



Acid and Alkali Modified Cow Hoof Powder as Adsorbents for Chromium (VI) Removal from Aqueous phase

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PAPER INFO

Paper history:

Received 9 May 2015

Accepted in revised form 21 July 2015

Keywords:

Adsorption isotherm

Chemical modification

Cow hoof

Biosorption

ABSTRACT

In this work, the feasibility of batch studies using hydrochloric acid modified cow hoofs (HCH), citric acid modified cow hoofs (CACH) and sodium hydroxide modified cow hoofs (SCH) for removing Cr (VI) from aqueous solution were investigated. Equilibrium data at four different temperatures (25, 35, 45 and 55°C), by contacting Cr (VI) solution at different concentrations with CACH, HCH and SCH were also conducted. The results of this study showed that SCH recorded higher percentage Cr (VI) removal than both HCH and CACH. The pH of 2 was required for maximum removal of Cr (VI) by the three biosorbents. The data obtained for both CACH and SCH were best fitted by Langmuir model while the data obtained for HCH were best fitted by Freundlich model. Thermodynamic parameters for the removal of Cr (VI) revealed the process to be spontaneous and exothermic for HCH and SCH but endothermic for CACH. Therefore, the removal of Cr (VI) from wastewater using these low-cost biosorbents (particularly HCH and SCH) would be economically feasible.

doi: 10.5829/idosi.ijee.2015.06.04.07

INTRODUCTION

Heavy metals pollution, dyes and other organic and inorganic pollutants became a global threat that needs to be combated considering the role of water for life sustenance. Heavy metals are known to be injurious to human health when ingested because they are not biodegradable and tend to accumulate in living tissues after ingestion into the body system.

Chromium (especially trivalent chromium) is an essential nutrient for the maintenance of normal glucose, fat and metabolism and cholesterol level in human body [1]. Chromium can be encountered by man in three different forms- metallic chromium (Cr), trivalent chromium (Cr (III)) and hexavalent chromium (Cr (VI)). It has been reported that exposure to metallic chromium is not common and no health hazards of this form of chromium. Cr (III) is mainly encountered in foods and does not have any injurious effects unless if ingested in excess [1]. Chromium (VI), which can be

introduced into the environment majorly through various industrial processes such as electroplating, steel production, leather tanning, wood preservation and textile industries. Cr (VI) has been particularly indicted in causing lung perforation, carcinoma, asthma, dermatitis, ulcer, lungs cancer, etc. [1, 2].

Industrial wastewater must be treated before being discharged to the environment to avoid unnecessary human and plant exposure to such toxic metal. To this end, a lot of methods have been used for this purpose. These methods are: chemical precipitation, ultrafiltration, electro deposition, electrodialysis, reverse osmosis, ion exchange, etc. All these water treatment techniques are grossly incapacitated due to their inherent disadvantages such as: incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or waste products [3].

Adsorption is one of the most economically favourable and a technically easy method [4]. Adsorption using activated carbon has proved to be the most efficient. But activated carbon is very expensive; therefore, the search for low-cost adsorbents is imperative particularly in developing countries. Several

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low cost-adsorbents have been investigated for the removal of Cr (VI) from aqueous solution. These include: *Bacillus thuringiensis* [5], carbonaceous adsorbents prepared from sunflower waste [6], neem sawdust [7], orange peel [8], green algae *spirogyra* species [9], maple sawdust [10], unmodified cow hooves [2], exhausted coffee, wall nut shell, waste tea, nut shell, Turkish coffee [11], etc.

But many of these tested naturally occurring low-cost adsorbents have low chromium adsorption capacity. Therefore, there is a need to develop or enhance the adsorption efficiency of these low-cost adsorbents for a better Cr (VI) removal from aqueous solution [3]. To achieve this, the different tested cheaply available adsorbents should be subjected to some kind of modifications. Different modification methods have been reported to enhance the adsorption capacity of adsorbents. Generally, these methods can be classified into physical and chemical methods. Physical modification method is normally used for carbonaceous agricultural solid wastes to produce activated carbon while the chemical method involves the treatment of the adsorbent with certain chemical agents before the adsorption process [12]. The pre-treatments/modifications of adsorbents are usually carried out to achieve one or more of the following:

- Improvement of the texture, surface area and pore sizes of adsorbents,
- Elimination of impurities, waxes or fats, and ions blocking the binding sites/active functional group(s) present on adsorbents [13, 14],
- Conversion of less important functional groups into active binding groups,
- Introduction of unavailable active functional groups into an adsorbent [14].

Several chemical treatment methods are known. The current research was undertaken using ground cow hooves samples that were separately reacted/ treated with citric acid, hydrochloric acid and sodium hydroxide with a view to improving the removing impurities and fats that might block the binding sites of the hooves. Cow hooves, being a keratin containing spare part of cows, will contain hydroxyl, carboxyl and amine functional groups which are among the principal groups that have been reported as highly important in the adsorption of heavy metals [15]. The effects of operation parameters like: pH, contact time, adsorbent mass, temperature and concentration of Cr (VI) were also investigated. Equilibrium data obtained were analysed using three isotherm models- Langmuir, Freundlich and Dubinin-Raduskevich (D-R) models. The possible involvement of the functional groups present on the chemically modified cow hooves in the biosorption of Cr (VI) was also studied by taking the FTIR spectral of CACH, HCH and SCH before and after biosorption of the metal.

MATERIALS AND METHODS

Materials and preparation of samples

Cow hooves were obtained from a local abattoir in Ado-Ekiti, Nigeria. The hooves were thoroughly washed and rinsed with distilled water. The hooves were sun dried for a month. After sun drying, the hooves were washed again with distilled water and oven dried at 105^o C. The dried hooves were ground and sieved using sieve of mesh size 212 μm . The powdered cow hoof was subjected to acid and alkaline modifications using the methods described by Marshall [16] to obtain the citric acid modified sample and Li et al. [17] to obtain both HCH and SCH. A stock solution containing 1000 mgL^{-1} of Cr (VI) was prepared by weighing 2.82 g of analytical grade $\text{K}_2\text{Cr}_2\text{O}_7$ into a 1 L standard flask. This was dissolved and made to mark with distilled water. Standard solutions of different concentrations as might be required were prepared by stepwise dilution from this stock solution.

Determination of point of zero charge (pHpzc)

This was determined by solid addition method [18]. Forty five millilitres (45 mL) of KNO_3 solution of known concentration was transferred into a series of 100 mL conical flasks. The initial pH (pH_0) values of the solutions were roughly adjusted from 2 to 12 by adding either 0.1M HNO_3 or NaOH . The total volume of the solution in each flask was made exactly to 50 mL by adding the KNO_3 solution of the same concentration. The pH_i of each solution was then accurately noted, and 0.1 g of each biosorbent was added to each flask differently. The flasks were securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquid were noted. The difference between the initial and final pH (pH_f) values ($\Delta\text{pH}=\text{pH}_i - \text{pH}_f$) was plotted against the pH_i . The point of intersection of the resulting curve on pH_i gave the pH_{PZC} . The procedure was repeated for another concentration of KNO_3 .

FTIR analysis

FT-IR analysis was performed on the three samples in solid state before and after Cr (VI) removal using Fourier Transform infrared spectrometer (Perkin-Elmer Spectrum GX, Beaconsfield, UK). This was done to obtain qualitative information on the functional groups that could be involved in the process of Cr (VI) biosorption by these samples. This was carried out by mixing 5 mg of each biosorbent homogeneously with dry potassium bromide and made pellets in disc by applying pressure. The spectra of the biosorbents were measured within the range of 4000–400 cm^{-1} .

Batch studies

Unless otherwise stated, all experiments were carried out in 150 mL Erlenmeyer flasks using 0.5 g of each adsorbent and 50 mL of 50 mgL⁻¹ Cr (VI) solution. The mixture was then agitated at a constant speed for 60 minutes at 25 °C. Afterwards, the resultant solution was filtered using a filter paper and its concentration was determined using Atomic Absorption Spectrometer (AAS). The effects of the different operation parameters considered were studied as follows: The effect of initial pH was conducted at pH values ranging from 2.0 to 7.0. Solution pH was adjusted by adding 0.1 M HCl or 0.1 M NaOH solution using HI 2210 pH metre (Hanna Instruments). The effect of contact time was conducted using different contact times of 5, 10, 20, 30, 60, 90, 120 and 150 minutes. The effect of biosorbent dosage was conducted by varying the amounts of the different biosorbents from 0.1-1.0g.

Biosorption isotherm studies

Equilibrium studies were carried out at different temperatures of 25, 35, 45 and 55^o C using different initial Cr (VI) concentrations ranging from 15-100 mgL⁻¹ whose initial pH was maintained at 2. The mixture in this case was agitated for 120 minutes so as to allow all adsorbents-metal solution to attain equilibrium. The resultant solution after filtration was also analysed for the amount of Cr (VI) present using AAS. The amount of Cr (VI) adsorbed (q_e) and the percentage removal (%R) by each biosorbent (CACH, HCH and SCH) were calculated using equations (1) and (2), respectively.

$$q_e = \frac{(C_i - C_f)V}{m} \quad (1)$$

$$\%R = \frac{(C_i - C_f) \times 100}{C_o} \quad (2)$$

Where, m is the mass of biosorbent (g), V is the volume of the solution (L), C_i is the initial concentration of Cr (VI) (mgL⁻¹), and C_f is the final concentration of Cr (VI) in the liquid phase (mgL⁻¹).

RESULT AND DISCUSSION

Point of zero charge and FTIR analysis of adsorbents

pHpzc is an important parameter for a given biosorbent as it indicates the acidity/basicity of the adsorbent and the net surface charge of the biosorbent in solution [19]. The results of pHpzc determination for the three biosorbents are presented in Fig. 1a-1c. The respective pHpzc values for CACH, HCH and SCH are, 4.6, 5.22 and 7.0. This indicates that the net surface charge of CACH, HCH and SCH would be zero at pH of 4.6, 5.22 and 7.0, respectively. This also implies that the surface

of each biosorbent becomes positively charged at pH < pHpzc to favour the removal of negatively charged ions and becomes more negatively charged at pH greater than the pHpzc to favour the biosorption of positively charged ions.

The FTIR spectra of CACH, HCH and SCH recorded before and after biosorption are given in Fig. 2A-2C. The spectra reveal the presence of certain functional groups on the surfaces of the biosorbents before and after Cr(VI) removal. It can be observed that many peaks were shifted while few were retained after Cr (VI) biosorption by the three biosorbents. However, for CACH a new peak was observed at 1529.78 cm⁻¹ and for SCH the absorption band at 1544.04 cm⁻¹ disappeared after Cr (VI) biosorption. The functional groups that can be ascribed to these different absorption bands have been summarized in Table 1a-c.

TABLE 1a: FTIR spectral characteristics of CACH before and after biosorption of Cr⁶⁺

IR peak	Frequency before adsorption (cm ⁻¹)	Frequency after adsorption (cm ⁻¹)	Difference	Assignment
1	3431.00	3449.00	-18.00	Bonded -OH group
2		2931.42	0	C-H groups
3	2371.42	2371.42	0	S-H stretching
4	1638.00	1647.33	-9.33	C=O of an amide
5	-	1529.79	-1529.79	Amino group
6	1387.30	1387.30	0	Amino group
7	1239.11	1230.56	8.55	C-N stretching
8	1045.33	1039.63	5.70	C-O stretching

Effect of initial pH

Solution pH is an important factor known to play a major role in biosorption because it affects the solution chemistry of metals (speciation), the extent of dissociation of functional groups on the active sites of biomaterials and the overall surface charge of a biosorbent [14, 20, 21]. The effect of pH on the biosorption of Cr (VI) by CACH, HCH and SCH is presented in Fig. 3. The figure clearly indicates that maximum removal of Cr (VI) took place at pH of 2. All other experiments were performed at this pH. Increase in solution pH from 2 to 7 brought about decrease in the biosorption efficiency of Cr (VI) by the three biosorbents. When pH was increased from 2-7, biosorption efficiency of CACH, HCH and SCH for chromium (VI) decreased from 73.3 -30.05, 86.9 - 54% and 89.08 - 77.9%, respectively. This obviously indicates that the percentage removal recorded for SCH

at every pH was higher than those recorded for other two biosorbents. In fact, the percentage removal of Cr (VI) by the three biosorbents followed this order: SCH>HCH>CACH.

The pH dependence of Cr (VI) biosorption by these biosorbents can be explained based on the type of functional groups present, the overall charge on each

TABLE 1b: FTIR spectral characteristics of HCH before and after biosorption of Cr⁶⁺

IR peak	Frequency (cm ⁻¹) before adsorption	Frequency (cm ⁻¹) after adsorption	Difference	Assignment
1	3451.42	3440.00	11.42	Bonded -OH
2	2948.57	2937.14	11.43	C-H groups
3	2377.14	2377.14	0	S-H stretching
4	1649.48	1649.48	0	C=O of an amide
5	1541.19	1541.19	0	Amino
6	1398.70	1395.85	2.85	C-N

TABLE 1c: FTIR spectral characteristics of SCH before and after biosorption of Cr⁶⁺

IR peak	Frequency (cm ⁻¹) before adsorption	Frequency (cm ⁻¹) after adsorption	Difference	Assignment
1	3428.00	3460.00	-32.00	-OH group
2	2931.42	2937.14	0	C-H groups
3	2382.85	2365.71	17.14	S-H stretching
4	1653.33	1649.00	4.33	C=O of an amide
5	1544.04	-	-	Amino
7	1239.11	1239.11	0	C-N
8	1090.93	1068.13	22.8	C-O stretching

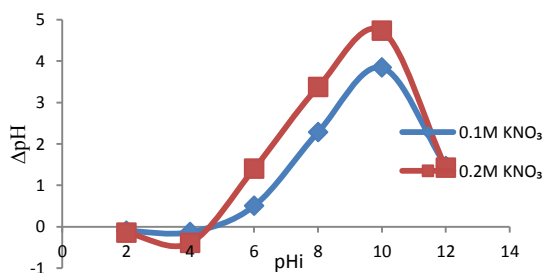


Figure 1a: Point of zero charge for CACH

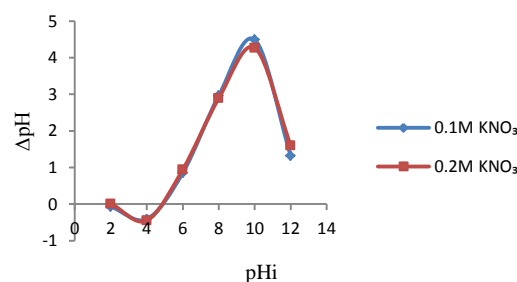


Figure 1b: Point of zero charge for HCH

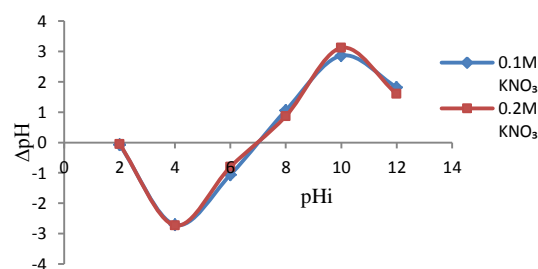
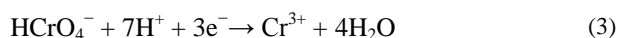


Figure 1c: Point of zero charge for SCH

biosorbent's surface and chromium speciation in solution. It has been reported that, in the pH range of 1.0–6.0, chromium ions co-exist in different forms, such as HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$, $\text{Cr}_3\text{O}_{10}^{2-}$, $\text{Cr}_4\text{O}_{13}^{2-}$ of which HCrO_4^- predominates [3, 6]. As the pH of the solution increases predominant species becomes CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ [6]. Therefore, at low pH values, there is high concentration of H^+ on the biosorbent surface and this brings about high biosorption efficiency because of the strong electrostatic attraction between the positively charged surface and the negatively charged chromium oxyanions. However, at high pH values, the surface of the biosorbent is saturated with abundant negative ions (OH^- ions). This discourages the biosorption of the chromium oxyanions on to the biosorbent surface since there will be mutual repulsions between the negatively charged biosorbent surface and that of the chromium oxyanions. Additionally, the pH dependence of the biosorption of Cr (VI) by CACH, HCH and SCH can also be explained based on the values of the pH_{pzc} . It has been reported that biosorption of cations is favoured at $\text{pH} > \text{pH}_{\text{pzc}}$, while biosorption of anions is favoured at $\text{pH} < \text{pH}_{\text{pzc}}$. The results obtained for chromium in this study agree perfectly with this phenomenon. Furthermore, Gupta and Babu, [3] reported that in acidic medium, Cr (VI) is reduced to Cr (III) according to the following equation:



This obviously reduces the percentage of chromium

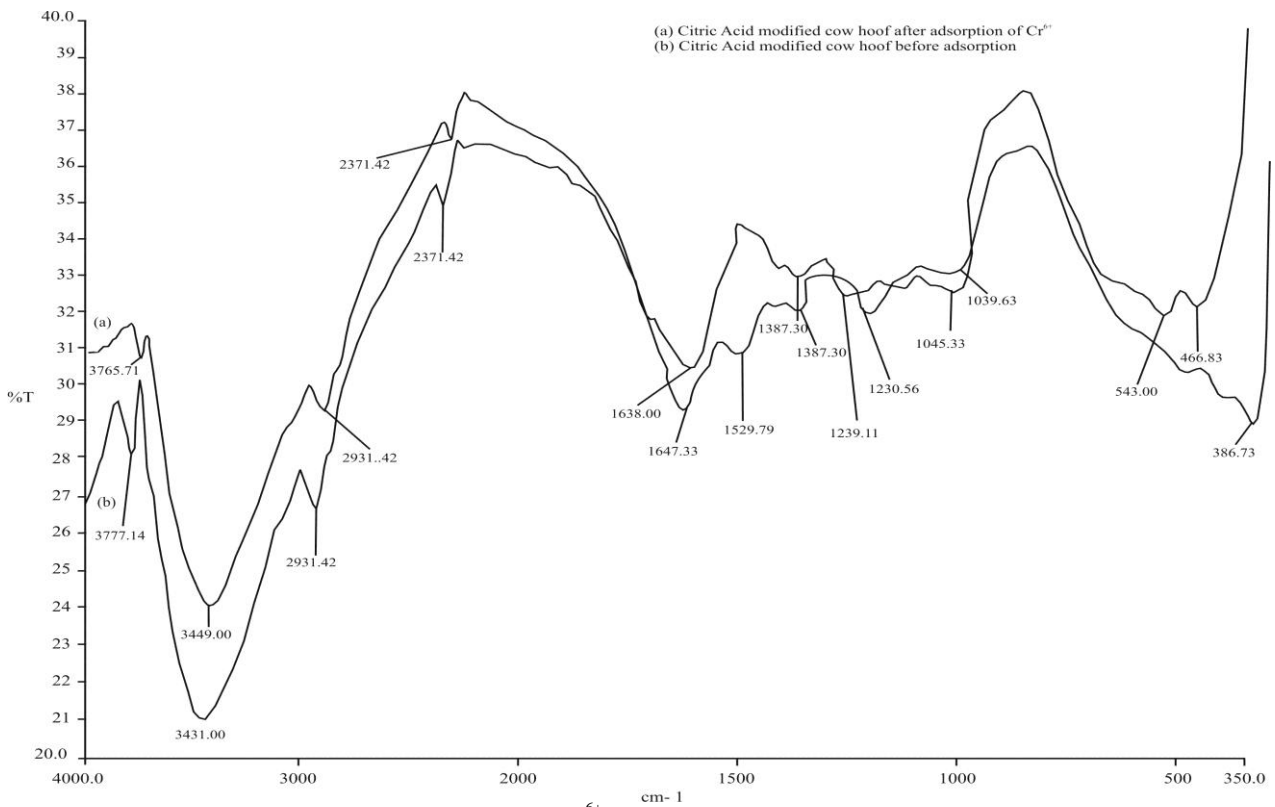


Figure 2A: FTIR spectra of (a) unloaded CACH and (b) Cr⁶⁺ loaded CACH

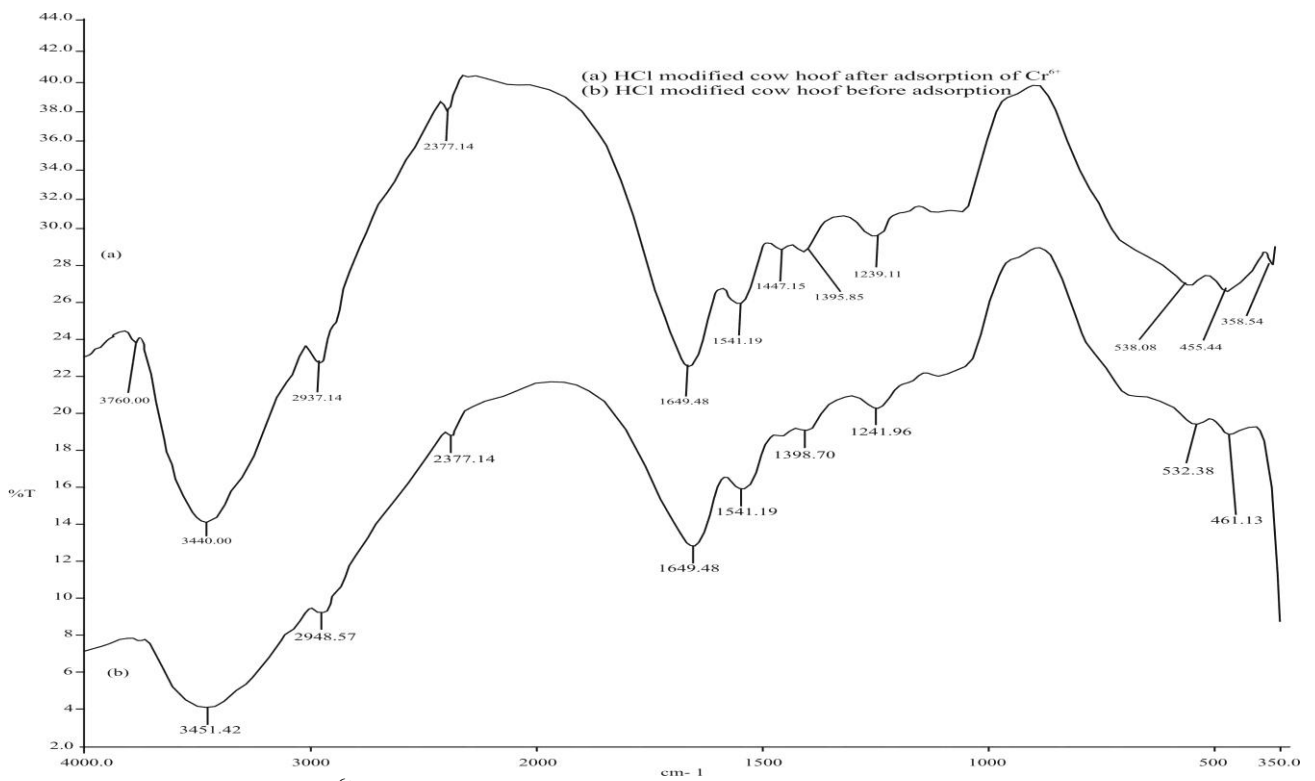


Figure 2B: FTIR spectra of (a) Cr⁶⁺ loaded HCH and (b) unloaded HCH

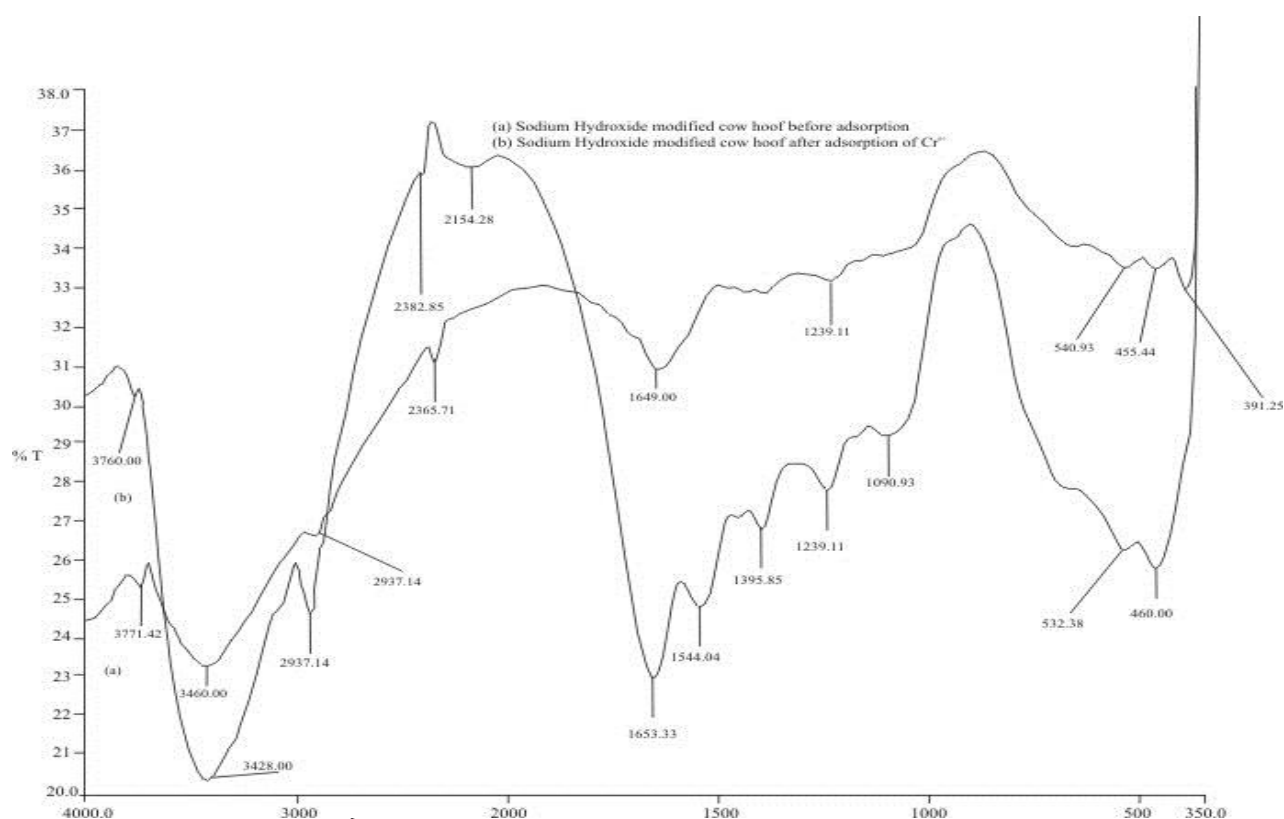


Figure 2C: FTIR spectra of (a) Cr⁶⁺ loaded SCH and (b) unloaded SCH

(VI) to be biosorbed in the solution. This directly decreases the amount of Cr (VI) left in the filtrate after biosorption and indirectly increases the percentage of chromium (VI) supposedly removed due to loss of Cr (VI) ions to reduction process.

Furthermore, the presence of the -OH functional group (Fig. 2A-2C and Table 1a-1c) on the surface of each of the biosorbents (CACH, HCH and HCH) can make one assume that the biosorbents are carbonaceous material which can be represented as C_xOH [22]. According to Hu et al., [22] hydroxylated surface groups are greatly influenced by protonation and deprotonation during pH adjustment as depicted below.

At low pH protonation occurs as indicated below:



This favours adsorption of anions (chromium oxyanion). At high pH deprotonation occurs. i.e.



This does not favour biosorption of anions because of the mutual repulsion that exists between the negatively charged chromium ion and C_xO⁻.

Biosorption kinetics

The removal of Cr (VI) by the three biosorbents increased with time. Sorption rate was observed to be

rapid within the first ten minutes for all biosorbents and then continued steadily until equilibrium was established after 30, 60, and 90 minutes of agitation for CACH, SCH and HCH, respectively (Fig. 4).

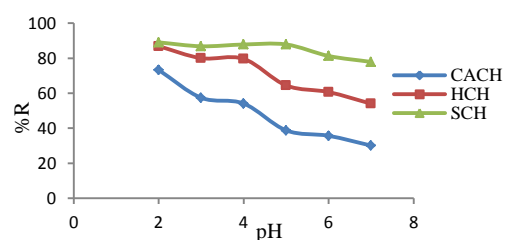


Figure 3: Effect of pH on the removal of Cr (VI) using HCH and SCH (at 298 K, biosorbent dosage: 0.5 g; initial Cr (VI) concentration: 50 mgL⁻¹).

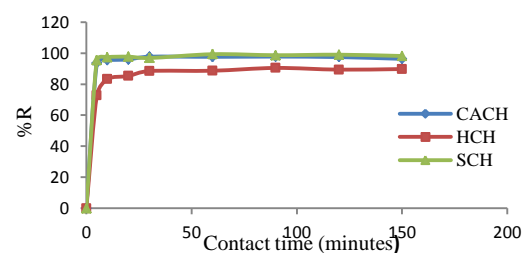


Figure 4: Effect of contact on the removal of Cr (VI) using CACH, HCH and SCH (pH: 2, temperature: 298 K, biosorbent

dosage: 0.5 g; initial Cr (VI) concentration: 50 mgL⁻¹).

The data obtained by varying the contact time were regressed against the linear forms of the pseudo-first-order kinetic equation, Eq. (6) and the pseudo-second-order kinetic equation Eq. (4) as shown below:

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \frac{k_1 t}{2.303} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

Where q_t is the metal uptake per unit weight of biosorbent (mg g⁻¹) at time t , q_e is the metal uptake per unit weight of biosorbent (mg g⁻¹) at equilibrium, and k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the rate constants of the pseudo-first-order and pseudo-second-order kinetic equations, respectively. The values of k_1 and its corresponding q_e values were respectively determined from the slope and intercept of the plot of $\log q_e - q_t$ versus time (Eq. 3). While k_2 and its corresponding q_e values were respectively determined from the intercept and slope of the plot of t/q_t versus time (Eq. 4). The values of these parameters are presented in Table 2.

TABLE 2: Kinetics parameters for the biosorption of Cr (VI) using CACH, HCH and SCH at 298K

Sample	First-order			Second-order			
	$q_e(\text{exp})$ mg g ⁻¹	$q_e(\text{cal})$ mg g ⁻¹	k_1 min ⁻¹	R^2	$q_e(\text{cal})$ mg g ⁻¹	k_2 gmg ⁻¹ min ⁻¹	R^2
CACH	4.89	-	-	-	4.85	6.74	0.999
HCH	4.52	0.38	0.03	0.73	4.52	1.00	0.999
SCH	4.97	0.077	0.02	0.53	4.93	0.14	0.999

The calculated values of $q_e(\text{cal})$ (Table 2) from the first-order kinetics model were obviously lower than the experimental $q_e(\text{exp})$ values for HCH and SCH. The pseudo-first-order kinetic equation could not be applied to the kinetic data obtained for CACH because the removal of Cr (VI) by CACH was brought to equilibrium at a faster rate than others. The kinetics parameters obtained from linearized pseudo-second-order kinetics model (Fig. 5 and Table 2) clearly indicates that the removal of Cr (VI) from aqueous solution could better be described by pseudo-second-order. This is because the model provided much better R^2 values than those for the first-order model. Besides this, the calculated q_e values obtained from the pseudo-second-order kinetics are in good agreement with the experimentally determined q_e for all the biosorbents.

Effect of biosorbent mass

The results of the effect of biosorbent mass on the removal of Cr (VI) from aqueous solution by CACH, HCH and SCH are presented in Fig. 6. The results

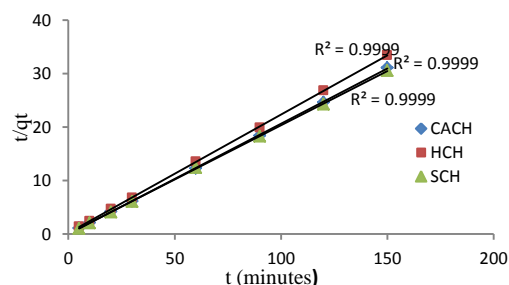


Figure 5: Pseudo-second-order kinetic plot for the removal of Cr (VI) by CACH, HCH and SCH at 298 K

showed that biosorption efficiency increased with increase in the amount of biosorbent dosed. Biosorption efficiency increased from 45.85% to 96.5% (CACH), 53.05 to 97.95% (HCH) and 98.1 to 99.85% (SCH) when the amount of biosorbent used increased from 0.1 to 1 g. This can be explained based on the fact that increase in the amount of biosorbent dose brings about increase in the number of exchangeable sites available for metal biosorption [22]. However, biosorption capacity recorded for the three biosorbents decreased with increase in biosorbent dosage (Table 3). The uptake capacity of Cr (VI) decreased from 11.46 to 2.29 mg g⁻¹ (CACH), 13.26 to 1.22 mg g⁻¹ (HCH) and 24.53 to 2.49 mg g⁻¹ (SCH) when the amount of biosorbent was increased from 0.1 to 1 g (Table 3). This may be due to interferences among the binding sites at high concentrations of biosorbent which can be caused by over-crowding of the biosorbent particles[6].

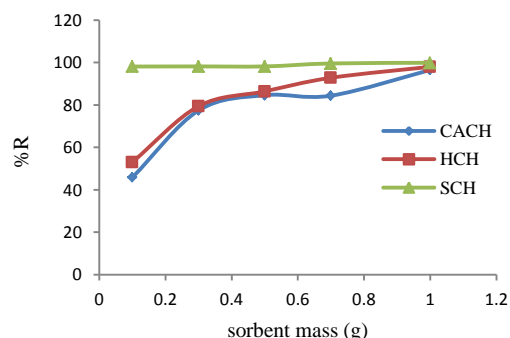


Figure 6: Effect of sorbent mass on biosorption of chromium (VI) using CACH, HCH and SCH (pH: 2, temperature: 298 K, initial Cr (VI) concentration: 50 mgL⁻¹).

Effect of temperature and concentration

The results for the effect of concentration and temperature are illustrated in Fig. 7a-c. The general observation is that the amount of Cr (VI) biosorbed per

TABLE 3: Biosorption capacity of CACH, HCH and SCH at different biosorbent doses.

Biosorbent dose g	CACH mg g ⁻¹	HCH mg g ⁻¹	SCH mg g ⁻¹
0.1	11.46	13.26	24.53
0.3	6.45	6.62	8.18
0.5	4.23	4.32	4.91
0.7	3.01	3.31	3.56
1.0	2.29	1.22	2.49

milligram of each biosorbent increased with increase in the initial concentration of Cr (VI) ion. For example, when the metal concentration was increased from 15-100 mgL⁻¹ at 298 K, the amount of Cr (VI) biosorbed increased from 1.46 to 7.52 mg g⁻¹ (CACH), 1.41 to 9.09 mg g⁻¹ (HCH) and 1.43 to 9.25 mg g⁻¹ (SCH). The same trend was also observed at other temperatures considered. These findings can be explained based on

Sample	TK	ΔG° kJ.mol ⁻¹	ΔH° kJ.mol ⁻¹	ΔS° J.mol ⁻¹
CACH	298	-6.15	8.15	48
	308	-6.63		
	318	-7.11		
HCH	328	-7.59	-28.79	-72
	298	-7.33		
	308	-6.61		
SCH	318	-5.89	-19.93	-40
	328	-5.17		
	298	-8.01		
	308	-7.61		
	318	-7.20		
	328	-6.81		

mass transfer driving force because as the initial metal concentration increases, the mass transfer driving force becomes larger, hence resulting in higher metal biosorption [23].

The uptake capacity of HCH and SCH for Cr (VI) decreased with increase in temperature while uptake capacity of CACH increased with increase in temperature. When the temperature was increased from 298 to 328 K, for initial concentration of 50 mgL⁻¹, uptake capacity of HCH and SCH decreased from 4.76 to 4.36 mg g⁻¹ and 4.81 to 4.63 mg g⁻¹, respectively. While, within the same temperature range for CACH, uptake capacity increased (4.64 to 4.74 mg g⁻¹). This indicates that the removal of chromium ions from aqueous solution by HCH and SCH is exothermic while its removal by CACH is endothermic.

Biosorption thermodynamic

The thermodynamic parameters for the obtained equilibrium data on temperature variation by the use of equations (8-10) were evaluated [24, 25]. The

equilibrium constant K_e was calculated based on C_{Ae} and C_e values:

$$K_e = C_{Ae}/C_e \quad (8)$$

Where, C_{Ae} represents adsorption in mgL⁻¹ at equilibrium; and C_e is the equilibrium concentration of the metal in mgL⁻¹. The respective values of ΔH and ΔS were obtained from the slope and intercept of the plot of $\ln K_e$ against $1/T$ (Eq. 9) while the values of ΔG^0 at different temperatures were obtained using equation (10).

$$\ln K_e = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (9)$$

Where, T is Temperature in Kelvin and R is the gas constant (kJmol⁻¹K⁻¹).

The summary of results for thermodynamic parameters are presented in Table 4. The positive value of ΔH^0 for Cr (VI) adsorbed on CACH further confirms the endothermic nature of the biosorption of Cr (VI) by CACH while the negative values recorded for HCH and SCH also confirm the exothermic nature of the biosorption of Cr (VI) by HCH and SCH. The ΔG values recorded for the three biosorbent indicate that the biosorption of Cr (VI) was spontaneous at all temperatures considered.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

A comparison of the adsorption capacities for the adsorption of metal ions on different biosorbents used in the literature with cow hoof (modified and unmodified) is summarized in Table 7. Although direct comparison of adsorption capacities of different biosorbents is

TABLE 4: Thermodynamic parameters for the biosorption of Cr⁺⁶ on CACH, HCH and SCH

Biosorption isotherm

The most commonly used models to represent adsorption equilibrium data from solution are Langmuir and Freundlich isotherm models. In this work, both models and Dubinin–Radushkevich were used to describe the relationship between the amount of chromium (VI) ion adsorbed and its equilibrium concentration. The applicability of the isotherm models to biosorption study was judged by the correlation coefficient, R^2 value of each plot. The high the R^2 value represents the desired data fit. The linear forms of Langmuir, Freundlich and Dubinin–Radushkevich (D-R) models are presented in equations (11, 12 and 13), respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (11)$$

Where, q_m (mg g⁻¹) is the maximum adsorption capacity, K_L (Lmg⁻¹) is a constant related to the affinity

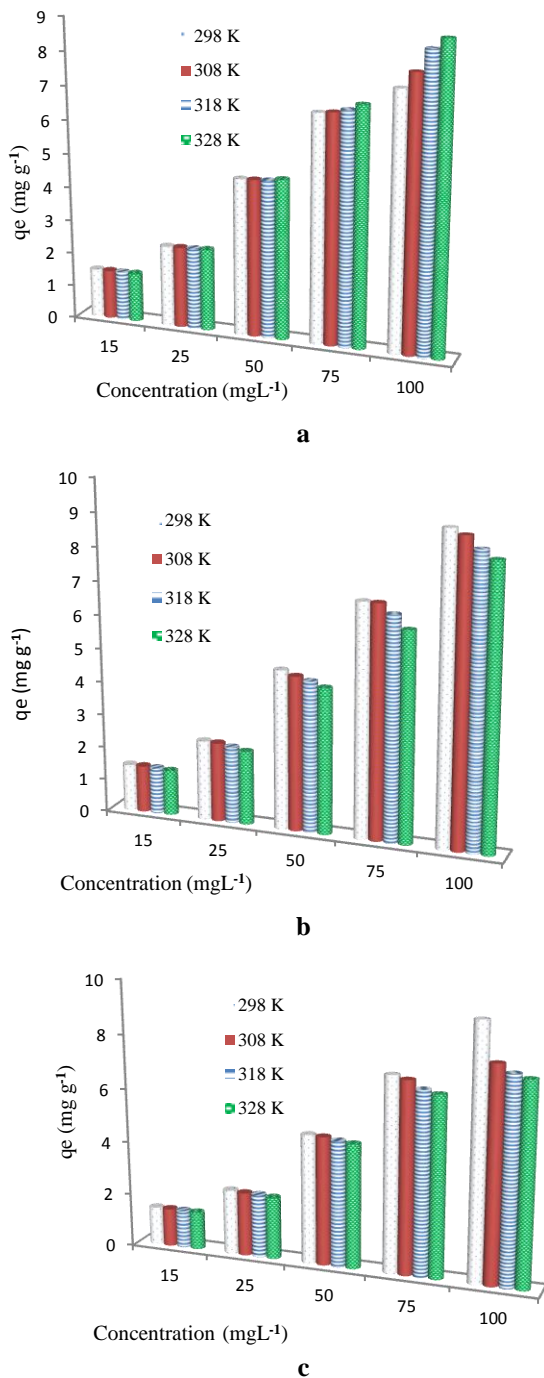


Figure 7: Effect of temperature and concentration on the removal of Cr⁶⁺ by (a) CACH (b) HCH and (c) SCH.

of binding sites or bonding energy. The respective values of q_m and K_L were obtained from the slope and intercept of the linear plots of C_e/q_e versus C_e and their values are presented in Table 5.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (12)$$

Where q_e (mg g^{-1}) is the metal uptake at equilibrium, C_e (mg L^{-1}) is the equilibrium concentration of the metal, and K_f and n are the Freundlich constants related to adsorption capacity and affinity between the adsorbent and the metal, respectively. The respective values of n and K_f were obtained from the slope and intercept of the linear plots of $\log q_e$ versus $\log C_e$ and their values are also presented in Table 5.

The linear form of Dubinin Raduskevich isotherm model stated as follows:

$$\ln q_e = \ln q_D - K_D \varepsilon^2 \quad (13)$$

Where ε is the Polanyi potential = $RT \ln(1 + 1/C_e)$, q_D is the Dubinin Raduskevich adsorption capacity of the adsorbent (mg g^{-1}), K_D is Dubinin Raduskevich constant relating to the adsorption energy ($\text{mol}^2 \text{kJ}^{-2}$), R is the gas constant ($\text{kJ K}^{-1} \text{mol}^{-1}$), and T is the temperature (K). Linear plots of $\ln q_e$ versus ε^2 were obtained and the values of K_D and q_D were evaluated from the slope and intercept, respectively. The mean adsorption energy can be determined from D-R model using the relationship:

$$E = (-2K_D)^{-1/2} \quad (14)$$

The maximum adsorption capacities (q_m for Langmuir, K_f for Freundlich and q_D for D-R), adsorption constants (K_L and n), mean adsorption energies and the correlation coefficients obtained for the three isotherm models at different temperatures are presented in Table 5.

It is obvious from the results presented in Table 5 that biosorption of Cr (VI) by CACH and SCH was best described by Langmuir. The maximum monolayer adsorption capacity evaluated for CACH increased from 8.14 to 10.52 mg g^{-1} but the maximum monolayer adsorption capacity obtained for SCH decreased from 15.87 to 8.55 mg g^{-1} for temperature ranged 298 to 328 K. For HCH, the removal of Cr (VI) was best described by Freundlich model and its corresponding maximum adsorption capacity (K_f) decreased from 2.05 to 1.09 $\text{L}^{1/n} \text{g}^{-1} \text{mg}^{-1/n}$.

The values of Freundlich constant n are important for predicting the favourability of any adsorption process [27]. An adsorption process is said to be favourable if $1 < n < 10$. All the values of n obtained for all samples at all temperatures fall within this range (Table 5). Similarly, the values of Langmuir constant K_L can predict the affinity between the sorbate and sorbent using the dimensionless separation factor R_L , defined as follows:

$$R_L = \frac{1}{1 + K_L C_o} \quad (15)$$

Where C_o is the initial concentration of Cr (VI) (mg L^{-1}) and K_L is Langmuir constant. Separation factor describes the affinity between sorbent and adsorbate as:

Irreversible, if $R_L = 0$; favourable, if $0 < R_L < 1$; linear if $R_L = 1$ and unfavourable if $R_L > 1$. The R_L values in this study are shown in Table 6. The values indicate that the biosorption of chromium by the biosorbents was favourable at all temperatures and this became more favourable at high initial metal concentration at all temperatures considered. The mean adsorption energy (E) calculated from D-R isotherm model (Equation 11) can be used to determine the nature of biosorption process. If E is $< 8 \text{ kJmol}^{-1}$, the adsorption process is dominated by physisorption mechanism and if E is between 8 and 16 kJmol^{-1} , the adsorption process is dominated by chemisorption mechanism and if E is $> 16 \text{ kJmol}^{-1}$, the sorption process is dominated by particle diffusion [27, 28]. The ranges of mean adsorption energies for the different biosorbents studied are as follows (Table 5): 1.80 to 2.15 kJmol^{-1} (CACH), 0.81 to 4.14 kJmol^{-1} (HCH) and 1.14 to 1.26 kJmol^{-1} (SCH). This observation clearly suggests that the biosorption of

TABLE 6: Separation factor (R_L) values for chromium ion biosorbed on CACH, HCH and SCH

Sample	Co mgL ⁻¹	298 K	308 K	318 K	328 K
CACH	15	0.120	0.137	0.160	0.132
	25	0.075	0.087	0.103	0.083
	50	0.039	0.045	0.055	0.043
	75	0.026	0.031	0.036	0.029
	100	0.020	0.023	0.028	0.022
HCH	15	0.323	0.357	0.426	0.499
	25	0.222	0.250	0.308	0.374
	50	0.125	0.143	0.182	0.230
	75	0.087	0.100	0.129	0.166
	100	0.067	0.077	0.100	0.130
SCH	15	0.250	0.156	0.172	0.198
	25	0.167	0.100	0.111	0.129
	50	0.091	0.053	0.059	0.069
	75	0.063	0.036	0.040	0.047
	100	0.048	0.027	0.030	0.036

chromium in this study was dominated by physisorption at all temperatures. difficult due to the differences in experimental conditions, yet the adsorption capacities of biosorbents in this study compare favourably well with those reported in the literature.

CONCLUSION

Investigation was conducted on the ability of citric acid modified, hydrochloric acid modified and sodium hydroxide modified cow hoof powder to remove Cr (VI) from aqueous solution. Our results revealed that Cr (VI) adsorption by these samples depended on pH, initial concentration of Cr (VI), adsorbent dose, contact time and temperature. Percent removal was 73.3% for CACH, 86.9% for HCH and 89.08% for SCH at pH 2.0. Uptake capacity (mg g^{-1}) of the samples for Cr (VI) increased with increase in initial Cr (VI) concentration

but decreased with increase in biosorbent dose. Kinetic studies showed that biosorption of Cr (VI) by all the samples was rapid at initial stages and decreased with increase in biosorption time until equilibrium was attained. The kinetic studies further revealed that removal of Cr (VI) fitted perfectly with the pseudo-second order model for the three biosorbents. The evaluated thermodynamic parameters revealed that the sorption of Cr (VI) by both HCH and SCH was exothermic while the sorption process was endothermic for CACH. The removal of Cr (VI) by the three biosorbents was observed to be feasible judging from the values of the Gibb's free energy obtained in this study. But biosorption of Cr (VI) from aqueous solution by both SCH and HCH is likely to be more economically feasible than sorption using

CACH. TABLE 7: Comparison of adsorption capacity (q_m) evaluated from Langmuir isotherm model of CACH HCH and SCH for Cr (VI) with that of other low-cost adsorbents

Biosorbent	Temperature K	q_m mg g ⁻¹	Ref.
Cow hoof	298	3.57	[2]
Acid treated sun flower head	298	53.4	[6]
Acid treated sun flower stem	298	47.3	[6]
Modified oak saw dust	293	1.7	[26]
	303	1.72	[26]
	313	1.74	[26]
<i>Aeromonas caviae</i>	NA	124.6	[27]
<i>Chryseomonas luteola</i>	NA	3.0	[28]
Wool	303	41.15	[29]
Coal	303	6.78	[29]
Cactus	303	7.08	[29]
Almond	303	10.62	[29]
Tea factory waste	298	27.24	[30]
	318	36.90	[30]
	333	54.65	[30]
CACH	298	8.14	Current study
HCH	298	16.18	Current study
SCH	298	15.87	Current study

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Persian Abstract

DOI: 10.5829/idosi.ijee.2015.06.04.07

چکیده

در این مطالعه، مطالعات امکان سنجی فرآیند batch با استفاده از اسید هیدروکلریک اصلاح شده ی سم گاو (HCH)، اسید سیتریک اصلاح شده ی سم گاو (CACH) و سدیم هیدروکسید اصلاح شده ی سم گاو (SCH) برای حذف Cr(VI) از محلول آبی مورد بررسی قرار گرفت. داده های تعادلی در ۴ دمای مختلف (۲۵،۳۵،۴۵ و ۵۵) درجه سانتی گراد، از طریق تماس با محلول Cr(VI) در غلظت های مختلف با SCH و HCH، CACH به دست آمد. نتایج حاصل از این مطالعه نشان داد که SCH درصد بالاتری از حذف Cr(VI) را نسبت به HCH و CACH ثبت کرده است. pH برابر ۲ برای حداکثر حذف Cr(VI) توسط سه جاذب زیستی مورد نیاز بود. داده های به دست آمده برای هر دو جاذب SCH و CACH بهترین برازش را با مدل لانگمیر دادند در حالی که داده های به دست آمده برای HCH بهترین برازش را با مدل فرندلیچ دادند. پارامتر های ترمودینامیکی برای حذف Cr(VI) فرآیند خود به خودی و گرمای را برای HCH و SCH و فرآیند گرماگیر را برای CACH نشان دادند. بنابراین، حذف Cr(VI) از پساب با استفاده از این جاذب های زیستی کم هزینه (به خصوص HCH و SCH) از لحاظ اقتصادی امکان پذیر خواهد بود.