsorption capacity (mg/g) is illustrated in a comparative plot (Fig. 2) for UMS and TMS. The plot shows a quick uptake of Pb(II) initially, followed by the equilibrium and decrease in adsorption capacity with increase in adsorbent dose. UMS shows that 53.75% adsorption efficiency of Pb(II) at a dose of 0.1 g/50 mL becomes increasing with the increase in dose rising to a maximum of 89.76% at a dose of 1.0 g/50 mL. While using TMS, the adsorption efficiency went from 74.11% at a dose of 0.1 g/50 mL to a maximum of 95.26% at 0.4 g/50 mL, remaining almost constant
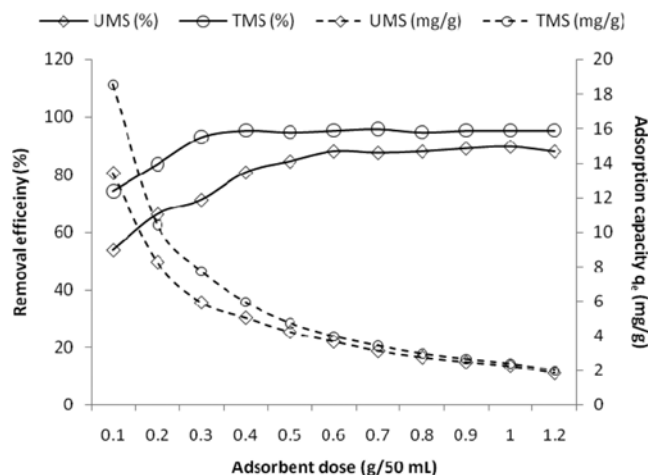
Fig. 2. Influence of UMS and TMS dosage on Pb(II) adsorption. Solution concentration (50 mg/L); contact time (25 mins); agitation speed (125 rpm); temperature (25 °C).
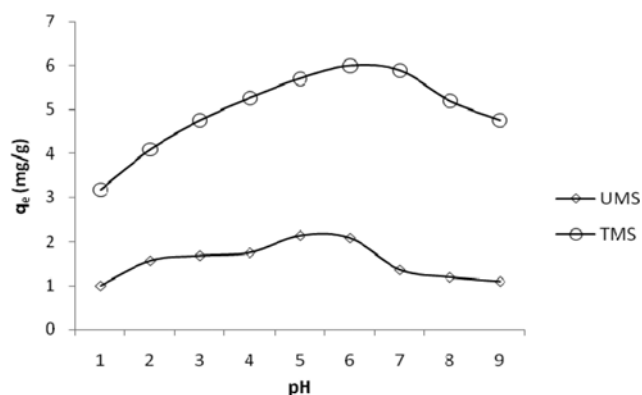
Fig. 3. Effect of pH on Pb(II) adsorption. Solution concentration (50 mg/L); adsorbent dosage (1.0 g/50 mL for UMS and 0.4 g/50 mL for TMS); contact time (25 mins); agitation speed (125 rpm); temperature (25 °C).

at higher dosages. The increase in adsorption with the increase in adsorbent dose is attributed to the availability of adsorption sites for metal adsorption [35,36].

Fig. 2 also illustrates that under similar condition (say 0.3 g/50 mL), the thiourea modified adsorbent (TMS) showed high adsorption efficiency (92.94%) and adsorption capacity (7.75 mg/g) relative to unmodified adsorbent (UMS), i.e., 71.26% and 5.94 mg/g, respectively. This implies that modification of sorghum with thiourea provides two major advantages: a decrease in adsorbent dose and increase in adsorption efficiency by providing more active sites for Pb(II) binding. Based on this study, a dose of 0.4 g/50 mL and 1.0 g/50 mL for TMS and UMS was selected for the further study.

3. Effect of pH

The pH of an aqueous medium is perhaps the most significant factor for metal ion adsorption to biomass. It affects both the adsorbent and metal ions present in the solution. Competitive ability of hydrogen ions and metal ion is directly related to solution pH.

Effect of solution pH on Pb(II) binding to UMS and TMS was checked by varying it in a range of 1-9, keeping other parameters constant, and the results are shown in Fig. 3. The maximum adsorption capacity of UMS was found at pH=5 (2.14 mg/g), while for TMS the maximum adsorption capacity was obtained at pH=6 (5.99 mg/g). At very low pH values (1-2), the adsorption capacity was found at its minimum in both the cases. The reason is the protonation of available binding sites on adsorbent materials as well as the increase in competitive adsorption of H^+ ions with respect to Pb^{2+} ions due its higher concentration at low pH. With the increase in pH values, the concentration of H^+ ions decreases, thus decreasing the probability of competitive adsorption of H^+ ion. This results in an increase in adsorption capacity of the adsorbent materials for Pb^{2+} ions. At higher pH values, the adsorption capacity in both cases decreases. This can be attributed to the formation of insoluble hydroxides $(Pb(OH)_2)$ becoming less available for adsorption. From this study, pH 5 and 6 were selected as optimum values for UMS and TMS, respectively. Study of pH also indicates the benefit of thiourea modification, which causes an increase in adsorption capacity of TMS to more than twice as compared to UMS.

4. Adsorption Kinetics - Effect of Time

The study of contact time gives the information about the mini-
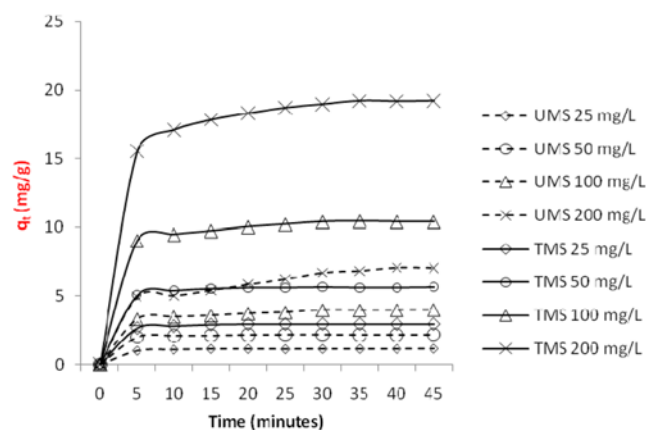
Fig. 4. Influence of contact time on Pb(II) adsorption. Solution concentration (25-200 mg/L); adsorbent dosage (1.0 g/50 mL for UMS and 0.4 g/50 mL for TMS); temperature (25 °C).

mum time required to establish equilibrium as liquid-solid interface for metal ion binding. The equilibrium time helps to study the rate of adsorption process.

The effect of contact time on Pb(II) adsorption at different initial concentrations ranging from 25-200 mg/L using UMS and TMS is illustrated in Fig. 4. The adsorption capacity (q_t) increases with the increase in time up to a certain limit, then becomes parallel to the x-axis in all the cases. At the point, a dynamic equilibrium has been established between the amount of Pb(II) adsorbed by the adsorbent materials (UMS and TMS) and the amount of Pb(II) desorbed form the adsorbent materials. Considering UMS as adsorbent, the minimum contact time needed for Pb(II) solution with initial concentration of 25 mg/L to establish equilibrium was 15 minutes; 25 minutes for Pb(II) solution with initial concentration of 50 mg/L; for the initial concentration of 100 and 200 mg/L, the minimum contact time required to attain equilibrium was 30 and 40 minutes,

respectively. While for TMS the time to reach equilibrium was 15, 20, 30 and 35 minutes for initial concentration of Pb(II) solution 25 mg/L, 50 mg/L, 100 mg/L and 200 mg/L, respectively. The reason is the available active sites at adsorbent surface uptake Pb(II) ions more quickly at lower initial concentration. At higher initial Pb(II) ion concentration, Pb(II) ions needs more time to diffuse to the inner active sites of the adsorbent material. Fig. 4 also indicates that the adsorption process is uniform with time and can be considered very rapid. Various studies have reported the equilibrium time for Pb(II) adsorption from its aqueous solution range on different biological material is in the range of 45-240 min [37-43]. The present study using TMS shows much less equilibrium time for Pb(II) adsorption (15-35 min), indicating the advantage of the proposed modification over the previous studies. In addition, the q_t value for TMS was found to be increased significantly for Pb(II) adsorption in each of its initial concentrations relative to q_t obtained for UMS. This increase again reinforces the same advantage of the proposed modification.

Active binding sites are not the only factor responsible of kinetic properties; the accessibility of Pb(II) ions without hindrance is also important. So, the adsorption mechanism depends both on the physico-chemical properties of adsorbent material and mass transfer. Most famous kinetic models, i.e., pseudo-first-order (Eq. (1)) and pseudo-second-order (Eq. (2)), were applied to examine the mechanism of adsorption.

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \tag{1}$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \tag{2}$$

where, q_e and q_t (mg/g) are the amounts of metal adsorbed at equilibrium and at the given the time t, respectively, and k_1 (1/min) and k_2 (mg/g*min) are the first- and second-order rate constants, respectively.

A pseudo-first-order kinetic model is based on the assumption that adsorption is directly related to number of free active sites. The

Table 2. Kinetic parameters for Pb(II) adsorption

| Adsorbents	Pseudo 1st order kinetics			q_e (mg/g) (Experimental)	Pseudo 2nd order kinetics		
	k_1 (min^{-1})	R^2	q_e (mg/g)		k_2 (mg/g*min)	R^2	q_e (mg/g)
UMS	0.157	0.891	0.446	**2.202**	0.974	0.999	2.227
TMS	0.149	0.949	1.113	**5.661**	0.341	0.999	5.724

Table 3. Comparison of adsorption capacity of TMS and UMS with various natural adsorbents for Pb(II) adsorption

Biomass	q_m (mg/g)	Equilibrium model	Kinetic model	Reference
Symphricarpus albus	21.78	Langmuir	Pseudo 2nd order	[52]
Thiourea- modified *Sorghum* (TMS)	17.82	Langmuir	Pseudo 2nd order	[Present study]
Cereal chaff	12.5	Langmuir	-	[53]
T. resupinatum	10.38	Langmuir	Pseudo 2nd order	[46]
Nigella sativa seeds	8.08	-	-	[41]
Solid waste of olive oil OS	6.57	Langmuir	-	[54]
Sorghum	6.289	Langmuir	Pseudo 2nd order	[Present study]
Acacia nilotica leaves	2.51	Langmuir	Pseudo 2nd order	[55]
Sisal fiber	1.34	Freundlich	-	[56]
Dried water hyacinth (roots)	0.097	-	Pseudo 2nd order	[57]
Dried water hyacinth (shoots)	0.096	-	Pseudo 2nd order	[57]

equilibrium data obtained from the effect of time using 50 mg/L Pb(II) ions concentration was plotted according to the linear equation of pseudo-first-order kinetic model (Eq. (1)) and the parameters were calculated (Table 2). The coefficient of determination (R^2) was 0.891 in case of UMS, and 0.949 using TMS as adsorbent indicates the inferior fit of the pseudo-first-order model to equilibrium data. In addition, the q_e calculated from the pseudo-first-order model was not in good agreement with experimentally determined q_e value (Table 2). It can be inferred that the adsorption of Pb(II) ions onto UMS and TMS did not follow a pseudo-first-order kinetic model. Literature also indicates that most of the divalent ions don not follow a pseudo-first -order kinetic model (Table 3).

The pseudo-second-order kinetic is based on the fact that the rate of adsorption is directly related to the square of the number of active sites present on the adsorbing specie and metal ion concentration. Linear equation of the pseudo-second-order was applied to kinetic data obtained from 50 mg/L lead ions concentration, and the parameters, k_2 and q_e, were calculated (Table 2). The correlation coefficient (R^2) was found 0.999 for both adsorbing materials (UMS and TMS), indicating the goodness of fit of the pseudo-second-order model to equilibrium data. The q_e value calculated from the pseudo-second-order plot was also found in close agreement to experimentally determined q_e value (Table 2). So, it can concluded here that adsorption of Pb(II) ions on UMS and TMS follows pseudo-second-order kinetics. Literature also reveals a similar aspect as represented in Table 3.

On the basis of theoretical consideration, the adsorption of divalent metal ions (M) onto two free active sites (B) can be explained by the following:

$$M + 2B \rightarrow B_2M$$
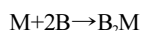
It means that the adsorption rate would be proportional to the concentration of metal ions and the square of the number of active sites onto UMS and TMS, which corresponds to the term $(q_e - q_t)^2$

in the pseudo-second-order model. The best fit of the pseudo-second-order model reveals that one divalent metal ion binds to two monovalent active sites [44].

5. Equilibrium Modeling - Effect of Pb(II) ion Concentration

An important feature of modern engineering is the ability to satisfactorily model the behavior of an adsorption system prior to committing an industrial-scale investment [45]. Equilibrium modeling represents the relationship between amount of adsorbate adsorbed on the adsorbent and the amount of adsorbate remaining in the solution. The most frequently used equilibrium models, Langmuir (Eq. (3)), Freundlich (Eq. (4)), Temkin (Eq. (5)) and D-R (Eq. (6)) isotherm models, were employed to examine the equilibrium process. A non-linear approach was attempted to explain the equilibrium models for Pb(II) adsorption using UMS and TMS. The stated models were compared using RMSE--the root mean square errors- (Eq. (7)) values.

$$q_e = \frac{b \cdot q_m \cdot C_e}{1 + b \cdot C_e} \tag{3}$$

$$q_e = K_F \cdot C_e^{1/n} \tag{4}$$

$$q_e = B_T \cdot \ln K_T \cdot C_e \tag{5}$$

$$q_e = q_m \cdot \exp(-\beta \varepsilon^2) \tag{6}$$

$$RMSE = \sqrt{\frac{\sum (q_{e(cal)} - q_{e(exp)})^2}{N}} \tag{7}$$

The Langmuir model presumes that Pb(II) ions form a monolayer coverage on the outer surface of the adsorbent [46]. The Langmuir model also provides the maximum adsorption capacity of the adsorbent to adsorb metal ions. RMSE values, maximum adsorption capacity-qm (mg/g) and b (L/mg), a constant related to the free energy of adsorption are in Table 4. The RMSE value calculated from the non-linear plot was found minimum in case of Langmuir model,

Table 4. Isotherm parameters for Pb(II) adsorption

Langmuir isotherm parameters				
Adsorbents	RMSE	q_m (mg/g)	b (L/mg)	R_L
UMS	0.062	6.289	0.047	0.515-0.141
TMS	0.223	17.82	0.041	0.549-0.075

Freundlich isotherm parameters			
Adsorbents	RMSE	N	K_F
UMS	0.237	1.43	0.387
TMS	0.331	1.93	1.431

Temkin isotherm parameters			
Adsorbents	RMSE	B_T (kJ/mol)	K_T (L*mol/kJ*g)
UMS	0.126	0.992	1.367
TMS	3.029	4.382	4.212

Dubinin-radushkevich isotherm parameter			
Adsorbents	RMSE	E (kJ/mol)	q_m (mg/g)
UMS	0.109	15.81	3.74
TMS	0.473	12.30	14.61

indicating its goodness of fit to the equilibrium data. It means that Pb(II) ions bind on the outer surface of UMS and TMS uniformly, forming a monolayer coverage. A significant increase in maximum adsorption capacity was observed using of TMS as adsorbent, i.e., 17.82 mg/g as compared to UMS (6.289 mg/g). This increase is attributed to the increase in number of binding sites on the surface of TMS due to thiourea-modification of UMS.

The factor b was used to find a dimensionless constant, called separation factor or equilibrium parameter, R_L (Eq. (8)), to monitor the feasibility of the Langmuir model.

$$R_L = \frac{1}{1 + b \cdot C_e} \tag{8}$$

The R_L value indicates the favorability of the process: $R_L > 1$ means unfavorable, $R_L = 1$ signifies linear, $R_L = 0-1$ entails favorable and $R_L < 0$ implies irreversible [47]. R_L values, 0.515-0.141 for UMS and 0.549-0.075 for TMS, obtained in the present study show the favorability of the process and Langmuir model for its proper representation.

Monolayer coverage of the surface by the metal ions can be used for the calculation of the specific surface area S according to following equation [48]:

$$S = \frac{q_{max}NA}{M} \tag{9}$$

where S is the specific surface area, m^2 (g adsorbent)$^{-1}$; q_{max} the monolayer adsorption capacity, g Pb(II) (g adsorbent)$^{-1}$; N the Avogadro number, 6.02×10^{23}; A the cross-sectional area of metal ion, m^2; M the atomic weight of Pb(II). The atomic weight and the cross-sectional area of Pb(II) are 207.2 g·mol^{-1} and 5.56 Å^2 in a close packed monolayer (Pb(II) radius is 1.33 Å), respectively. The maximum specific surface area calculated from Eq. (9) for Pb(II) adsorption is 1.016 m^2 (g UMS)$^{-1}$ and 2.878 m^2 (g TMS)$^{-1}$. It can inferred here that modification of sorghum biomass with thiourea significantly increases the specific surface area for Pb(II) adsorption.

The Freundlich expression assumes that the Pb(II) binds to the heterogeneous surface of the adsorbent forming multilayers [46]. The Freundlich model in its nonlinear form was used to analyze the equilibrium data. Table 4 contains the constant indicative of relative adsorption capacity (K_F) and factor indicative of adsorption intensity (n). The value of the factor n represents the favorability of adsorption process. The n values, 1.428 and 1.935, for adsorption of Pb(II) ions using UMS and TMS, respectively, represents good adsorption characteristics [47,49]. The RMSE values obtained from the nonlinear plot of the Freundlich model also indicates its fitness to equilibrium data.

The Temkin isotherm assumes that the decline of the heat of sorption as a function of temperature is linear rather than logarithmic, as entailed in the Freundlich model. The RMSE value in case of TMS was found relatively high, indicating its inferior fit to equilibrium data. Temkin parameters, K_T (adsorption potential) and B_T (heat of adsorption) are illustrated in Table 4. Heat of adsorption (B_T) is an important parameter in predicting the nature of attractive forces. The B_T values, 0.992 kJ/mol for UMS and 4.383 kJ/mol for TMS (less than 8 kJ/mol), obtained in the present study, suggest a weak interaction between Pb(II) ions and the adsorbing species (UMS and TMS) [50].

The D-R (Dubinin-Radushkevich) model was also used to evaluate the nature of adsorption. The values of D-R parameters q_m, β and RMSE for Pb(II) adsorption obtained D-R expression are tabulated in Table 4. E values (kJ/mol), calculated from Eq. (10), for Pb(II) adsorption were found less than 16 kJ/mol, depicting the surface attraction phenomenon rather particle diffusion [12]. An increase in q_m (mg/g) value for Pb(II) adsorption on TMS relative to UMS was also observed, indicating greater relative adsorption capacity of TMS as already represented in the Langmuir model.

$$E = \frac{1}{\sqrt{2\beta}} \tag{10}$$

A comparative plot of nonlinear modeling for Pb(II) adsorption on UMS and TMS is shown in Fig. 5(a) and 5(b), respectively. It can be concluded by observing the figures and RMSE value that Langmuir model explanation of the equilibrium data is superior to other models.

6. Thermodynamic Studies - Effect of Temperature

The effect of temperature also provides important information about the process of adsorption. Adsorption capacity of UMS and TMS for Pb(II) adsorption increases with the increase in temperature as illustrated in Fig. 6. This increase may be attributed to the development of new active sites at high temperature or to the increase of the chance of metal ions diffusion into the adsorbent. The observed pattern also suggests that TMS can be considered as a more effective adsorbent for Pb(II) adsorption than UMS at studied temperature ranges. Thermodynamic parameters--free energy, enthalpy and
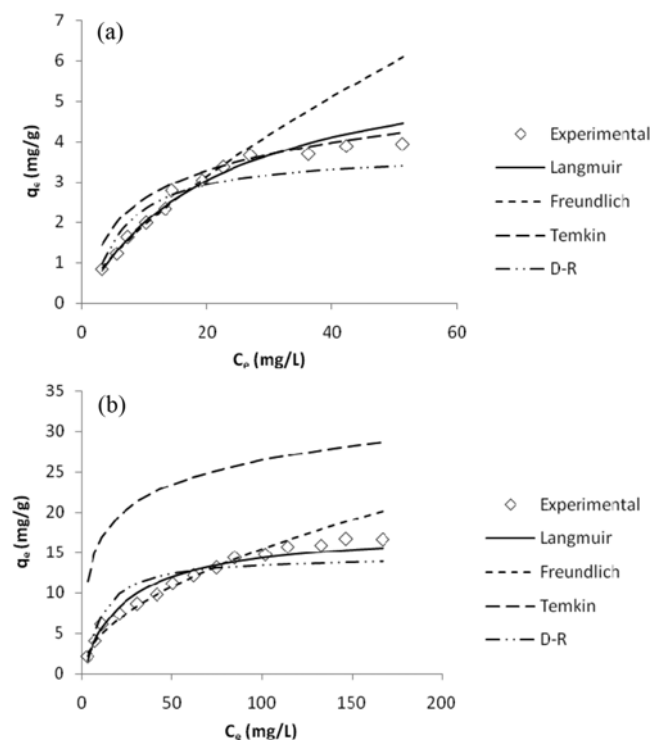

Fig. 5. (a) Nonlinear isotherms plot for Pb(II) adsorption on UMS. Initial concentration (20-130 mg/L); Adsorbent dosage (1.0 g/50 mL); Temperature (25 °C); Contact time (60 mins). (b) Nonlinear isotherms plot for Pb(II) adsorption on TMS. Initial concentration (20-300 mg/L); Adsorbent dosage (0.4 g/50 mL); Temperature (25 °C); Contact time (60 mins).
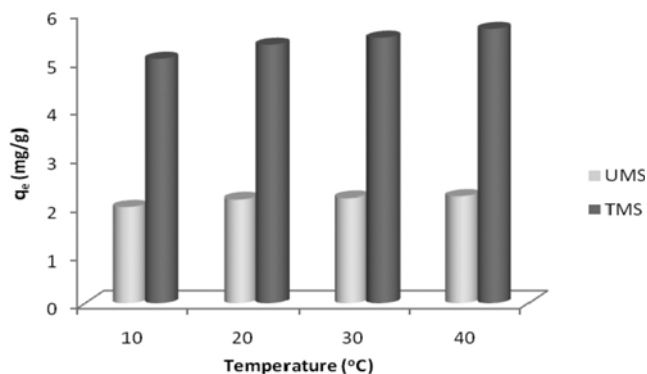
Fig. 6. Effect of temperature on Pb(II) adsorption. Solution concentration (50 mg/L); adsorbent dosage (1.0 g/50 mL for UMS and 0.4 g/50 mL for TMS); contact time (25 mins).

Table 5. Thermodynamic parameters for Pb(II) adsorption

Metal ions	Temperature (°C)	ΔG^o	ΔH^o	ΔS^o
UMS	10	−49.54	213.8	0.93
	20	−58.84		
	30	−68.14		
	40	−77.44		
TMS	10	−48.70	290.7	1.19
	20	−60.69		
	30	−72.68		
	40	−84.67		

entropy--were calculated using Eqs. (11), (12) and (13) and tabulated in Table 5.

$$\Delta G^o = -RTlnK_D \qquad (11)$$

$$lnK_D = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \qquad (12)$$

where, R is the universal gas constant (8.3134 J mol^{-1} K^{-1}), T is the temperature (K), and K_D is the distribution coefficient, obtained from Eq. (13):

$$K_D = \frac{C_o - C_e}{C_e} \qquad (13)$$

The negative values of ΔG^o for the adsorption of Pb(II) by UMS and TMS at the studied temperature range affirmed the feasibility of the process and suggest that the process would be a spontaneous one. Moreover, the increase in magnitude of ΔG^o depicts the endothermic nature of the adsorption process. Also, the magnitude of the ΔG^o values observed in case of TMS was greater as compared to UMS, suggesting TMS as a more feasible adsorbing specie as compared to UMS. The calculated value of ΔH^o also corroborated this statement. Positive values of ΔS^o showed the increased randomness at the solid-solution interface during the adsorption of Pb(II) onto UMS and TMS [51].

CONCLUSION

Thiourea, which was used for modifying the sorghum biomass

under microwave irradiation, remarkably enhanced its adsorption capacity. They study clearly established that microwave assisted modification of sorghum biomass with thiourea is an effective method. This paper also presents an extensive study of reaction equilibrium and kinetics. The equilibrium and kinetic modeling represents that the adsorption process follows the Langmuir model and pseudo-second-order kinetics. The study of operation parameters suggests that maximum adsorption of Pb(II) occurred at pH 5 and 6 using UMS and TMS, respectively. An appreciable increase in Pb(II) uptake capacity of TMS (17.82 mg/g) relative to UMS (6.29 mg/g) shows the effectiveness of thiourea modification. Thermodynamic parameters revealed that the adsorption of Pb(II) on UMS and TMS was spontaneous and endothermic. Hence, it can be inferred that modification of sorghum biomass with thiourea produces an effective and eco-friendly adsorbing specie for Pb(II) adsorption.

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