Microwave-assisted urea-modified sorghum biomass for Cr (III) elimination from aqueous solutions

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Abstract–The present study concentrated on the use of an agro-waste biodegradable sorghum biomass in its simple and modified forms for the binding of Cr (III) ions. A relatively new method of modification was adopted using urea under microwave irradiation. FTIR analysis showed the presence of oxygen and nitrogen bearing functional groups in unmodified (UMS) and modified (MS) sorghum biomass. The appearance of new bands and shifts in the peaks confirmed the modification. The influence of different process parameters such as the adsorbent dose, solution pH, contact time, agitation speed and initial metal ion concentration was studied thoroughly to evaluate optimum conditions for adsorption. Maximum adsorption for Cr (III) ions occurred at pH 5.0-6.0 using UMS and MS. Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models in a non-linear fashion were used to explain the phenomenon. Maximum adsorption capacity was 7.03 and 16.36 mg of Cr (III) per gram of UMS and MS, respectively. Adsorption mechanism was explored by pseudo-first- and pseudo-second-order kinetic models, and it was found that the process followed pseudo-second-order kinetics. Thermodynamic study indicated the process favorability. The study concluded that urea modification under microwave irradiation produces a non-toxic and more effective adsorbent for Cr (III) remediation by inducing new nitrogen bearing functional groups to sorghum biomass.

Key words: Sorghum, Urea Modification, Non-linear Equilibrium, Surface Area, Thermodynamics

INTRODUCTION

Water contamination from heavy metals is a very serious problem [1-3]. Heavy metals can enter an aqueous ecosystem either from industrial activities like electroplating, battery manufacturing, and metallurgical processes, or through acid rain breaking down soil and releasing heavy metals into streams, lakes, and rivers [4]. Heavy metals are considered to be highly toxic and persistent against biodegradation [5]. Industrial sources of chromium are electroplating, leather tanning, mining, steel, and pigment manufacturing [6]. USEPA made a list of 13 hazardous metals in 1978 including chromium (antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc) [7]. Among these, chromium plays an important role in polluting the environment [8]. The permissible concentration of chromium in drinking water suggested by USEPA is 0.1 mg/L [9].

Numerous methods are available to remove toxic metals from water: ion exchange, reverse osmosis, precipitation, solvent extraction, membrane technologies, electrochemical treatment, adsorption, etc. Adsorption is by far the most adaptable and broadly used, and activated carbon is the most frequently used adsorbent. However, its use is very expensive, so there has been substantial concern in the use of other adsorbents [10]. Literature indicates the removal of heavy metals by inexpensive biological materials such as rice straw [11], wheat straw [12], banana peels [13], and bagasse [14].

Usually, biological materials in raw form offer a low adsorption capacity and also limited information about the adsorption mechanism [15,16]. Several physical and chemical methods have been employed to increase the adsorption capacity, to have information about the adsorption sites, and to unite known functional groups with the biological materials [17-21]. Chemical modification changes the surface chemistry of adsorbent by incorporation of new functional groups or by changing the already existing functional groups. These modified functional groups act as complexing/chelating agents for metals [22]. Thus, chemical modification produces adsorbents having greater active sites for metal binding as compared to raw adsorbent. A relative new medication of biological materials has been reported under microware irradiation. The reported method is beneficial because of easy handling and eco-friendly nature. Also, the method does not require any solvent for modification [23-26].

We used sorghum biomass as a cost-effective adsorbent for Cr (III) remediation. Sorghum biomass is a plentiful waste agro-material because it is the fifth major cereal crop grown in the world [27]. We also concentrated on evaluating the ability of urea modified sorghum (MS) to remove toxic Cr (III) ions from aqueous solution in a batch procedure. The effect of process parameters like adsorbent dose, contact time, solution pH, and temperature for unmodified (UMS) and modified sorghum (MS) was studied. A non-linear approach has been adopted to study the adsorption equilibrium using Langmuir, Freundlich and Dubinin-Radushkevich models in order to reveal the information about the binding of Cr (III). Besides, kinetic models and thermodynamic parameters were also used to explain the adsorption mechanism.

MATERIALS AND METHODS

1. Preparation of Adsorbent

Fresh *Sorghum bicolor L.* was collected from a local market of Lahore, Pakistan. Later, the mass was washed with distilled water

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and subsequently dried in an incubator at 70 °C till it became moisture free. The material was ground to a fine powder in a laboratory grinder and was sieved in the particle size range of 60-80 mesh (ASTM). The processed material was stored in airtight plastic containers. This material was designated as unmodified sorghum biomass (UMS).

Sorghum biomass (UMS) and urea (Sigma-Aldrich) were blended in a ratio of 1 : 2 by mass and were exposed to microwave radiation (2,450 MHz) for 12 minutes by using a microwave oven (Dawlance). It was then boiled in water for 25-30 min and filtered while hot. The residue was further washed with hot water to remove any excess of urea. The residue was dried in an oven at 70 °C to constant mass. This was designated as modified sorghum (MS) and used for further experiments.

2. Chemicals, Equipment and Apparatus

High purity chemicals and reagents, purchased from Sigma-Aldrich (Taufkirchen, Germany), were used during the study. The glassware was thoroughly washed with chromic acid, caustic soda, soda ash, tap water, distilled water, in that order, and dried in an oven prior to use. Batch experiments were performed in 250 ml conical flasks on top of orbital shaker (VORTEX Model-OSM-747). The pH was adjusted with 0.1 M NaOH or 0.1 M HCl solutions with a digital pH meter (HANNA, Model-8417). A Perkin Elmer atomic absorption spectrophotometer (Model-AAnalyst 100) was used to determine the concentrations of Cr (III) at 357.9 nm. FTIR (Perkin Elmer Spectrum-RX1) was used to characterize the adsorbent materials. Vario EL III Elementar was used for elemental (carbon, nitrogen and hydrogen) analysis.

3. Optimization of Process Parameters

Using the initial concentration of 50 mg/L for Cr (III) ions, a series of experiments were performed to check the effects of various process parameters (adsorbent dose, contact time, pH, and agitation speed) on metal adsorption using unmodified (UMS) and modified sorghum (MS) as adsorbent. The effect of a certain parameter was studied by varying it gradually, keeping all other parameters constant. The glassware used in the study was successively washed with acid and distilled water and then oven dried at 105 °C for 1 h. The atomic absorption spectrometer was used for the analysis of Cr (III) ions concentration after adsorption under certain conditions. The effect of adsorbent dose was studied by varying the adsorbent amount from 0.1 g/50 mL to 0.9 g/50 mL for both adsorbent materials: UMS and MS. pH was varied from 1-9 to investigate the optimum pH for metal adsorption. The effect of contact time and agitation speed on Cr (III) adsorption was studied under gradually varied conditions of 1-45 min (for different initial metal ion concentrations i.e. 25 mg/L, 50 mg/L, 100 mg/L and 200 mg/L) and 50-250 rpm for contact time and agitation speed, respectively. Effect of temperature was also studied for the temperature range 10-40 °C.

4. Study of Adsorption Isotherms

Solutions of varying concentration (20-180 mg/L) of Cr (III) ions were taken in nine Erlenmeyer flasks (250 mL). Adsorption of Cr (III) ions was carried out under the optimum conditions obtained from the prior study of process parameters. Various equilibrium models including Langmuir (Eq. (1)), Freundlich (Eq. (2)), Temkin (Eq. (3)) and Dubinin-Radushkevich (Eq. (4)) were used to evaluate the
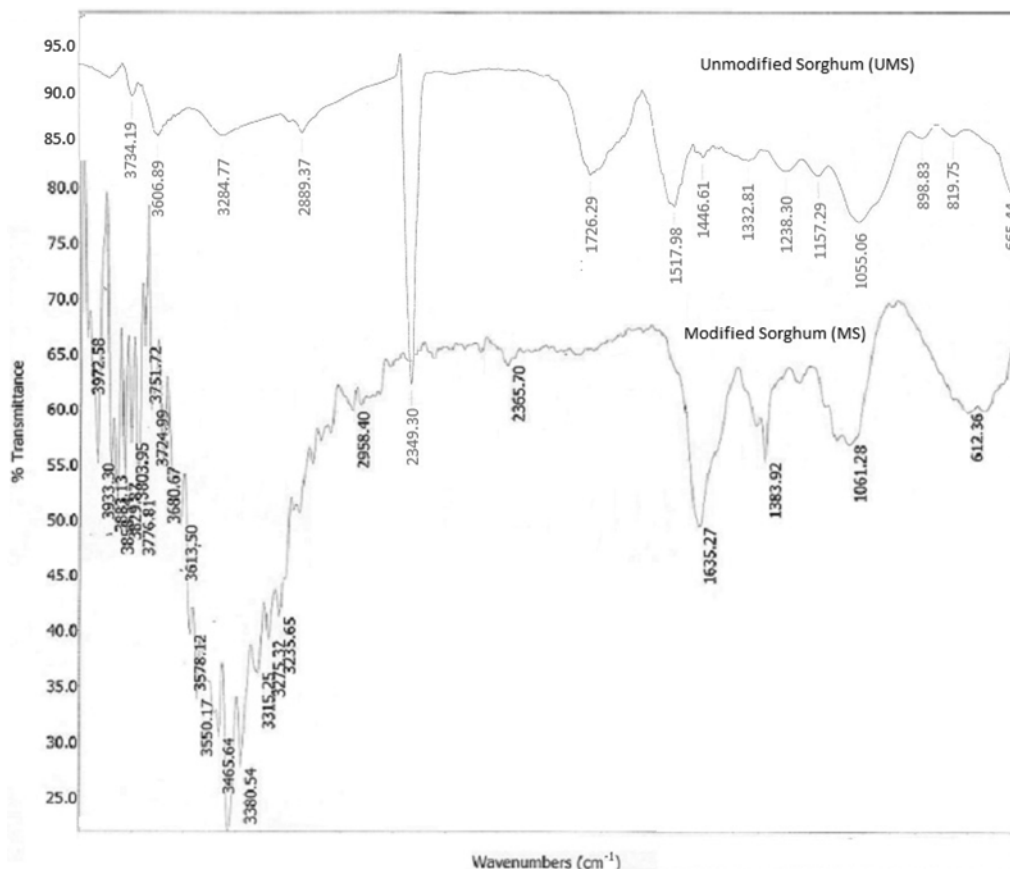

**Fig. 1. FT-IR spectrum of UMS and MS.**

equilibrium data and their corresponding parameters were calculated from their respective plots.

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 provides the absorbance peaks at 1,726.29, 1,517.98, 1,446.61, 1,332.81, 1,238.30, 1,157.29 and 1,055.06 cm^{-1}, all being stretching of carboxyl group [28]. Another broad peak at 3,284.77 cm^{-1} indicates the presence of hydroxyl group.

The urea modified sorghum (MS) was also subjected to solid phase FTIR analysis. A notable change in spectrum was observed as illustrated in Fig. 1. The peak at 1,635.27 cm^{-1} indicates the presence of secondary amides. Peaks at 3,315.25, 3,275.32 cm^{-1} also confirm the presence of secondary amides. Another peak at 612.36 cm^{-1} affirms the presence of aliphatic secondary amides, which absorbs between the region 610-625 cm^{-1} [28]. It can be concluded from the peak data that most of the functional groups are converted into secondary amides, thus increasing the nitrogen content due to the binding of urea with sorghum biomass. In other words, the functionality the MS has been increased as compared to UMS, eventually increasing more binding sites on surface of MS for Cr (III) remediation.
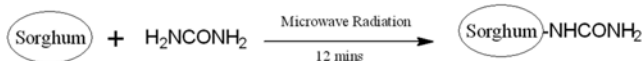
The elemental analysis showed virtually similar results for the C and H content in both UMS and MS adsorbents as shown in Table 1. It also illustrates that modification with urea has increased the nitrogen content significantly from 0.86% in UMS to 8.24% in MS. This increase indicates the grafting of urea to the functional groups present in the sorghum biomass.

2. Effect of Adsorbent Dose

Effect of adsorbent dose on the removal of Cr (III) from its aqueous solution was studied at initial concentration of 50 mg/L of Cr (III) by varying the amount of UMS and MS adsorbent from 0.1-0.9 g/50 mL at solution pH. Percentage removal efficiency and adsorption capacity (mg/g) with increase in dose of UMS and MS is illustrated in Fig. 2. Initially, there was a quick uptake of Cr (III) followed by the equilibrium and decrease in adsorption capacity with increase in adsorbent dose. Percentage adsorption efficiency of UMS for Cr (III) started from 21.36% at a dose of 0.1 g/50 mL, rose to a maximum of 56.26% at 0.7 g/50 mL then slightly decreased up to 49.26% at 0.9 g/50 mL. Using MS as adsorbent it went up from

Table 1. Elemental analysis of modified and unmodified sorghum biomass

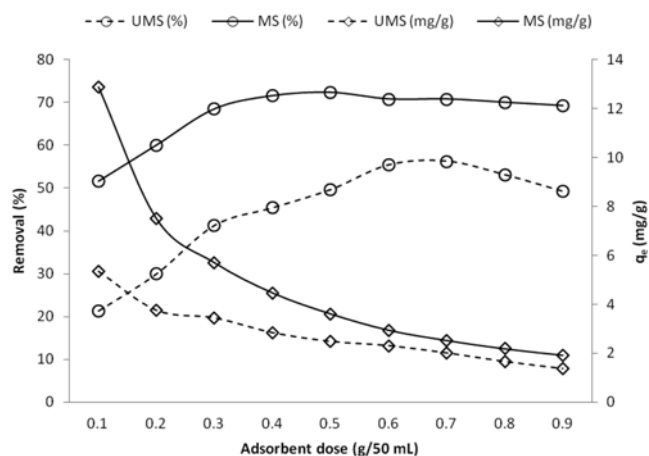| Elements	Unmodified sorghum (UMS)	Modified sorghum (MS)
C (%)	44.51±0.50	43.16±0.30
H (%)	6.97±0.05	7.12±0.04
N (%)	0.86±0.05	8.24±0.05

Fig. 2. Influence of UMS and MS dosage on Cr (III) adsorption. Solution concentration (50 mg/L); contact time (30 mins); agitation speed (125 rpm); temperature (298 K).

51.54% at a dose of 0.1 g/50 mL to 69.23% at 0.9 g/50 mL with a maximum of 72.31% at 0.5 g/50 mL. The increase in adsorption with the increase in adsorbent dose was attributed to the availability of adsorption sites for metal adsorption [29,30]. After a certain value of dose, the adsorption of metals decreased to some extent with further increase in adsorbent dose. This may be attributed to overlapping or aggregation of adsorption sites, resulting in decrease in total adsorbent surface area available to metal ions and an increase in diffusion path length. The decreasing trend in the adsorption capacity of UMS and MS was due to the interference between binding sites at higher dose or insufficiency of Cr (III) ions in solution with respect to available binding sites [31,32].

From Fig. 2, under similar conditions (0.5 g/50 mL) modification with urea caused the adsorption efficiency of the MS to increase from 49.62% to 72.31% relative to UMS. Similar trend was found in adsorption capacity as well. At the optimum values of dose of MS (0.5 g/50 mL) and UMS (0.7 g/50 mL), the increase in percentage adsorption efficiency and adsorption capacity can be attributed to the increase in binding sites for Cr (III) in MS as compared to UMS. So it can be inferred that modification of sorghum with urea is responsible for two major advantages: increase in adsorption efficiency and a decrease in adsorbent amount. After studying the effect of adsorbent concentration, we chose a dose of 0.5 g/50 mL for MS and 0.7 g/50 mL for UMS as optimum dose in further experiments.

3. Effect of pH and Agitation Speed

The pH of the medium has a significant effect on the adsorption of metal ions on different adsorbents. pH affects both the adsorbent and adsorbate present in the solution. Cr (III) ions exist in solution as Cr^{3+} in acidic pH range (1-6). After pH 6 it starts precipitating as $Cr(OH)_3$, thus becoming less available in for adsorption. At very low pH, either H+ ions compete with Cr^{3+} for binding sites in adsorbent or protonate the available functional groups available for Cr^{3+} binding [25].

Experiments were conducted to investigate the effect of solution pH on Cr^{3+} binding to UMS and MS by varying it from 1-9 while the rest of the factors were kept constant. Fig. 3 shows the increase in adsorption capacity of UMS and MS with rise in pH up to 6. After that adsorption capacity decreases due to the reason discussed above
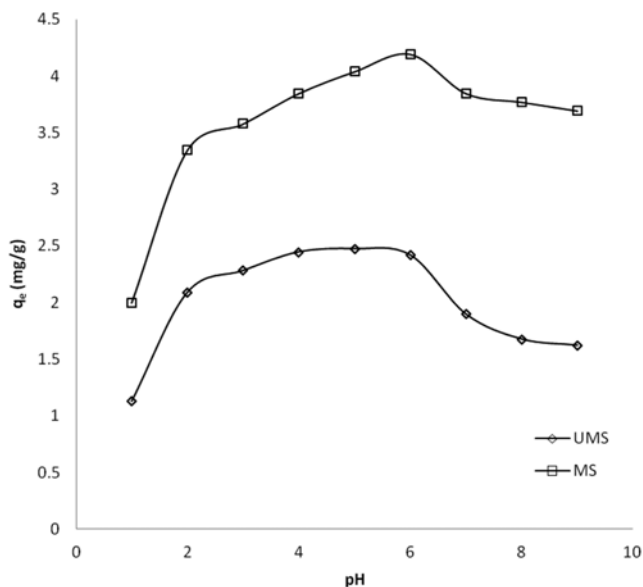
Fig. 3. Influence of pH on Cr (III) adsorption. Solution concentration (50 mg/L); adsorbent dosage (0.7 g/50 mL for UMS and 0.5 g/50 mL for MS); contact time (30 mins); agitation speed (125 rpm); temperature (298 K).

already. The maximum uptake of Cr^{3+} was observed at pH=5 (2.47 mg/g) using UMS as adsorbent, while for MS it was pH=6 (4.19 mg/g). From this study, pH 5 and 6 were selected optimum values for UMS and MS, respectively. Almost similar results of optimum pH for Cr (III) binding for various adsorbents have been reported [9,13,33,34]. Study of pH also indicates the advantage of urea modification, which causes the increase in adsorption capacity of MS to almost double relative to UMS.

Experiments were also performed to monitor the effect of agitation speed by varying it in 50-250 rpm on Cr (III) adsorption from aqueous solution at optimum pH and dose calculated form previ-
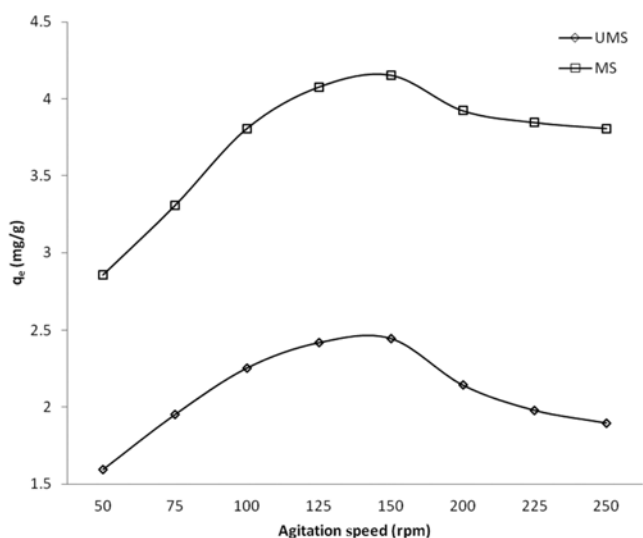

Fig. 4. Influence of Agitation speed on Cr (III) adsorption. Solution concentration (50 mg/L); adsorbent dosage (0.7 g/50 mL for UMS and 0.5 g/50 mL for MS); contact time (30 mins); temperature (298 K).

ous study for both UMS and MS. The trend of adsorption capacity with agitation speed is shown in Fig. 4. Agitation speed of 150 rpm was found to be optimum for Cr (III) adsorption in both the cases. The reason is that at very slow agitation speed, the adsorbent aggregates at the bottom, which results in the unavailability of adsorption sites. Also, at very high speed centrifugal forces overcome the ion-dipole forces (physisorption), resulting in desorption of the adsorbate. Adsorption capacity of MS (2.44 mg/g) was found appreciably more than UMS (4.15 mg/g) for Cr (III) removal from aqueous solution, indicating the presence of more binding sites for Cr (III) ions on MS.

4. Adsorption Isotherms

Before committing to large-scale investment, the ability to satisfactorily model the behavior of the system is considered to be an important feature of modern engineering [35]. Proper analysis and design of an adsorption system requires appropriate adsorption equilibrium as a critical piece of information. The study of adsorption equilibrium at a given temperature is referred to as adsorption isotherm. Several adsorption isotherms are available and readily adopted to correlate adsorption equilibrium. In the present study, Langmuir (Eq. (1)), Freundlich (Eq. (2)), Temkin (Eq. (3)) and D-R (Eq. (4)) isotherm models were used to explain the relationship between concentration of adsorbed specie and adsorption capacity of adsorbent. A non-linear approach has been attempted to explain the equilibrium models for Cr (III) adsorption using UMS and MS. The stated isotherms were compared by using RMSE -the root mean square errors- (Eq. (5)) values.

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

$$q_e = K_F \cdot C_e^{1/n} \tag{2}$$

$$q_e = B_T \cdot \ln K_T \cdot C_e \tag{3}$$

$$q_e = q_m \cdot \exp(-\beta \varepsilon^2) \tag{4}$$

Table 2. Isotherm parameters for Cr (III) adsorption

Langmuir Isotherm Parameters

Adsorbents	RMSE	q_m (mg/g)	b (L/mg)	R_L
UMS	0.304	7.03	0.017	0.0008-0.0071
MS	0.378	16.36	0.011	0.0003-0.0031

Freundlich Isotherm Parameters

Adsorbents	RMSE	n	K_F
UMS	0.415	1.593	0.262
MS	0.489	1.411	0.353

Temkin Isotherm Parameters

Adsorbents	RMSE	B_T (KJ/mol)	K_T
UMS	7.07	2.443	1.479
MS	15.79	4.590	2.717

Dubinin-Radushkevich Isotherm Parameters

Adsorbents	RMSE	E (KJ/mol)	q_m (mg/g)
UMS	0.442	8.908	4.648
MS	0.826	8.838	8.251

Table 3. Comparison of different modified biomass materials for Cr(III) binding

Biomass	Modifying agent	Adsorption capacity (mg/g)	Reference
S. condensate	Hydrochloric acid	14.00	[48]
R. hieroglyphicum	Hydrochloric acid	11.81	[48]
Reanut husk	Sulfuric acid	7.67	[49]
Bagasse fly ash	Hydrogen peroxide	4.35	[50]
Palm flower	Sulfuric acid	1.41	[51]
Sorghum biomass	Urea	**16.36**	Present study

$$RMSE = \sqrt{\frac{\sum(q_{e(cal)} - q_{e(exp)})^2}{N}} \qquad (5)$$

The Langmuir model presumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Table 2 contains the RMSE, q_m (mg/g) -the maximum adsorption capacity- and b (L/mg), a constant related to the free energy of adsorption. The lowest RMSE value indicates that Langmuir equation represented the adsorption process very well in both the cases. This indicates a homogeneous distribution of active sites on the surface of UMS and MS. The maximum adsorption capacity as calculated from the Langmuir plot was 7.03 and 16.36 mg of Cr (III) per gram of UMS and MS, respectively. An appreciable increase in the q_m value for MS indicates the increase in the number of active sites or relative activity of already existing active sites. A comparison between the adsorption capacities of urea modified sorghum and other adsorbents with different modifying agents to uptake Cr(III) is presented in Table 3. The comparison shows the effectiveness of urea modification on metal binding.

The factor b was used to find a dimensionless constant called separation factor or equilibrium parameter, R_L (Eq. (6)).

$$R_L = \frac{1}{1 + b \cdot C_e} \qquad (6)$$

The value of R_L points out the favorability of the process: $R_L > 1$ means unfavorable, $R_L = 1$ signifies linear, $R_L = 0\text{-}1$ entails favorable and $R_L < 0$ implies irreversible [36,37]. In the present study, values were in the range 0.0008-0.0071 for UMS and 0.0003-0.0031 for MS implies favorability of the process and Langmuir isotherm for its proper depiction.

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 [38]:

$$S = \frac{q_{max}NA}{M} \qquad (7)$$

where S is the specific surface area, m² (g adsorbent)⁻¹; q_{max} the monolayer sorption capacity, g Cr (III) (g adsorbent)⁻¹; N, Avogadro's number, 6.02×10^{23}; A, the cross-sectional area of metal ion, m²; M, the atomic weight of Cr (III). The atomic weight and the cross-sectional area of Cr (III) are 51.99 and 1.247 Å² in a close packed monolayer (Cr (III) radius is 0.63 Å), respectively. The maximum specific surface area calculated from Eq. (7) for Cr (III) adsorption is 1.015 m² (g UMS)⁻¹ and 2.36 m² (g MS)⁻¹, indicating the effectiveness of urea

modification towards increment in specific surface area.

The Freundlich expression is an exponential equation that assumes the increase in concentration of adsorbate on the adsorbent surface with increasing adsorbate concentration in the solution. Non-linear form of Freundlich model was used to analyze the equilibrium data. The constant indicative of relative adsorption capacity (K_F) and factor indicative of adsorption intensity (n) were calculated and illustrated in Table 2. The magnitude of the factor n is an indication of the favorability of adsorption. Values of n in the range 2-10 represent better, 1-2 good, and less than one average adsorption characteristics [36,39]. In the present study, the magnitude of the factor n was found 1.593 and 1.411 for Cr (III) adsorption using UMS and MS as adsorbing specie, respectively. The values represent the good adsorption characteristics. The low RMSE values obtained in both cases indicate the goodness of fit for Freundlich model.

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 equation. Slope and intercept of the Temkin isotherm equation were calculated form its respective linear plot and tabulated in Table 2. The highest RMSE values indicate inferior fitness of the Temkin isotherm equation for the equilibrium data for both adsorbing species. Temkin parameters K_T and B_T were calculated to study the adsorption potential and heat of adsorption, respectively. K_T values obtained from Temkin isotherm equation were: 1.479 for UMS and 2.717 for MS depicted satisfactory adsorption potential for Cr (III). Also the B_T values for Cr (III) adsorption; 2.442 kJ/mol (UMS) and 4.590 kJ/mol (MS), less than 8 suggest weak interaction between Cr (III) and UMS and MS indicating that process would be physisorption [40].

The nature of the adsorption (physisorption or chemisorption) was determined by using D-R (Dubinin-Radushkevich) model. The values of D-R parameters q_m, β, E and RMSE for C (III) adsorption obtained from the of Eq. (4) are in Table 2. E values (kJ/mol) less than 8 imply the presence of physical and van der Waal's forces indicating physisorption. Values in between 8-16 indicate ion exchange mechanism, whereas E>16 depicts particle diffusion [41]. The E values for Cr (III) under study described physisorption as the operating phenomenon for both adsorbents. An increase in q_m value for Cr (III) adsorption on MS as compared to UMS was also observed, indicating the more relative adsorption capacity of MS as depicted in the Langmuir model.

Fig. 5(a) and 5(b) show the comparison of non-linear isotherm modeling for Cr (III) adsorption on UMS and MS, respectively. The figures clearly indicate that the Langmuir isotherm explains the experimental data clearly. The order of fit in relation to RMSE was Langmuir>Freundlich>Dubinin-Radushkevich>Temkin.

5. Effect of Contact Time - Kinetic Studies

The adsorption data for the uptake of Cr (III) versus contact time at different initial concentration ranging from 25-200 mg/L using UMS and MS as adsorbents are represented in Fig. 6, respectively. In both the cases adsorption capacity (q_e) increased with time and at some point, it reached a constant value where no more Cr (III) was removed from the solution. At this point, the amount of Cr (III) being absorbed by the UMS and MS was in a state of dynamic equilibrium with the amount of Cr (III) being detached from the UMS and MS. Using UMS as adsorbing specie, the contact time needed for Cr (III) solution with initial concentration of 25 ppm to reach
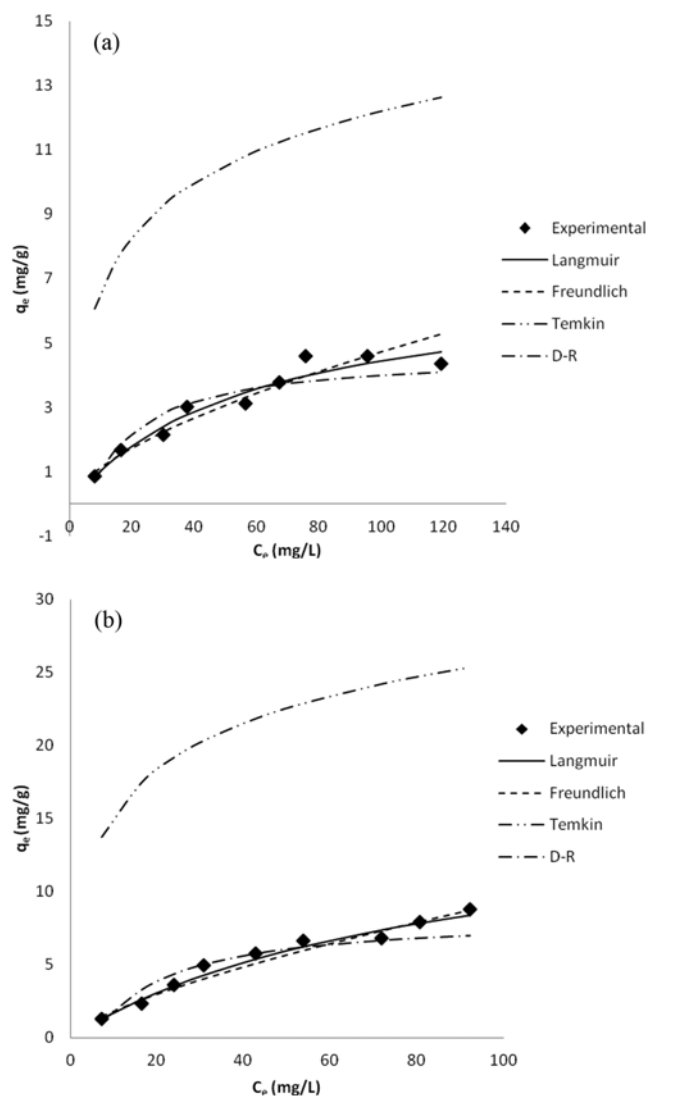
Fig. 5. (a) Nonlinear isotherms plot for Cr (III) adsorption on UMS. Initial concentration (20-180 mg/L); Adsorbent dosage (0.7 g/50 mL); Temperature (298 K); Contact time (60 mins). (b) Nonlinear isotherms plot for Cr (III) adsorption on MS. Initial concentration (20-180 mg/L); Adsorbent dosage (0.5 g/50 mL); Temperature (298 K); Contact time (60 mins).
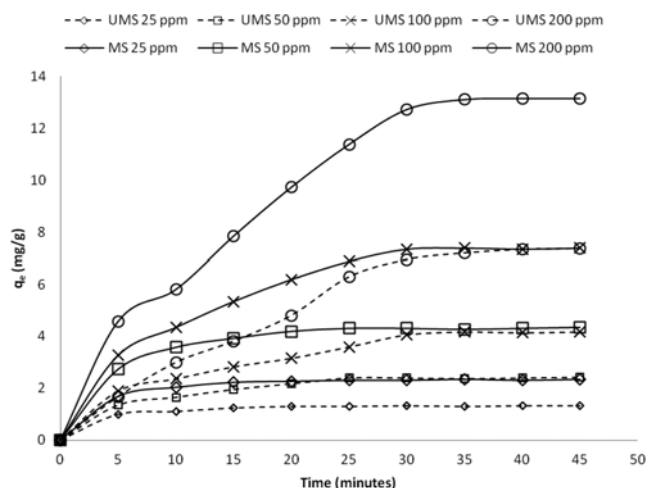

Fig. 6. Influence of contact time on Cr (III) adsorption. Solution concentration (25-200 mg/L); adsorbent dosage (0.7 g/50 mL for UMS and 0.5 g/50 mL for MS); temperature (298 K).

ions more quickly at lower concentrations, but metal needed to diffuse to the inner sites of the sorbent for higher concentrations. The kinetic results also showed that the adsorption process was uniform with time for both adsorbents and can be considered very fast. In addition, the q_e value for MS was found to be increased significantly for Cr (III) adsorption in each of its initial concentration relative to q_e obtained for UMS. This increase indicates the high surface activity of MS due to increase in active sites on its surface (secondary amides induced due to urea modification) compared to MS.

The mechanism of adsorption processes such as mass transfer and chemical reaction was examined by using pseudo-first-order (Lagergren) and pseudo-second-order kinetic models.

The linear equation of the pseudo-first-order model is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 \cdot t \qquad (8)$$

where q_e and q_t (mg/g) refer to the amount of metals adsorbed on UMS and MS at equilibrium and t (min), respectively; k_1 represents the first order rate constant (min^{-1}). Table 4 illustrates the data calculated from the pseudo-first-order kinetic model.

The linear form of pseudo-second-order model is given by:

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{t}{q_e} \qquad (9)$$

where k_2 is the second-order rate constant. The kinetic data calculated from the above Eq. (5) is in Table 4.

The coefficient of determination (R^2) observed for the pseudo-first-order model (0.97 for UMS and 0.98 for MS) was found less than 0.99 for UMS and MS as observed using pseudo-second-order.

equilibrium was 20 minutes, 25 minutes for Cr (III) solution with initial concentration of 50 ppm, for the initial concentration of 100 and 200 ppm, the contact time needed to reach equilibrium was 35 and 40 minutes, respectively. While for MS the time to reach equilibrium was 15, 20, 30 and 35 minutes for initial concentration of Cr (III) solution 25 ppm, 50 ppm, 100 ppm and 200 ppm, respectively.

The reason is that adsorption sites took up the available Cr (III)

Table 4. Kinetic parameters for Cr (III) adsorption

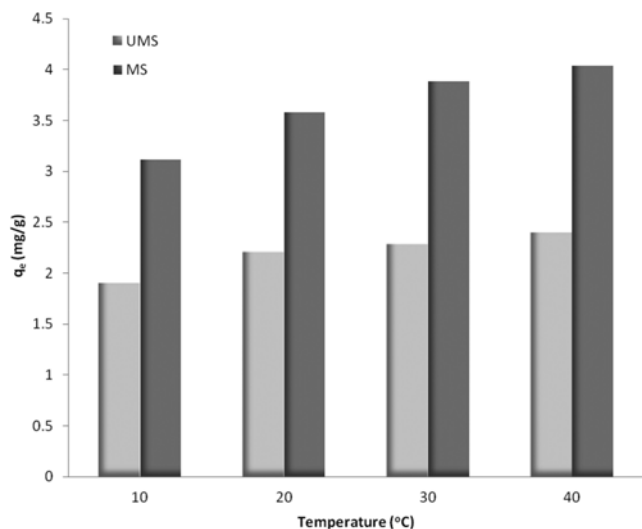| Adsorbents	Pseudo 1st order kinetics			q_e (mg/g) (experimental)	Pseudo 2nd order kinetics		
	k_1 (min^{-1})	R^2	q_e (mg/g)		k_2 (min^{-1})	R^2	q_e (mg/g)
UMS	0.081	0.98	1.853	2.527	0.066	0.99	2.747
MS	0.169	0.98	3.968	4.461	0.076	0.99	4.651

Fig. 7. Influence of temperature on Cr (III) adsorption. Solution concentration (50 mg/L); adsorbent dosage (0.7 g/50 mL for UMS and 0.5 g/50 mL for MS); contact time (30 mins).

The value approaching to 1 clearly showed a perfect fit for pseudo-second-order model as compared to pseudo-first-order model. In addition, the q_e values calculated from pseudo-second-order model was in close accordance to the experimental values for Cr (III) for both UMS and MS. So the conclusion can be made that the adsorption mechanism for Cr (III) removal using UMS and MS as adsorbing specie was governed by pseudo-second-order kinetic model. Several studies showed that the adsorption of metal ions on various adsorbents mostly followed pseudo-second-order kinetic model [42-44].

6. Effect of Temperature - Thermodynamic Parameters

Temperature is an important parameter which affects the adsorption process. Fig. 7 shows the influence of temperature on the adsorption of Cr (III) on UMS and MS, showing increased adsorption capacity with temperature. Increased Cr (III) removal at high temperature indicated the adsorption process to be endothermic in nature. The observed trend suggested that MS can be considered as more effective adsorbent for Cr (III) removal than UMS at high temperatures. Eqs. (10), (11) and (12) were used to calculate the thermodynamic parameters such as changes in standard free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o). The calculated parameters depict the nature of the process.

$$\Delta G^o = -RT\ln K_D \quad (10)$$

$$\ln K_D = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (11)$$

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

$$K_D = \frac{C_o - C_e}{C_e} \quad (12)$$

where, q_e is the equilibrium amount of metal adsorbed (mg/g) and C_e is the concentration of metal in solution at equilibrium (mg/L) [45,46]. Calculated thermodynamic parameters are given in Table

Table 5. Thermodynamic parameters for Cr (III) adsorption

Metal ions	Temperature (^{o}C)	ΔG^o	ΔH^o	ΔS^o
UMS	10	−6.19633	197.9	0.721
	20	−13.4069		
	30	−20.6176		
	40	−27.8282		
MS	10	−18.5813	334.5	1.247
	20	−31.053		
	30	−43.5248		
	40	−55.9965		

5. The negative values of ΔG^o for the adsorption of Cr (III) by UMS and MS at the studied temperature range affirmed the feasibility of the process and suggest that process would be a spontaneous one. In addition, the increase of ΔG^o values with negative sign depicts that the adsorption process was endothermic. The magnitude of ΔG^o values observed in case of MS was more as compared to UMS, indicating suggesting MS as for feasible adsorbent relative 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 Cr (III) onto UMS and MS [47]. ΔS^o values from Table 5 pointed to the greater randomness at surface of MS as compared to UMS due to urea modification thus increasing in relative adsorption capacity of MS.

CONCLUSION

The present study focuses on the use of unmodified (UMS) and urea modified (MS) sorghum biomass for Cr (III) removal from aqueous medium. The calculated optimum process parameters showed that the Cr (III) ions can be effectively removed in slightly acidic environment (pH=5-6) using both UMS and MS. The equilibrium study showed an appreciable uptake capacity of the adsorbents: 7.03 and 16.36 mg of Cr (III) per gram of UMS and MS, respectively. The increase in q_e value for MS in all the equilibrium experiments enables us to say that urea induces new binding sites on the surface of sorghum biomass. The adsorption mechanism for both adsorbents was governed by the pseudo-second order kinetic model. Thermodynamic parameters indicated that the process was energetically feasible and endothermic. So, urea modification of sorghum biomass makes it an effective, low-cost and eco-friendly adsorbent for the removal of Cr (III) form aqueous systems. Another positive feature found during the study was that there exist weak inter-active forces between adsorbent and adsorbate, which leads to the idea of adsorbent regeneration.

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