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Peanut shells and talc powder for removal of hexavalent chromium from aqueous solutions

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In this work, talc powder and peanut shells were investigated as potential adsorbents for the removal of hexavalent chromium from aqueous solutions. The effect of important parameters, such as contact time, solution pH and adsorbent dosage were also evaluated for the adsorption process of chromium (IV). The experimental data showed that a contact time of 30 min for peanut shells and 70 min for talc powder and pH of 4 were optimum for the adsorption to reach equilibrium. Furthermore, FT-IR, SEM and BET measurements were made in order to assess the physicochemical properties of the substrates. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models were used to fit the equilibrium data, heat and energy of adsorption of both adsorbents. Determinations of the rate of adsorption using kinetic models follow pseudo-first order for peanut shells and talc powder with intraparticle diffusion.

Keywords: Talc powder, peanut shell, hexavalent chromium, removal, wastewater.

INTRODUCTION

The presence of heavy metals in the environment has been of great concern due to the increased concentration of downstream discharge with toxic nature on various habitats affecting many living organisms. Toxicity levels of heavy metals depend on the type of metal, its valence state, its biological role and volume or concentration [1]. Chemical and biological properties of an element species depend very much on its oxidation state, and an accurate determination of different species of a given element is important for the comprehension of its biological and physiological functions, as well as potential toxicity [2]. The occurrence of heavy metals such as chromium derives either from anthropogenic or geogenic activities, in the former case it is mainly from chemical process industry emissions while in the latter it is through natural generation from rock-bearing materials. The transition metal chromium is found in aqueous streams such as wastewater, groundwater, seas and lakes released from different industrial sources and contaminants such as steel and other alloy forming materials and elements, electroplating, dyes and pigments for painting and printing, leather tanning, wood preservation and textiles, photography and surface treatment work as well as chromite from ultramafic rocks [3, 4].

Chromium usually exists in either hexavalent or trivalent form in aqueous media and is considered to be non-degradable. Hexavalent chromium is more toxic than the trivalent one owing to its high mobility across biological cell membrane and its oxidizing potential [5]. Hexavalent chromium is a mutagen, teratogen and carcinogen; chronic inhalation and exposure affect the respiratory tract with ulcerations of the body system and also affect the immune system [3, 6]. Therefore, differentiation and quantification of chromium in the two oxidation states are important in developing a strategic approach to deal with drainage of the wastewater and effluent disposal into the environment.

Various methods have been reported in the literature to remove hexavalent chromium such as reduction [7, 8], electro-coagulation [9], membrane and photocatalysis [10], co-precipitation [11], ion-exchange separation [12, 13] and adsorption, the latter being the most commonly employed method [14-17]. Traditional techniques using commercially available activated carbon for removal of the heavy metal chromium have been the preference of choice due to their accessible high surface area and porous structure leading to high adsorption capacity. However, high cost and dependence on importation of activated carbon by most developing countries would mean that alternatives that are on par with the surface characteristics and efficiency have to be sought for. Nowadays, low cost, environmentally benign and abundant resources are getting

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widespread attention for chromium effluent treatment, where agricultural waste and biomass products are converted into a value-added system as effective adsorbents. Owing to their chemical composition and complex structures of cellulose, hemicellulose and lignin, lignocellulosic materials can be used for adsorbing chromium-with slight or no modifications or treatment through physical and chemical means to have similar properties as activated carbons. Various lignocellulosic and agricultural wastes have been forwarded to maximize the adsorption capacity of Cr(VI) from wastewaters [17-24]. The potential for using complex minerals for the adsorption process of chromium (VI) has not been investigated except sand with major constituent of silica [25]. Talc mineral deposits exist in Egypt and its use as adsorbent material is for the first time presented. Therefore, the aim of this work was to study the possibility of using peanut shells and talc powder as adsorbents for removal of hexavalent chromium from waste water; to assess the important parameters that affect the adsorption process (such as time, pH, and dosage of adsorbents), as well as surface characteristics and properties of the adsorbents. Kinetic models and equilibrium studies were also carried out to substantiate the relationship with the experimental data for both adsorbents.

MATERIALS AND METHODS

Materials

$K_2Cr_2O_7$, sodium diphenylamine sulfonate, NaOH, and H_2SO_4 were all of analytical grade and were used as received. A stock solution of the adsorbate, hexavalent chromium of 10000 mg L^{-1} was prepared by dissolving an appropriate quantity of AR grade $K_2Cr_2O_7$ in 1000 ml of distilled water. The stock solution was further diluted to the desired concentration for obtaining the test solutions. Initial metal ion concentrations ranging from 70 to 3000 mg L^{-1} were prepared. A set of experiments was conducted to optimize and determine the Cr(VI) removal from aqueous solutions under varying process conditions of pH, contact time, amount of adsorbent and adsorbate concentration.

Characterization methods

The surface morphology of peanut shells and talc powder was analyzed using different magnifications by scanning electron microscopy (SEM, JEOL JSM 6360LA). The surface functional groups with binding sites and structure of the solid materials were studied by Fourier transform infrared spectroscopy (FTIR-8400S, Shimadzu). The FT-IR spectra of talc powder and peanut shells were recorded between 500 and 4000 cm^{-1}. The specific surface areas of peanut shell and talc powder were also characterized by the Brunauer-Emmet-Teller (BET) method, where the samples were degassed at120^{o}C and nitrogen was adsorbed at liquid nitrogen temperature (-196 ^{o}C). Specific surface areas were calculated from the linear region of the isotherms in a relative P/Po pressure range of 0.06–0.20. Pore size distributions were derived from the adsorption branch of the isotherms by the Barrett–Joyner–Halenda (BJH) method. The total pore volumes were estimated from the amount adsorbed at a relative pressure of P/Po = 0.98.

Preparation of adsorbents and adsorption studies

Two adsorbents, one a biomass waste of peanut shells and another a mineral composite of talc powder, were used for Cr(VI) removal. The peanut shells were collected from local sources, washed with distilled water, cut into suitably sized pieces and dried in an oven at 80 ^{0}C for 2 h. The dried materials were then crushed and sieved into different sizes ranging from 4 mm to 500 μm. The talc powder was washed with distilled water and was subjected to sedimentation in order to remove any surface impurities. After this step, it was dried at 60^{o}C in an oven for 1 h and then stored in a desiccator.

Batch adsorption experiments were conducted in 250 mL conical flasks at a solution pH of 4.0. The adsorbent, each in a different experiment, (0.5, 1, 2 and 3 g L^{-1}) was thoroughly mixed with 100 mL of hexavalent chromium solution (3000 mg L^{-1}) and the suspensions were stirred using IKA RT5 model magnetic stirrer operated at 400 rpm at room temperature. Duplicate samples of 1.0 mL each were collected from the supernatant at predetermined time intervals of 5 to 180 min to verify the reproducibility. These samples were then centrifuged for 5 min and the clear solutions were analyzed for the residual hexavalent chromium concentration. The spectrophotometric technique developed by Dong *et al*. [26] was used to determine the residual hexavalent chromium in the solution. This method is based on the reaction of hexavalent chromium with sodium diphenylamine sulfonate in an acidic medium to form a purple complex (λmax = 550 nm).

The amount of solute adsorbed per unit gram of adsorbent q (mg g^{-1}), was evaluated from the following equation:

$$q = \frac{(C_i - C_f)V}{M} \qquad (1)$$

where: V is the volume of the solution, C_i is the initial concentration of the adsorbate solution (mg L^{-1}), C_f is the final concentration (mg L^{-1}) of the solute in the bulk phase at a time (t) and M is the mass of the adsorbent.

RESULTS AND DISCUSSION

Characterization of the adsorbents

Talc powder $Mg_3[Si_4O_{10}](OH)_2$ is a hydrous silicate material consisting of two major parts of oxides of silicon and magnesium with the chemical composition shown in Table 1.

Table 1. BET-surface area and chemical properties of the talc powder used.

Type	Value
Specific surface area (m^2/g)	4.3
SiO_2 (%)	63.26
MgO (%)	26.71
Al_2O_3 (%)	1.47
Fe_2O_3 (%)	0.54
CaO (%)	0.75
K_2O (%)	0.31
Na_2O (%)	0.13

It is one of the softest minerals ever known, having a hardness of 1 according to the Mohs scale. Its available surface area for adsorption or other wider area industrial application markedly depends on the particle size of the powder. Its specific surface area was found to be 4.3 m^2 g^{-1}. A schematic diagram of the chemical structure of talc powder is shown in Fig. 1. The particle size distribution for talc powder used was between 30 and 350 nm and the mean particle size was 158 nm with a pore volume corresponding to 0.09 cm^3 g^{-1}.

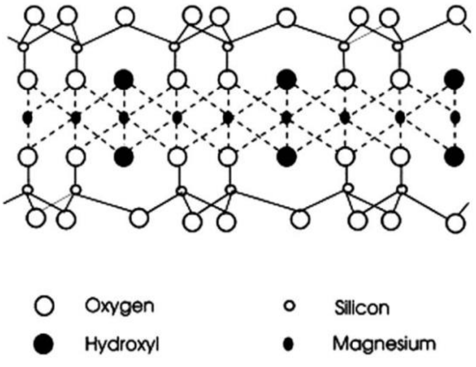
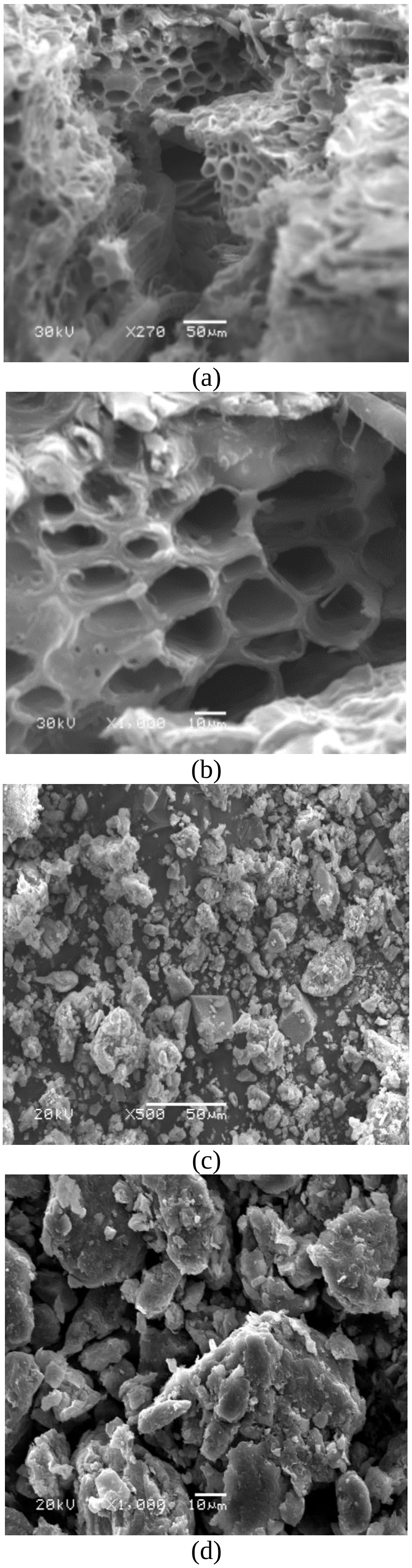


Fig. 1 Schematic diagram of the crystal structure of talc powder as viewed along the x-axis [27].

Peanut shells after the treatment steps had a specific surface area of 0.861 m^2 g^{-1}, a pore volume of 0.0036 cm^3 g^{-1} and an average particle diameter of 100 μm. Morphological analyses of the peanut shells and talc powder samples were performed by scanning electron microscopy (SEM) and are presented in Figs. 2a-2d for the respective adsorbent under different magnifications.



(a)

(b)

(c)

(d)

Fig. 2. a) SEM images for peanut shells with magnification of 270 times b) magnification of 1000 times c) SEM images for talc powder with magnification of 270 times d) magnification of 1000 times

At high magnification (Fig. 2b), peanut shells surface shows high roughness with hollow cavities of porous structures in the range of 7 to 25 µm, while Figs. 2c and 2d show talc powder having both small and big particle aggregates with sharp edges.

Like all vegetable biomass, peanut shells are composed of cellulose, hemicellulose and lignin. Peanut shells mainly consist of polysaccharides, proteins, and lipids, offering many functional groups such as carboxyl, carbonyl, hydroxyl and amino with characteristic chemical structures. The peaks in the FT-IR spectrum on Fig. 3 for peanut shells prior to adsorption were assigned to various groups and bands in accordance to their respective wave numbers (cm^{-1}) showing the complex nature of the adsorbent. The broad band around 3388 cm^{-1} is attributed to the surface hydroxyl groups (-OH), which are most probably due to the interaction and presence of alcoholic, phenolic, amino, and carboxylic derivatives. The peak at 2920 cm^{-1} is assigned to C–H asymmetrical stretching band of most aromatics, aliphatics and olefins [28]. These groups are also present in the lignin structure [29]. The peaks located at 2138 cm^{-1} are characteristic of the C−C stretching band, representing alkyne groups. The peak associated with the stretching in C=O (carbonyl compounds) and C=C is verified at 1629 cm^{-1} and is ascribed to ketones, aldehydes alkenes, esters and aromatic groups, respectively. The absorption peaks at 1480 and 1271 cm^{-1} could be due to C−O, C−H or C−C stretching vibrations. The peak observed at 1051 cm^{-1} is due to the C−O group in carboxylic and alcoholic groups. The band of the C−O group in Fig. 3 was more intense than that of the C=O group, possibly due to the presence of more C−O groups in peanut shells. The peak at 588 cm^{-1} is due to the vibrational bending in the aromatic compounds of lignin.

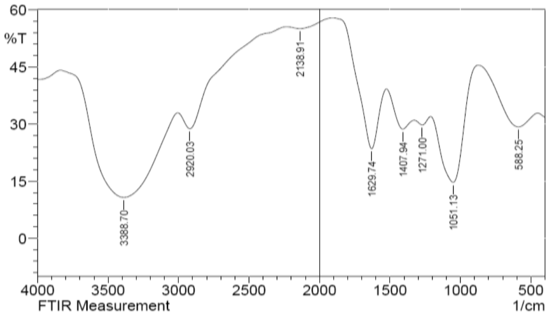


Fig. 3. FT-IR spectrum of raw peanut shells.

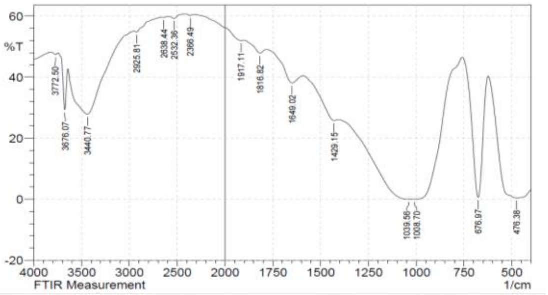


Fig. 4. FTIR spectrum of talc powder

The vibrations in the bands of the FT-IR spectrum for talc powder are shown in Fig. 4, where wave numbers of 3676, 3441, 1040, 677 and 476 cm^{-1} dominate. The siloxane group (Si-O-Si) stretching vibrational bands exist with intense peaks at 476 and 1040 cm^{-1}, respectively, while the band at 677 cm^{-1} reflects the Si-O-Mg bond [30]. The bands at 3441 and 3676 cm^{-1} are ascribed to the vibrations of hydroxyl groups linked to Si (Si-OH) and Mg (Mg-OH), respectively [31].

Effect of contact time

Contact time has a strong effect on the adsorption process of chromium as the interaction depends on the physicochemical properties and volume of the adsorbent, as well as the distribution and flow rate in the adsorption column. Thus, higher flow rates and small volumes would mean less contact time with low adsorption capacity, while *vice versa* is valid for higher adsorption capacity. The effect of adsorption time on hexavalent chromium removal with comparative data for both adsorbents (0.5 g) is shown in Fig. 5. The amount of adsorbed hexavalent chromium increased with contact time for the two adsorbents used and equilibrium was attained within 30 min for peanut shells and 70 min for talc powder. The latter showed higher adsorption capacity for hexavalent chromium than peanut shells, because of its smaller average particle diameter, higher pore volume, higher surface area and the probable complexation with the compounds present in the mineral.

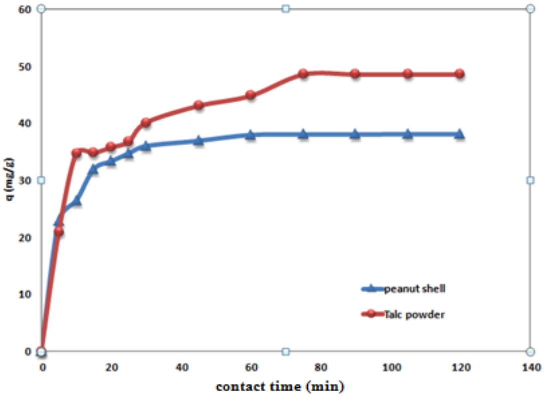


Fig. 5. Effect of contact time on the adsorption capacity of talc powder and peanut shells for hexavalent chromium (initial conc. 3000 mg L^{-1}, adsorbent dosage 0.5 g L^{-1}, temp. 25^{o}C, pH=4.0, 400 rpm)

Effect of adsorbent dosage

Under optimum conditions of stirring and pH, the effect of adsorbent dosage on the adsorption of hexavalent chromium was studied by stirring 100 mL of 3000 mg L^{-1} of hexavalent chromium solution with 0.5 – 3 g L^{-1} of adsorbent for 1 h at 25ºC and constant pH 4. The results of the experiments with varying adsorbent dosage are presented in Fig. 6. It was found that the % removal for talc powder increases from 50 to 77 % as the adsorbent dosage is increased from 0.5 to 3.0 g L^{-1}, while that for peanut shells increased from 36 to 72 %. This can be explained by the fact that the more the mass of adsorbent available, the more contact surface is offered to adsorption, resulting in an adsorbate-adsorbent equilibrium. Interestingly, up to 1.5 g L^{-1} both talc powder and peanut shells show similar % removal. However, talc powder shows higher efficiency resulting from the higher surface area exposure for adsorption and lower mass transfer resistance due to the available porous structure and volume.

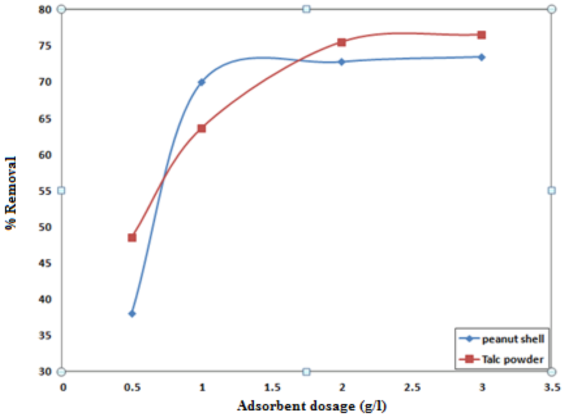


Fig. 6. Effect of dosage of talc powder and peanut shells on hexavalent chromium removal (initial conc. 3000 mg L^{-1}, pH=4.0, temp. 25ºC, 400 rpm)

Effect of pH of the solution

In order to optimize the pH for maximum removal efficiency, batch experiments at 25ºC were carried out using 100 mL of 3000 mg L^{-1} hexavalent chromium solution with 0.5 g of the adsorbents. The solution pH was continuously adjusted with H_2SO_4 and NaOH solutions for 1 h at pH values of 1, 3, 4, 7 and 9. The results obtained are shown in Fig. 7 which depicts the significant effect of pH on the adsorption of hexavalent chromium on talc powder and peanut shells. Solution pH is one of the most important variables affecting the adsorption characteristics and mechanism. The adsorption of hexavalent chromium was favored when the initial solution pH was between 3.5 and 5.0; the adsorption efficiency decreased slightly as the solution pH increased from 4 to 5. However, a sharp decline in hexavalent chromium adsorption occurred when pH was lower than 3.0 or higher than 5. The pH dependence of metal adsorption is largely related to the ionic forms of chromium in the solution and the surface properties of the adsorbent [32]. Thus, not only pH affects surface modifications of the available functional groups on the adsorbent, but it also disposes the proper ionic formation of the type of chromium to be accessible for the adsorption process.

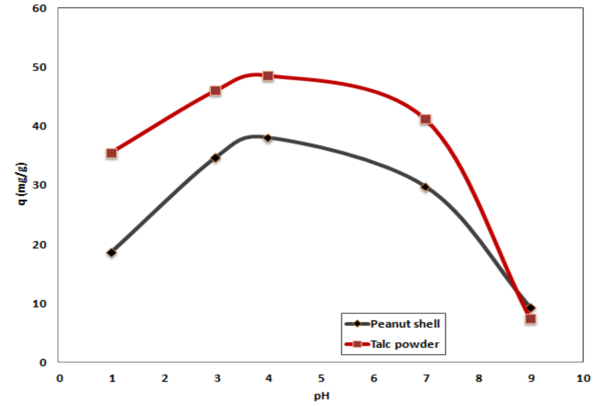


Fig. 7. Effect of pH on sorption capacity of talc powder and peanut shells for hexavalent chromium (initial conc. 3000 mg L^{-1}, adsorbent dosage 0.5 g L^{-1}, temp. 25º C, 400 rpm)

Hexavalent chromium exists in different ionic forms in solution. The most important hexavalent chromium states in solution are chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$) and hydrogen chromate ($HCrO^{4-}$), depending on the solution pH and total chromate concentration. From the stability diagram of the Cr(VI)–H_2O system, it is evident that at low pH, acid chromate ions ($HCrO_4^{-}$) are the dominant species which might interact strongly with the surface hydroxyl groups in peanut shells and mineral acidization is followed by chemical complex formation. The optimum pH value was found to be 4, which fits well with similar results obtained with agricultural nuts and shells and biomass-derived active carbons in the literature [33, 34, 24]. When the pH was further increased, a sharp decrease in the adsorption capacity was observed. This might be due to the weakening of the electrostatic force of attraction between the oppositely charged adsorbate and adsorbent and ultimately leads to a reduction in sorption capacity. When the pH was increased beyond 6, a decrease in the percentage adsorption was observed. This might be due to the competition between OH^{-} and chromate ions (CrO_4^{2-}), the former being the dominant species in the pH range outweighing the reaction. The net positive surface potential of the adsorbent decreased with increasing pH resulting in weakening of the electrostatic force between adsorbate and adsorbent which ultimately led to lowering of the adsorption capacity. Talc powder is insoluble in many mineral acids. However, in dilute acids it might slightly dissolve at pH 4 and 5, which might result in chemical interaction with the other elements in the solution.

Modeling of adsorption isotherms

Equilibrium adsorption isotherms are mathematical equations which are used to describe the relationship between the distribution and concentration of adsorbate and adsorbent. Rate expressions and reaction mechanisms of adsorption are of importance in understanding and designing adsorption systems, provided that a set of assumptions is taken into account, such as heterogeneous, homogeneous, surface coverage, diffusion, and interactions between sorbate and sorbent. Due to the complex physicochemical properties of micro/mesoporous structures, flow patterns and chemical nature of the liquid-solid phase process, adsorption models differ to some extent for practical application. The most widely accepted surface adsorption models for single-solute systems are the Langmuir and the Freundlich models. The correlation between the adsorbed amount and the liquid-phase concentration was tested with Langmuir, and Freundlich, whereas Temkin and Dubinin–Radushkevich (D–R) provided further information on the energy of adsorption and mechanism. The applicability of isotherm equations is compared by relating the correlation coefficients that fit the experimental data.

The Langmuir isotherm

Langmuir equation is the most widely applied model for isotherm adsorption as it considers that the adsorption energy of each molecule is constant on the finite number of identical adsorption sites and that adsorption takes place only on a monolayer until saturation with no interactions between the molecules**.**

The adsorption data were tested using Langmuir isotherm equation in the linearized form:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{1}{q_{max}} C_e \qquad (2)$$

where: C_e is the equilibrium concentration of hexavalent chromium in solution (mg L^{-1}), q_e is the adsorption capacity at equilibrium (mg g^{-1}), and b (L mg^{-1}) and q_{max} (mg g^{-1}) are Langmuir constants, related to the binding constant and the maximum adsorption capacity, respectively.

A plot of the specific sorption (C_e/q_e) *versus* C_e gives a straight line with a slope ($1/q_{max}$) and an intercept ($1/q_{max}$ b). The correlation coefficients shown in Table 2 (R^2 varying between 0.76 and 0.89 for talc powder, and R^2 >0.95 for peanut shells) suggest that the Langmuir adsorption isotherm does not fit well the situation for talc powder whereas it describes the case of adsorption on peanut shell very well.

The Freundlich isotherm

The Freundlich isotherm can be derived assuming a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites and is commonly given by the following non-linear equation:

Table 2. Isotherm models for adsorption of hexavalent chromium on talc powder

Isotherm equation	Isotherm parameters	Temperature (°C)			
		15	25	35	45
Langmuir $Ce/qe=1/b\ q_{max}+Ce/q_{max}$	b (L mg^{-1})	0.0025	0.0030	0.00321	0.00390
	q_{max} (mg g^{-1})	25.2525	25.3164	26.3852	26.5957
	R^2	0.7557	0.8322	0.8486	0.89
Freundlich $\log q_e = \log K_f+(1/n) \log C_e$	$1/n$	0.470	0.472	0.391	0.468
	K_F(L mg^{-1})	0.6889	0.032	1.0744	0.87437
	R^2	0.935	0.9538	0.8539	0.9482
Temkin $q_e=B_1 \ln K+B1 \ln Ce$	B_1	4.2867	4.447	3.4233	4.7988
	K (L mg^{-1})	0.0540	0.0587	0.0934	0.002288
	b(kJ mol^{-1})	115.241	108.252	103.513	101.316
	R^2	0.7977	0.84	0.6741	0.8808
D-R $\ln q_e=\ln Q_m - B\ \varepsilon^2$	Q_m (mg g^{-1})	12.98117	13.994	12.472	16.1577
	B (mol^2 kJ^{-2})	0.068	0.0243	0.0102	0.0068
	E (kJ mol^{-1})	2.7116	4.536	7.001	8.5749
	R^2	0.6991	0.7575	0.7746	0.8281

Table 3. Isotherm models for adsorption of hexavalent chromium on peanut shells

Isotherm equation	Isotherm parameters	Temperature (°C)			
		20	30	40	50
Langmuir $Ce/qe=1/b\ q_{max}+Ce/q_{max}$	b (L mg^{-1})	0.001085	0.001364	0.001589	0.001238
	q_{max} (mg g^{-1})	128.2051	135.1351	138.8889	147.0588
	R^2	0.9766	0.9534	0.9619	0.9697
Freundlich $log\ q_e= log\ K_f+(1/n)\ logC_e$	1/n	0.6965	0.6426	0.6228	0.6609
	K_F(L mg^{-1})	0.490456	0.82699	1.046405	0.64759
	R^2	0.9651	0.966	0.9641	0.9751
Temkin $q_e=B_1\ lnK+B1\ lnCe$	B_1	21.499	22.887	23.935	24.454
	K (L mg^{-1})	0.023343	0.028956	0.033082	0.027158
	b(kJ mol^{-1})	577.967	577.133	560.118	516.289
	R^2	0.9468	0.9297	0.9374	0.9314
D-R $lnq_e=lnQ_m - B\ \varepsilon^2$	Q_m (mg g^{-1})	60.71556	68.10155	73.61141	70.23874
	B (mol^2 kJ^{-2})	0.07	0.04	0.03	0.04
	E (kJ mol^{-1})	2.672612	3.535534	4.082483	3.535534
	R^2	0.8825	0.8756	0.8782	0.8651

$$q_e = K_F C_e^{1/n} \tag{3}$$

where K_F is a Freundlich constant related to the bonding energy. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of hexavalent chromium adsorbed onto the adsorbent for unit equilibrium concentration. The value of $1/n$ indicates the adsorption intensity of hexavalent chromium onto the sorbent with surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. A value for $1/n$ below 1 indicates a normal Langmuir isotherm while $1/n$ above 1 is indicative of cooperative adsorption. Eq. (3) can be linearized to the logarithmic Eq. (4) and the Freundlich constants can be determined:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

The applicability of the Freundlich sorption isotherm was analyzed using the same set of experimental data, by plotting log(q_e) *versus* log(C_e). The data obtained from the linear Freundlich isotherm plot for the adsorption of hexavalent chromium on talc powder are presented in Table 2, while those for the adsorption of hexavalent chromium on peanut shells are presented in Table 3. The correlation coefficients (>0.94) showed that the Freundlich model fits well to both types of adsorbents. A higher value of n between 2 and 10 (a smaller value of 1/n) indicates a favorable and stronger interaction during adsorption, n = 1 - 2 reveals moderate adsorption while less than 1 means poor performance [35]. The n value for talc powder is higher than 2 and thus shows favorable adsorption, while it is approximately 2 for peanut shells.

The Temkin isotherm

The Temkin adsorption isotherm model was used to evaluate the adsorption potentials of talc powder and peanut shells for hexavalent chromium. The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has been commonly applied according to the following equation [36, 37]:

$$\mathrm{q_e} = \frac{\mathrm{RT}}{\mathrm{b}} \ln(\mathrm{KC_e}) \tag{5}$$

The Temkin isotherm Eq. (5) can be simplified to the following equation:

$$q_e = B1 \ln(K) + B1 \ln(C_e) \tag{6}$$

where: B1= (RT)/b, T is the absolute temperature (K) and R is the universal gas constant, 8.314 J mol^{-1} K^{-1}. The constant b is related to the heat of adsorption. The adsorption data were analyzed according to the linear form of the Temkin isotherm equation (6) and the values of the linear isotherm constants and coefficients are presented in Tables 2 and 3, respectively.

Examination of the data obtained shows that the Temkin isotherm fitted the hexavalent chromium adsorption data on peanut shells better than those for talc powder. The heat of hexavalent chromium adsorption by talc powder was found to be less than that for peanut shells, where the correlation coefficient is also less pronounced. The correlation coefficients R^2 obtained from the Temkin model were less comparable to those obtained from the Langmuir and Freundlich equations for peanut shells.

The Dubinin–Radushkevich (D–R) isotherm

The D–R model was also applied to estimate the characteristic porosity of the adsorbent, the apparent energy of adsorption and the characteristics of adsorption on micropores rather than of layer-by-layer adsorption [38, 39]. The D–R isotherm does not assume homogeneous surface or constant sorption potential. The D–R model has commonly been applied by Eq. (7) with its linear form as shown in Eq. (8):

$$q_e = Q_m \exp(-B\varepsilon^2) \quad (7)$$

$$\ln q_e = \ln Q_m - B\varepsilon^2 \quad (8)$$

where B is a constant related to the adsorption energy (mol^2 kJ^{-2}), Q_m is the theoretical saturation capacity (mg g^{-1}), ε is the Polanyi potential, calculated from Eq. (9).

$$\varepsilon = RT\ln(1 + \frac{1}{Ce}) \quad (9)$$

The slope of the plot of lnq_e *versus* ε^2 gives B and the intercept yields the adsorption capacity Q_m (mg g^{-1}). The mean free energy of adsorption, E (kJ mol^{-1}), defined as the free energy change when one mol of ion is transferred from infinity to the surface of the solid, was calculated from the B value using the following relations [40]:

$$E = -\frac{1}{\sqrt{(2B)}} \quad (10)$$

The values of E calculated using Eq. (10) for the present case were found to vary between 2.67 and 4.08 kJ mol^{-1} for peanut shells and between 2.7 and 8.6 kJ mol^{-1} for talc powder. The values of the mean free energy of adsorption observed in this study for both adsorbents fall between 2.7 and 8.6 kJ mol^{-1}, showing the type of adsorption to be physisorption (physical sorption) [41]. The energy of adsorption also shows that it increases with temperature for the talc powder, while no significant dependence on temperature is shown for the peanut shells.

Kinetics of adsorption

Adsorption kinetics is important as it controls the process efficiency as the rate of uptake of the chromium species on the adsorbent is equilibrated with time. The kinetics of Cr(VI) adsorption on peanut shells and talc powder were analyzed using pseudo-first order, pseudo-second order and intraparticle diffusion models. The pseudo-first order Lagergren rate expression may be written as follows [42]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \quad (11)$$

where q_e and q_t are the amounts of hexavalent chromium adsorbed on the two adsorbents at equilibrium and at time *t*, respectively (both in mg g^{-1}), and k_1 is the rate constant (min^{-1}). The values of q_e and k_1 are obtained from the intercept and the slope of the plot of log (q_e-q_t) as a function of time (t) and these values are given in Table. 4

Table 4. Kinetic parameters of the adsorption of hexavalent chromium onto talc powder and peanut shells

Kinetics model	peanut shells	talc powder
Pseudo-first order		
k_1 (min^{-1})	0.128	0.1609
$q_{e\,Calc}$ (mg g^{-1})	39.6	42.476
$q_{Exp.}$(mg g^{-1})	38	45
R_1^2	0.9745	0.9936
Pseudo-second order		
k_2 (g mg^{-1} min^{-1})	0.0052	0.334
$q_{e\,Calc.}$(mg g^{-1})	38.87	39.88
$q_{Exp..}$(mg g^{-1})	38	45
R_2^2	0.9364	0.8929
Intraparticle diffusion		
k_d (mg g^{-1} min$^{-1/2}$)	6.5887	0.8865
c	0.5688	0.022
R^2	0.9886	0.9979

The pseudo-second order kinetic model is expressed by the following relationship [43]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (12)$$

where k_2 is the equilibrium rate constant (g mg^{-1}min^{-1}). The rate constant and q_e were obtained from the slope and the intercept of the t/q_t vs. time (t) dependence. The kinetic parameters along with the correlation coefficients of the kinetic models are also shown in Table (4).

As can be seen from Table 4, higher correlation coefficients (R_1^2) were obtained using the pseudo-first order equation and the calculated q_e values were reasonably close to the experimental data obtained, indicating that the pseudo-first order kinetic model is more suitable to describe the kinetics of the adsorption process of hexavalent chromium on talc powder and peanut shells.

The adsorbate transport from the bulk solution phase to the internal active sites occurs in several steps, where the rate of internal mass transfer is, in most cases, the rate-determining step in adsorption processes. Kinetic data were therefore used to check the possibility of intraparticle diffusion limitations by using the Weber and Morris equation [44], expressed by the following equation:

$$q_t = k_d\, t^{0.5} + c \quad (13)$$

where q_t (mg g^{-1}) is the amount of adsorbed Cr(VI) at time t and k_d is the intraparticle diffusion rate constant (mg g^{-1} min$^{-0.5}$), and c is a constant determined from the intercept.

If the plot of q_t *versus* $t^{0.5}$ gives a straight line passing through the origin, then the adsorption process is only controlled by intraparticle diffusion. However, if the data exhibit multi-linear plots, then two or more stages influence the adsorption process. Figs. 8 and 9 are the plots of q_t *versus* $t^{0.5}$ for peanut shells and talc powder, respectively, which clearly show multilinearity. The multi-linear behavior of the plots of q_t *versus* $t^{0.5}$ is due to the extensive pore size distribution of the studied adsorbents having micro-, meso- and macroporosity. The first one could be attributed to the adsorption of hexavalent chromium over the surface with macropore structure of both adsorbents, and hence it is the fastest adsorption stage. The second one could be ascribed to the intraparticle diffusion through the mesopores, while the third stage may be regarded as diffusion through micropores, and of course, this stage is followed forthwith by the establishment of equilibrium. Table 4 also gives the linear correlation coefficient (>0.98) showing high applicability of the kinetic model of the intraparticle diffusion for both adsorbents.

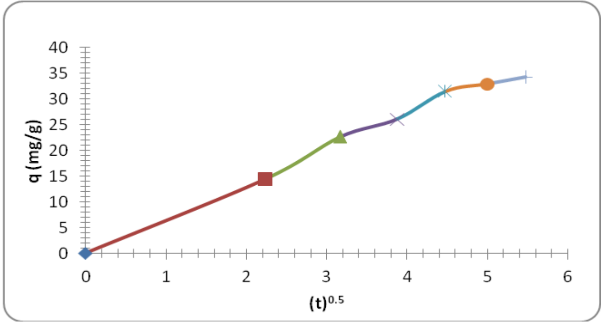


Fig. 8. Intraparticle diffusion for adsorption of hexavalent chromium on peanut shells

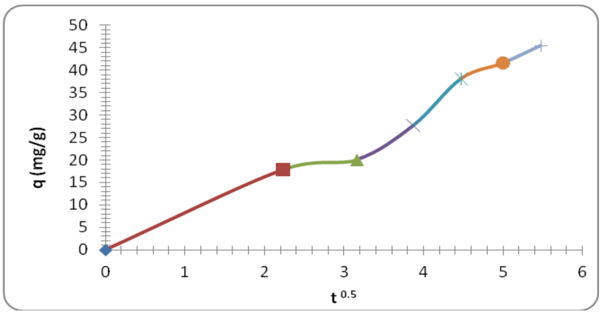


Fig. 9. Intraparticle diffusion for adsorption of hexavalent chromium on talc powder

CONCLUSION

In this study, two abundant natural resources (talc powder and peanut shells) were used as adsorbents for removing hexavalent chromium from simulated wastewater. Different parameters that are known to affect the adsorption process were studied, namely: contact time, amount of adsorbents, and pH of the solution. It was found that the adsorption process using the two adsorbents is simple, fast and reached equilibrium within 30 min for peanut shells and 70 min for talc powder. The adsorption capacity increased with increasing the amount of adsorbent. The optimum pH value for the adsorprion of hexavalent chromium was found to be 4.0. The experimental results were analyzed by using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models and the correlation coefficients showed that while Freundlich fitted well with talc powder, peanut shells showed validity for both Langmuir and Freundlich for the adsorption of Cr(VI). The kinetic study of the adsorption of hexavalent chromium on talc powder and peanut shells revealed that they are better described by the pseudo-first order with intraparticle diffusion models. It can be concluded that talc powder and peanut shells could be employed as low-cost adsorbents for the removal of hexavalent chromium from waste water.

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ИЗПОЛЗВАНЕ НА ЧЕРУПКИ ОТ ФЪСТЪЦИ И ПРАХ ОТ ТАЛК ЗА ОТСТРАНЯВАНЕ НА ШЕСТ-ВАЛЕНТЕН ХРОМ ОТ ВОДНИ РАЗТВОРИ

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(Резюме)

В настоящата работа са изследвани черупки от фъстъци и прах от талк като потенциални адсорбенти за отстраняването на шест-валентен хром от водни разтвори. Оценени са ефектите на значими параметри, като времето на контакт, pH на средата и дозировката на адсорбента върху степента на адсорбция на хром (IV). Освен това е извършено охарактеризиране с методите FT-IR, SEM и BET за оценяване н физико-химичните свойства на материалите. Експерименталните данни показват че оптималното време на контакт за достигане на равновесие са фъстъчените черупки е 30 мин., а за праха от талк -70 мин. Оптималната киселинност на средата отговаря на pH за двата сорбента. Изпитани са изотермите на Лангмюир, Фройндлих, Тьомкин и Дубинин-Радушкевич за описание на равновесните данни, топлината и енергията на адсорбция за двата адсорбента. Определена е скоростта на адсорбция с помощта на кинетика на реакция от псевдо-първи порядък с вътрешна дифузия за двата адсорбента.