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Humic acids elimination from aqueous media utilizing derived activated carbon from raw maize tassel on equilibrium, thermodynamic and kinetics

Mahboube Ebrahimi*, Saideh Bagheri*, Maryam Maleki Taleghani, Majid Ghorabani

Department of Agriculture Science, Payame Noor University, Tehran, Iran, email: Mahboube.ebrahimi@pnu.ac.ir (M. Ebrahimi), S_bagheri2010@yahoo.com (S. Bagheri), maryammaleki2022@yahoo.com (M.M. Taleghani), majid.ghorbani@ pnu.ac.ir (M. Ghorabani)

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ABSTRACT

In this paper activated carbon which was prepared from maize tassel was utilized to eliminate humic acids (HAs) from aqueous solutions. Fourier transform infrared spectroscopy and X-ray diffraction were employed to characterize the activated carbon. Batch adsorption technique was utilized to investigate on the elimination of humic acids (HAs) by the generated adsorbent. Additionally, all parameters affecting the elimination efficiency like pH, dose of adsorbent, and initial humic acids (HAs) concentration were taken into consideration. Under optimum conditions, diverse isotherm models were examined to fit the experimental equilibrium data. The appropriateness and applicability of Langmuir model was confirmed by the obtained results. Kinetic models including pseudo-first-order and pseudo-second-order diffusion models confirmed that the second-order equation model controls the kinetic of the adsorption process. Also, evaluation of thermodynamic parameters of adsorption process ($\Delta G°$, $\Delta H°$, $\Delta S°$) revealed little information. The negative $\Delta G°$ value revealed that the process is practicable and adsorption spontaneous in nature. The exothermic nature of adsorption was revealed by the negative $\Delta H°$ value. And finally the value of $\Delta S°$ revealed the change in the randomness of the active carbon from raw maize tassel solution interface during the sorption. The whole adsorption process was exothermic and spontaneous in nature. The outcomes demonstrated that HAs adsorption onto maize tassel might be a physical adsorption.

Keywords: Adsorption; Humic acids (HAs); Kinetic; Thermodynamic; Maize tassel

1. Introduction

Humic substances (mainly humic acids and fulvic acids) are present in almost all natural waters and often represent a major proportion of organic pollution (known in the literature as natural organic matter-NOM) [1]. Humic substances are complex high molecular weight organic compounds, with an aromatic-aliphatic character, that contain carbon, oxygen, hydrogen, nitrogen and sulfur. The relative molecular mass of humic substances ranges from a few hundred to tens of thousands [2]. Humic acid may cause water to have an undesirable taste and color. Moreover, it acts as a nutrient for the growth of bacteria in water distribution systems. Humic acid can cause blockage of membranes in membrane treatment processes, and therefore, increase the operational costs. Furthermore, humic acid can form complexes with chlorine, heavy metals, pesticides, and herbicides, creating carcinogenic compounds [3,4]. The factors that determine the composition of humic substances are location dependent and include the source of the organic matter, the water chemistry, temperature, pH, and biological processes, The elementary composition of humic substances [5].

Since 1974, a number of epidemiological surveys have confirmed the correlation between a variety of cancers in humans and animals and drinking of or contact with the chlorinated water. Humic acids (HAs) as the main chlorine disinfection byproducts are toxic, carcinogenic, and mutagenic [6]. The presence of organic compounds in water resources provokes numerous troubles during treatment processes specifically if conventional water treatments are practiced. NOM can affect water treatment and the leading effect of these materials is the creation of chlorination by

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*Corresponding author.

products due to their reaction with chlorine. The direct relationship between the formation of chlorination by products and the concentration of NOM as the most important precursor in the formation of these compounds has been confirmed. Only 30% of NOM precursors has been removed in the conventional water treatment processes [7].

The presence of humic substances (mainly humic acids) in almost all natural waters is often associated with major proportion of organic contaminations (known in the literature as natural organic materials – NOM) [8].

Humic substances belong to a class of organic compounds with high molecular weight and an aromatic/aliphatic character which contain carbon, oxygen, hydrogen, nitrogen and sulfur.

The reported relative molecular weight of humic substances is from a few hundred to millions of daltons. Location dependent factors like the source of the organic matter, the water chemistry, temperature, pH, and biological processes [9] are among the factors that ascertain the composition of humic substances. By surveying the chemical characteristics of humic substances, the presence of carboxylic acid and the hydroxy (phenol, alcohol), methoxy, and carbonyl groups can be specified that along with the aliphatic side chains are bound to the nucleus [10]. Carcinogenicity and toxicity of these substances have been confirmed [11]. Therefore, reducing the content of humic substances in water or changing the method of disinfection is indispensable in order to halt the development of chlorinated hydrocarbons.

Coagulation and flocculation followed by sedimentation/flotation and filtration are the commonest, cost effective and doable processes to abate NOM. Coagulation is effective in removing most of the NOM, although obviously hydrophilic, low molecular weight fractions of NOM (molecular mass up to 500) in comparison with hydrophobic, high molecular weight compounds are eliminated less efficiently (some fractions cannot be eliminated at all). Accordingly after coagulation, hydrophilic NOM and low molecular weight fractions dominate the residual organic matter. The best result is obtained in the treatment of humic waters by clarification earlier in the acidic range (pH 4–6), that produce large and well separated units [12].

However, as mentioned in the literature, high initial investment and operation cost, obstruction, formation of a large amount of sludge, abatement of water pH, generation of corrosive water, and the exigency for reduction operation are among the limitations presented if these methods are employed [13]. Coagulation and ion exchange [14], adsorption [15], ozonation and Air Oxidation [16], activated carbon filtration [17], and biosorption [18] are conventional wastewater treatment protocol based on physicochemical, chemical, and biological processes. Amongst the mentioned processes, adsorption is extensively employed for large scale chemical, biochemical, purification and environmental recovery applications [19]. Using effective, non-toxic and low-cost adsorbents along with simple design and ease of operation made this technique beneficial and popular. Appropriateness of the adsorbent depends on factors such as elimination capacity, treatment cost, and operating conditions [20]. Therefore, for the elimination of humic acids (HAs) and their precursors it is essential to exercise suitable methods. Amongst variety of methods, the adsorption process as a simple and standard method is considered advantageous for the elimination of organic pollutants like humic acid. Activated carbon in theory is the best adsorbent for humic acids (HAs) elimination however; in practice it exhibits low capacity for the elimination of high molecular organic compounds such as NOM [21].

Recently, the use of cost effective adsorbents has been a subject receiving close review since adsorbents are expensive and their feasibility has been investigated [22,23]. Chemical treatment and biodegradation procedures not only are based on expensive and complex processes but also produce noxious by-products. The derived activated carbon from maize tassel is very cost effective, energy effective and non-toxic because Cob as an agricultural tree grows in many regions. The mentioned characteristics of this carbon in comparison with the commercial activated carbon make it suitable for the elimination of water contamination. On the other hand elimination of humic acids (HAs) based on biological treatment and chemical precipitation has low efficiency and is not environmental friendly [24]. Therefore, preparing activated carbon sprang from maize tassel as an alternative to exorbitant or noxious adsorbents for the elimination of humic acids (HAs) from wastewater attracted our attention. To characterize this adsorbent, X-ray diffraction pattern and FTIR of the activated carbon were employed. Investigating and optimizing the experimental conditions including pH of solution, initial humic acids (HAs) concentration, contact time, and adsorbent dosage as well as the dye removal percentage as response were performed. Also investigation about the extent to which the experimental factors interact with each other was performed. The optimal conditions for the humic acids (HAs) elimination for pH, contact time, initial humic acids (HAs) concentration, and adsorbent dosage were estimated to be 5, 65 min, 10 mg/L and 50 mg respectively. To best fit the experimental equilibrium data, different isotherm models like Langmuir, Freundlich, and Dubinin–Radushkevich were employed. The obtained outcomes demonstrated the appropriateness and pertinence of the Langmuir model. By applying the kinetic models of pseudo-first-order and pseudo-second-order diffusion models, it was shown that the pseudo-second-order model regulates the kinetic of adsorption process. The effective use of the activated carbon sprang from maize tassel to eliminate the humic acids (HAs) from wastewater was confirmed.

2. Experimental procedure

2.1. Materials

The chemical compounds and reagents utilized in this work were of analytical grade and bought from Merck (Darmstadt, Germany). The stock solutions were watered down with deionized water in order to obtain the standard and experimental solutions. All through the study, deionized water (DI-water) was utilized [25].

2.2. Provision of biomass

The maize tassel powder as a valueless agricultural waste product was gathered. Maize tassel was removed from the woody parts of the maize plant and completely washed with water, and then it was sun dried for 5 d. The-dried biomass was grinded and then by means of 100–300 m analytical sieves was fractionated. Finally, it was washed twice with 0.01 M HCl to ensure any metals removal that might be on the biomass.

2.3. Provision of activated carbon

Based on the reported procedures, the provision of activate carbon was done [26,27]. Concisely, 200 g of the fractionated maize tassel powder was weighed in a 1 L capacity cleansed dry beaker containing (200 mL, 97% H_2SO_4 for 24 h) followed by refluxing in a fume hood for 4 h. Filtration of the reaction mixture was done after cooling and with ultrapure water the filtrate was washed over and over again and then drenched in 1% $NaHCO_3$ solution to neutralize any remaining acid. Thereafter, the sample was rinsed using distilled water until the pH of the activated carbon was between 6 and 7, dried overnight in an oven at 120°C, and retained in a glass bottle until use.

2.4. Batch adsorption experiments

Batch adsorption experiments were performed to ascertain the humic acids (HAs) adsorption isotherm onto active carbon sprang from raw maize tassel and its thermodynamic properties: after preparing 500 mL solution containing 10 mg/L concentration of humic acids (HAs), by the help of 0.01 N HCl/0.01 N NaOH aqueous solution, the initial pH of the solution was adjusted with no further adjustments during the experiments. The solution was divided into 10 samples of 50 mL and was poured in ten 250 mL flasks containing fixed adsorbent dose of 100 mg/L. Then at a steady rate of 200 rpm and a maintained temperature at 25°C, the flasks were shaken on an orbital shaker. One of the sample flasks was withdrawn from the orbital shaker after fixed time intervals (5, 10, 20, 30, 40, 50, 60, 70, 80 min) and analyzed for remaining humic acids (HAs) present in the adsorbate solution. By filtration and via Whatman No. 42 filter paper, the derived active carbon from raw maize tassel was separated from aqueous solution. With the help of a“U-Visible Shimadzu 160 Spectrophotometer” equipped with an air-acetylene flame, the analysis of the concentration of the humic acids (HAs) in solution samples was performed. The humic acids (HAs) removal (%A) or removal yield of humic acids (HAs) was assessed by the following equation:

$$\%A_t = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

In the above formula C_0 stands for the initial concentration of humic acids (HAs) in solution (mg/L), and C_e for the final concentration of humic acids (HAs) in solution (mg/L). The computation of the amount (mg/g) of humic acids (HAs) adsorbed at equilibrium was done using the ensuing equation:

$$q_t = \frac{(C_0 - C_t)V}{w} \quad (2)$$

In which C_o and C_t show the initial ion concentration and concentration of humic acids (HAs) at any time 't'. V stands for the volume of solution in litters and W shows the adsorbent dosage in mg/L. By adding 50 mg of derived active carbon from raw maize tassel into 10 mL initial humic acids (HAs) concentration ranging from 2 to 12 ppm in each experiment, the thermodynamic properties of the adsorption process was assessed. Each solution was agitated consecutively for 65 min at 25°C.

The humic acids (HAs) concentrations, after the solutions reached equilibrium, were estimated and then the results of desorption were acquired. In the present study, each experiment was performed in triplicate and the average results were presented.

3. Results and discussion

3.1. Physicochemical characteristics of activated carbon

The physicochemical characteristics like pH, moisture content.

Bulk density, surface area, and loss of mass on ignition are shown in Table 1. The bulk density affects the rate of adsorption of humic acids (HAs) solution onto activated carbon. In the present study, the bulk density was less than 2.0 indicating that the activated carbon materials are in fine nature and hence enhanced the adsorption of humic acids (HAs) solution from aqueous solution. The moisture content (0.3%) was determined, even though it does not affect the adsorption power, dilutes the adsorbents, and therefore necessitates the use of additional weight of adsorbents to provide the required weight. The surface area of the prepared activated carbon in the present research study was 250 m^2/g and is higher than a low-cost adsorbent such as palm pith carbon (188 m^2/g) [28] but lower than peanut hull carbon (354 m^2/g) [29]. The X-ray diffraction pattern of the activated carbon is shown in Fig. 1. The XRD spectrum of activated carbon is a typical diffraction pattern of an amorphous material which gives a continuous function and had two partially.

The FT-IR spectrum was obtained for treated activated carbon before (a) and after humic acids (HAs) solution bio sorption process (b) (Fig. 3). The comparisons of the FT-IR spectra of activated carbon and after humic acids (HAs) solution biosorption give the following bands and peaks. The spectrum shows a band at around 3500 cm^{-1}, which indicates the presence of hydroxyl functional groups on the surface of maize tassel activated carbon. The peaks at 1630 cm^{-1} and 1622 cm^{-1} can be attributed to and 1388 cm^{-1} carbonyl groups (C=O). The peaks at 1384 cm^{-1} were due to the presence of C=H aliphatic bending. The C=O functional

Table 1
Characteristics of the activated carbon derived from maize tassel

pH	5.0
Moisture (%)	0.3
Bulk density (g mL^{-1})	0.52
Surface area (m^2/g)	250
Particle size range (µm)	100–300
Loss of mass on ignition	0.7

Fig. 1. Schematic representation of the process involved in the derivation of activated carbon from raw maize tassel up to adsorption.

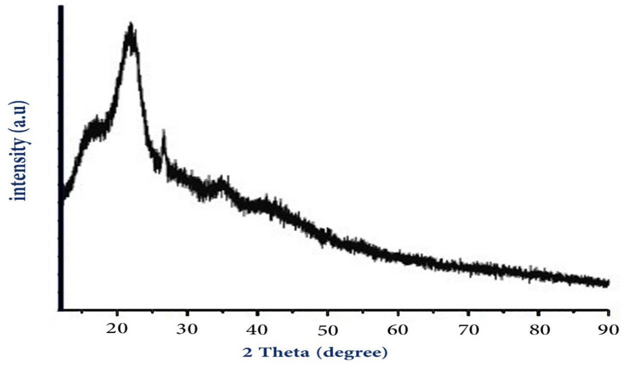

Fig. 2. X-ray diffraction of activated carbon derived from maize tassel.

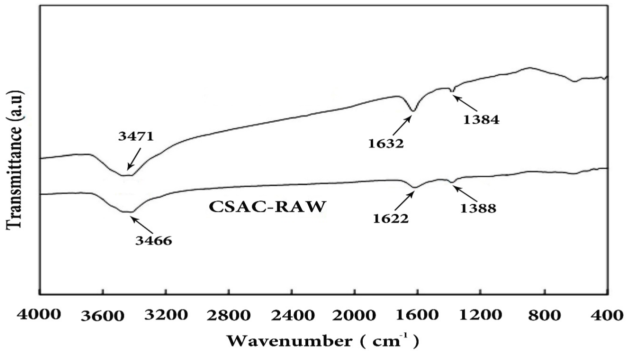

Fig. 3. FT-IR spectra of treated activated carbon (a) and humic acids (HAs) solution loaded activated carbon (b). defined resolved peaks at about 2 = angle of 22.6 and 26.4 degrees, respectively.

groups have been reported to show very high coordination with trace metals; hence it disappeared in the humic acids (HAs) solution loaded [30]. For this reason, the presence of these functional groups may be responsible for good adsorptive behavior of the activated carbon towards the humic acids (HAs) solution.

3.2. Impact of pH

The pH has been found to be one of the most leading and effective parameter on humic acids (HAs) sorption. Competition potentiality of hydrogen ions with humic acids (HAs) to active sites on the biosorbent surface has a direct relation with pH. Investigation about the impact of pH on the biosorption of humic acids (HAs) onto derived active carbon from raw maize tassel was done at pH 3.0–10.0 which is shown in Fig. 4. The pH of 5.0 provided the highest biosorption for humic acids (HAs). Therefore, this pH value was chosen to be the base pH for the all remained biosorption experiments [31]. The physio-chemical nature of the interaction of the solution was reflected by the biosorption mechanisms on the derived active carbon from raw maize tassel. When the whole surface charge on the active sites at highly acidic pH become positive, humic acids (HAs) and protons fight for binding sites on active carbon from raw maize tassel which culminates in lower uptake of humic acids (HAs). Upon the increase in the pH of the solution from 5.0, the biosorbent surface was more negatively charged. Deporotonization of the functional groups of the active carbon from raw maize tassel upon the increase in the make the scene for the humic acids (HAs). Therefore the reduction in biosorption yield at higher pH (=5) is not only pertain to the genesis of soluble hydroxylated complexes of the humic acids (HAs) but also to the ionized nature of the active carbon from raw maize tassel of the biosorbent under the studied pH. Also based on the prior surveys, the topmost biosorption yield of humic acids (HAs) on biomass was detected at pH 5.0.

3.3. Impact of initial humic acids (HAs) concentration

Investigation about the adsorption uptake of humic acids (HAs) was done for initial concentration range from 2 to 12 mg/L and exhibited in Fig. 5.

A rise in the initial concentration of humic acids (HAs) provokes the increase in the adsorption yield of these humic acids (HAs) by active carbon from raw maize tassel. The requisite driving force is provided by the initial concentration to defeat the resistance to mass transfer of adsorbent between aqueous and solid phases.

3.4. Impact of contact time

Over a time range of 5–80 min, the uptake of humic acids (HAs) ion was investigated and the impact of contact time on elimination yield demonstrated in Fig. 6. It was revealed that a very large amount of humic acids (HAs) was eliminated in the first 65 min and for this reason 65 min was taken for granted to be adequate for humic acids (HAs) to reach equilibrium.

3.5. Impact of temperature

Investigation about the adsorption of humic acids (HAs) on derived active carbon from raw maize tassel as

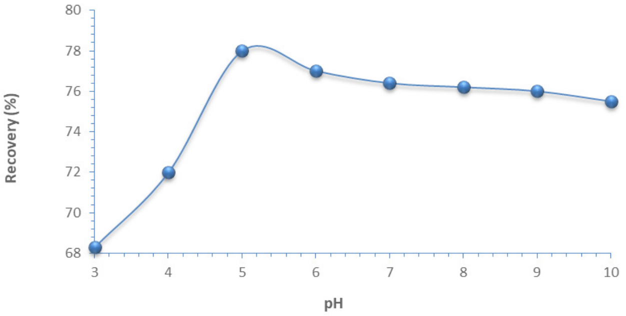

Fig. 4. Impact of pH on removal of humic acids (HAs) (conc = 10 mg/L; adsorbent dose = 50 mg, contact time = 65 min; stirring speed = 200 rpm; temp = 25°C).

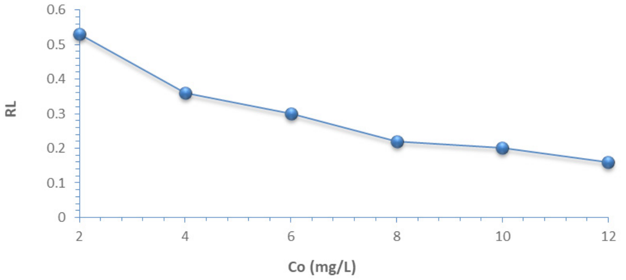

Fig. 5. Impact of Initial humic acids (HAs) concentration on metal uptake of adsorbent; adsorbent dosage = 50 mg, pH of solution = 5.0, contact time = 65 min.

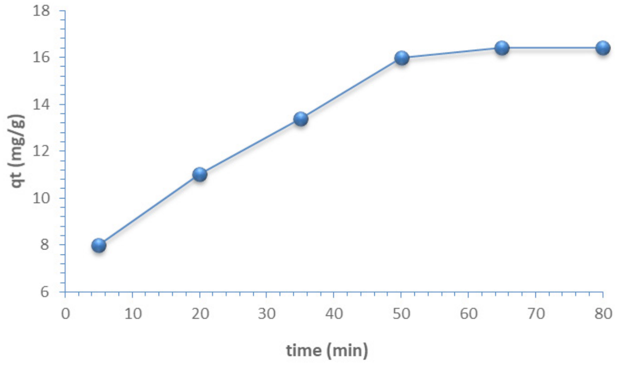

Fig. 6. Impact of contact time on removal of humic acids (HAs) by active carbon from raw maize tassel; Initial humic acids (HAs) concentration = 10 mg/L, adsorbent dosage = 50 mg, pH of solution = 5.0.

a function of temperature was performed and the topmost uptake was achieved at 25°C. Trials were carried out at temperatures of 25, 35, 45 and 55°C for the initial humic acids (HAs) concentration of 10 mg/L and at constant adsorbent dose of 50 mg and pH of 5.0. It was observed that with a rise in temperature from 25 to 55°C,the adsorption reduced from 80.0 to 60.0 % for the initial humic acids (HAs) concentration of 30 mg/L (Fig. 7). Decreased surface activity can be the main reason for this reduction proposing that adsorption between humic acids (HAs) and derived active carbon from raw maize tassel is an exothermic process.

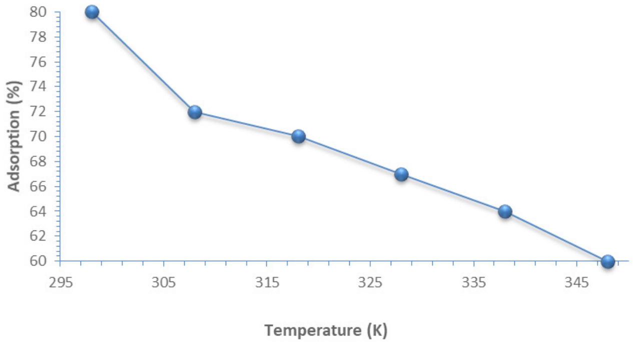

Fig. 7. Impact of temperature for adsorption of humic acids (HAs) by active carbon from raw maize tassel, initial humic acids (HAs) concentration = 10 mg/L, adsorbent dosage = 50 mg, pH of solution = 5.0.

3.6. Kinetics study

In order to evaluate the biosorption kinetics of humic acids (HAs) uptake onto derived active carbon from raw maize tassel, parameters from two kinetic models, pseudo-first-order and pseudo-second-order were fitted to experimental data.

3.6.1. Pseudo-first-order kinetics

The ensuing equation is the pseudo-first-order equation of Lagergren [32]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

In which q_e shows the sorption capacities at equilibrium and q_t shows the sorption capacities at time t (mg/g). K_1 in the above equation is the rate constant of pseudo-first-order sorption (1/min). The integrated form of equation after integration and applying boundary conditions, $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$ is expressed as follow [33]:

$$\ln(q_{e/\exp} - q_t) = \ln q_{e/cal} - \frac{K_1}{2.303}t \tag{4}$$

In two ways, the equation fitting to experimental results mostly differs from a true first-order equation: first, the number of available sites is not represented by the parameter $k_1(q_e - q_t)$; and second, the parameter $\ln q_e$ is frequently not found equal to the intercept of a plot of ln $(q_e - q_t)$ against t while it is an adjustable parameter. Indeed in a true first-order sorption reaction log, the equivalence of q_e to the intercept of ln $(q_e - q_t)$ against t is definite. The sorption capacity at equilibrium (q_e) must be known to fit the equation to experimental data.

When q_e is unknown and as chemisorption is apt to become excessively slow, the amount sorbed in comparison with the equilibrium amount is significantly smaller. Based on the literature, in many cases the pseudo-first-order equation of Lagergren does not fit properly for the entire range of contact time and is usually applicable over the initial 5–50 min of the sorption process. In addition, some means of extrapolating the experimental data to $t = \infty$ should be found on regarding q_e as an adjustable parameter to be ascertain by trial and error. Therefore, for analyzing the pseudo-first-order model kinetics, attaining the equilibrium sorption capacity by trial and error is necessary.

As it is shown in Fig. 8, obtaining the pseudo-first-order rate constant is possible from the slope of plot between log ($q_e - q_t$) against time (t). Table 2 summarizes the computed values and their corresponding linear regression correlation coefficient values. The value of $R^2 = 0.8331$ demonstrates that this model cannot be employed to foretell the adsorption kinetic model.

3.6.2. Pseudo-second-order kinetics

The ensuing equation is the pseudo-second-order rate expression which has been used for analyzing chemisorption kinetics rate [34]:

$$\frac{dq_t}{d_t} = k(q_e - q_t)^2 \tag{5}$$

In which q_e and q_t stand for the sorption capacity at equilibrium and at time t, respectively (mg/g), and k shows the rate constant of pseudo-second-order sorption, (g/mg min). The integrated formula of equation for the boundary conditions to $q_t = 0$ to $q_t = q_t$ at $t = 0$ to $t = t$, (12) is expressed as follow [35]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{e/cal}^2} + \frac{t}{q_{e/cal}} \tag{6}$$

In which t, q_e, and q_t stand for the contact time (min), the amount of the solute adsorbed at equilibrium (mg/g) and at any time, t (mg/g) respectively. Pseudo-second-order kinetics is applicable if there exist a linear relationship between the plot of t/q_t and t of Eq. (13) from which q_e and k_2 can be recognized from the slope and intercept of the plot (Fig. 9). Table 2 demonstrates a list for the pseudo-second-order rate constant k_2, the computed e value and the relative linear regression correlation coefficient value. The linear regression correlation coefficient R^2 at all initial metal concentrations equals 0.9814. The higher values reveal that pseudo-second-order kinetics can represent the adsorption data properly.

3.7. Adsorption isotherm

Linear plots of the Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (DR) models for adsorption of humic acids (HAs) on derived active carbon from raw maize tassel are exhibited in Figs. 10–13 and in Table 3, the parameters of these models are provided.

3.7.1. Langmuir isotherm

Monolayer adsorption on a homogeneous surface with a limited number of adsorption sites is presumed for the Langmuir isotherm [36]. No further sorption can transpire at a site which is filled and when the maximum adsorption takes place, the surface will finally reach a saturation point. The ensuing formula expresses the linear form of the Langmuir isotherm model [37]:

$$\frac{1}{q_e} = \frac{1}{K_L q_m}\left(\frac{1}{C_e}\right) + \frac{1}{q_m} \tag{7}$$

Fig. 10 exhibits the plots of C_e versus C_e/q_e for humic acids (HAs) and in Table 3, the linear isotherm parameters q_{max}, b_L and the correlation coefficient are presented. The maximum sorption capacity q_{max} of humic acids (HAs) 3.0 mg/g onto derived active carbon from raw maize tassel was observed.

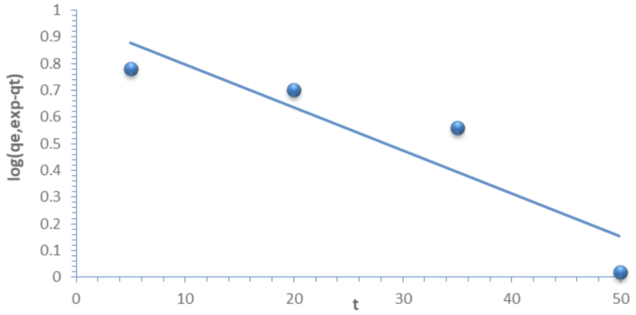

Fig. 8. Pseudo-first-order kinetics for humic acids (HAs) onto active carbon from raw maize tassel.

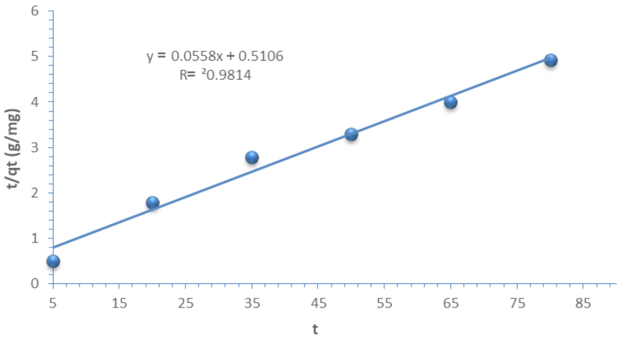

Fig. 9. Pseudo-second-order kinetics for humic acids (HAs) onto active carbon from raw maize tassel.

Table 2
Adsorption rate constants by kinetic equation

Kinetic model ion	Pseudo-first-order kinetic			Pseudo-second-order kinetic		
	q_e (mg g^{-1})	K_1 (1/min)	R^2	q_e (mg g^{-1})	$K_2 \times 10^{-3}$ (g/mg min)	R^2
Humic acids (HAs)	9.1	0.04	0.8331	18.0	6.1	0.9814

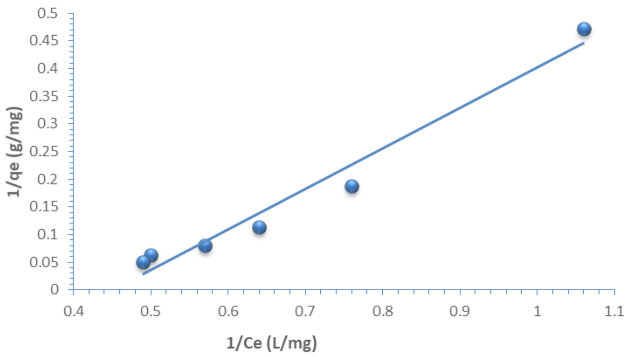

Fig. 10. Langmuir plot for adsorption of humic acids (HAs) by active carbon from raw maize tassel adsorbent dosage = 50 mg, pH of solution = 5.0, contact time = 65 min.

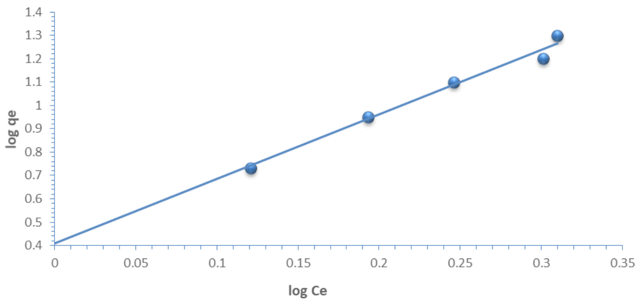

Fig. 11. Freundlich plot for adsorption of humic acids (HAs) by active carbon from raw maize tassel adsorbent dosage = 50 mg, pH of solution = 5.0, contact time = 65 min.

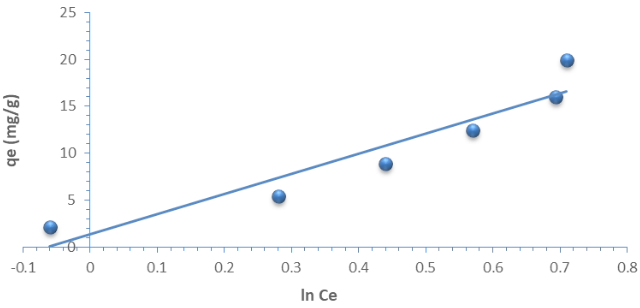

Fig. 12. Temkin plot for adsorption of humic acids (HAs) by active carbon from raw maize tassel adsorbent dosage = 50 mg, pH of solution = 5.0, contact time = 65 min.

3.7.2. Freundlich isotherm

The well-known Freundlich isotherm model is the earliest model that describes the adsorption process. For adsorption on non-uniform surfaces with the interaction between adsorbed molecules, Freundlich isotherm model is applied. Also based on the Freundlich equation, sorption energy shows a rapid decrease when the sorption centers of an adsorbent is completed. This isotherm as an empirical equation is used to define non-uniform systems and is expressed as follows in linear form [38]:

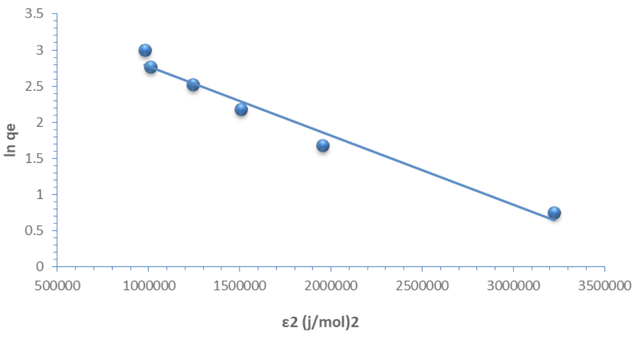

Fig. 13. Dubinin–Radushkevich (DR) plot for adsorption of humic acids (HAs) by active carbon from raw maize tassel adsorbent dosage = 50 mg, pH of solution = 5.0, contact time = 65 min.

Table 3
Adsorption isotherms parameters and correlation coefficients

Isotherms	Parameters	Values
Langmuir	q_m (mg/g)	3
	K_L (L/mg)	0.45
	R^2	0.9679
Freundlich	n	0.4
	$K_F (mg)^{1-n} L^n g^{-1}$	2.6
	R^2	0.995
Temkin	A_T (L mg^{-1})	1.07
	B_T	21.441
	R^2	0.8906
Dubinin - Radushkevich (DR)	q_d (mg/g)	42
	$K_D \times 10^{-6} (mol/J)^2$	1
	E (kJ/mol)	-700
	R^2	0.9714

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{8}$$

In the above formula K_F stands for the Freundlich constant pertain to the bonding energy. $1/n$ is the heterogeneity factor and n (g/L) is a quantity of the deviation from linearity of adsorption [39].

The $1/n$ and k_F show the slope and intercept of the plots ln (C_e) vs. ln (q_e) (Fig. 11). In Table 3, the values of N_f and k_F are demonstrated. The value of $1/n < 1$ for both humic acids (HAs) demonstrates desired adsorption. Sorption intensity shows an increase for higher k_F value. Thus, active carbon from raw maize tassel is a suitable and favorable sorbent for humic acids (HAs). The Freundlich isotherm with correlation coefficient of R^2 0.995 properly matched for adsorption of humic acids (HAs) on derived active carbon from raw maize tassel.

3.7.3. Temkin isotherm

In Temkin isotherm equation [40] it is presumed that the heat of biosorption of all the molecules in the layer reduces linearly with coverage owing to adsorbent–adsorbate interactions and that the adsorption is characterized by a homogeneous distribution of the binding energies up to some topmost binding energy [41]. The linear form of the Temkin isotherm is expressed as follows:

$$\log\left(\frac{1}{q_e}\right)=\log\left(\frac{k_L+1}{k_L q_m}\right)+\frac{1}{n}\log\frac{1}{C_e} \tag{9}$$

In Fig. 12 the plots of ln (C_e) versus q_e for humic acids (HAs) are exhibited and in Table 3, the linear isotherm parameters b_T, K_T and the correlation coefficient are summarized. The b_T constant relative to heat of sorption for humic acids (HAs) equals 21.441 J/mol.

3.7.4. Dubinin–Radushkevich (DR) isotherm

The biosorption nature of the sorbate on the biosorbent and calculation of the mean free energy of biosorption is described by the Dubinin–Radushkevich isotherm [42].

$$Lnq_e = Lnq_d - K_D\varepsilon^2 \tag{10}$$

where ε can be correlated

$$\varepsilon = RTLn\left(1+\frac{1}{C_e}\right) \tag{11}$$

in which R shows the gas constant (8.314 J/mol K). T shows the absolute temperature (K). As shown in Fig. 13, from the slope and intercept of the plot of ln q_e against ε^2, the D–R isotherm constants b and q_{max} can be acquired. The computed values are exhibited in Table 3. E or the mean free energy of biosorption which is defined as the free energy alters when 1 mol of ion is conveyed to the surface of the solid from infinity in solution and computed from the b value: [43].

$$E = -0.7{K_D}^{-0.5} \tag{12}$$

The plots of RT ln(1+1/C_e) versus ln(q_e) for humic acids (HAs) are shown in Fig. 13 and the linear isotherm parameters q_D, B_D and the correlation coefficient are given in Table 3.

3.8. Adsorption thermodynamics

At diverse temperatures of 25, 35, 45, and 55°C, thermodynamic parameters for adsorption of humic acids (HAs) onto derived active carbon from raw maize tassel were acquired. This was carried out via the ensuing equation to scrutinize the spontaneous nature of the adsorption process [44].

$$\Delta G_{ads} = -RTLnK \tag{13}$$

A graph (Fig. 14) is developed from a plot of lnK_e against 1/T, from the slope of which ΔG can be procured. In Tables 4 and 5, the summary of the thermodynamic parameter outcomes for the adsorption of humic acids (HAs) onto derived active carbon from raw maize tassel at different temperatures is shown.

Via applying the equation adsorption of humic acids (HAs), the ΔG° values were computed. As shown in Fig. 14, upon the increase in the temperature from 298 to 348K, maize tassel adsorbent diminished and therefore the exothermicity nature of the process was confirmed. The values of the thermodynamic parameters (Tables 4,5) [45] were computed using the plots. In the current study, the computed value for the enthalpy change (ΔH°) was –15.0 kJ/mol and for the entropy change (ΔS°) was –40.0 J/mol·K. The feasibility and spontaneity nature of the process was revealed by the negative value of ΔG°. The exothermicity nature of adsorption was proven by the negative value of ΔH° while the value of ΔS° was a good indication of change in the randomness at the derived active carbon from raw maize tassel solution interface during the sorption. The fact that ΔG° values up to –2.25 kJ/mol are accordant with electrostatic interaction between sorption sites and the humic acids (HAs) (physical adsorption) has been reported. The obtained ΔG° values in this article for humic acids (HAs) are <–5 kJ/mol suggesting the predominancy of the physical adsorption mechanism in the sorption process.

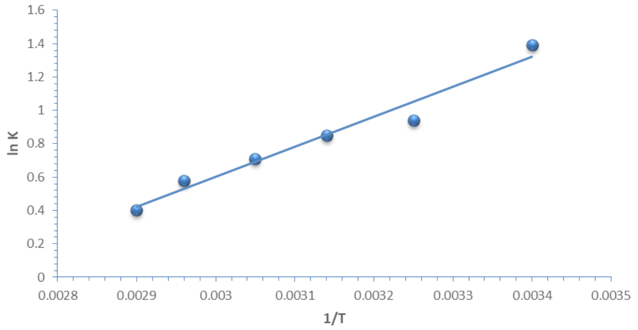

Fig. 14. Plot of ln K_c vs. 1/T for the estimation of thermodynamic parameters.

Further applications

The use of activated carbon in solving environmental problems affecting air and water is undeniable and since the process of deriving activated carbon from raw maize tassel is cost-effective, it is suggested to use it for removing other impurities from water. Also, the use of activated

Table 4
The distribution coefficients at different temperature

Humic acids (HAs) concn. (mg/L)	R^2	K_d					
		298K	308K	318K	328K	338K	348K
10 mg/L	0.936	4.0	2.6	2.33	2.03	1.87	1.5

Table 5
The thermodynamic parameters for the adsorption of humic acids (HAs) on maize tassel adsorbent

Humic acids (HAs) concn. (mg/L)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)					
			298K	308K	318K	328K	338K	348K
10 mg/L	–15.0	–40.0	–3.44	–2.40	–2.25	–1.94	–1.63	–1.16

carbon from raw maize tassel as a filter for drinking water should be tested. And since the subjects of decolorizing and deodorizing waste water lies at the heart of a number of many processes of water treatment, it is strongly suggested to test the use of activated carbon from raw maize tassel in decolorization and deodorization of waste water.

4. Conclusions

The prepared activated carbon from maize tassel was utilized as a successful, economical and non-toxic natural adsorbent for the elimination of humic acids (HAs) from aqueous solutions. The impacts of pH, adsorbent dosage, contact time, and initial humic acids (HAs) on the elimination of (HAs) were researched via batch experiments. After assessing the isotherm models of Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich (DR) models for the adsorption process, it was noted that Freundlich model could properly describe the equilibrium data. The maximum sorption capacity (q_{max}) of 3.0 mg/g and R^2 of 0.995 in Langmuir isotherm of humic acids (HAs) was observed onto maize tassel. The kinetics were detected to be adequately fitted to the pseudo-second-order kinetic model. The spontaneity of the adsorption of HAs at the temperatures under study was confirmed. On the one hand, the feasibility of the process and spontaneity of the adsorption was confirmed by the negative value of ΔG°. On the other hand, the exothermic nature of adsorption was confirmed by the negative value of ΔH° while the value of ΔS° indicated the alteration in the randomness at the derived active carbon from raw maize tassel solution interface during the sorption. The aim of the current work is to generate economical, accessible, and efficacious humic acids (HAs) adsorbents from natural leavings as an alternative to existing commercial adsorbents. Maize tassel showed a high adsorption capacity when juxtaposed to other adsorbents for humic acids (HAs) elimination from an aqueous medium.

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