

Application of Rice Husk to Remove Humic Acid from Aqueous Solutions and Profiting from Waste Leftover

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ABSTRACT: -Scrutinize to the feasibility of Rice Husk (RH) on the removal of humic acid pollutant from aqueous solutions using different design parameters by adsorption process is carried out. Results show that the higher removal efficiency was 98.24 % for humic acid from aquatic solution and this efficiency was decreased with increasing of initial concentration flow rate and pH while the removal efficiency increased with increasing absorbance material bed height and feeding temperature. One of the method of profiting from it was using as fertilizer for tomato harvest. The results show that the tomato was bloomed and gave greater weight crop. By this way we can possess different benefits which are: remove the humic acid contaminated the water, get rid of agricultural waste (RH), in the same time, and prepared a good and useful fertilizer for tomato harvest.

Key-Words: -Rice Husk, Humic Acid, Fertilizer, Aqueous Solutions, Adsorption, Residue and Wastewater

1 Introduction

A natural organic substance, in raw surface water, is best described as a complex mixture of organic compounds, mainly humic acid and fulvic acids. Organic substance itself is considered harmless; however the conversion of it into disinfection by-products when chlorine is used in water treatment can cause problems [1]. Humic substances are universally present in natural waters and soils. They are not well-defined substances, but generally can be subdivided into a humming, humic acids (HA) and fulvic acids (FA) based on their solubility under acidic or alkaline conditions in aqueous solutions. Humic substances can react with chlorine during drinking water treatment and produce disinfection by-products (DBPs), such as trihalomethanes with potential adverse health impacts [5].

Thus, the removal of humic substances from water is necessary and many methods have been developed such as chemical coagulation, membrane separation, advanced oxidation and adsorption [2]. Among these methods, adsorption is generally regarded as a promising method and has been extensively studied for removal of humic substances [6]. Various adsorbents, including activated carbon, unburned carbons, resin, Chitosan, Chitosan-coated granules, cross linked Chitosan epichlorohydrin beads, Mg/Al layered double hydroxides, Mg/Fe

layered double hydroxide, layer structured graphite oxide, amine modified polyacrylamide-bentonite composite, surfactant-modified bentonite and irradiation-cross linked carboxymethylchitosan, etc. have been tested for humic acid removal [6].

Natural zeolites are crystalline microporousaluminosilicates with very well defined structure that consist of a framework formed by tetrahedrons of SiO_4 and AlO_4 , and they possess permanent negative charge in their crystal structures that can be balanced by exchangeable cations such as Na^+ , Ca^{2+} , K^+ and Mg^{2+} . Thus, natural zeolites usually can exchange cations but not anions, which making them suitable for surface modification using cationic surfactants, such as hexadecyltrimethylammonium bromide (HDTMA-Br) and cetylpyridinium bromide (CPB) [3].

Although extensive studies on performance of HDTMA modified zeolite in removing anionic and organic contaminants and the intercalation of HDTMA into zeolite have been conducted, there are few reports concerning the performance of CPB modified zeolite in removing humic acid and the intercalation of CPB into zeolite. By loading cationic surfactant CPB onto one kind of natural zeolite, a composite adsorbent was prepared and applied to the removal of humic acid from aqueous solution[3]. In this paper the adsorption of humic acid using RH was tested and endeavour of utilizing

from the residue in a convenient, economical way and ecofriendly.

2 Methodology

2.1 Materials

2.1.1 Rice Husk (adsorbent media)

RH was collected from Al-Shanafia fields for rice in the Southern of Iraq. The rice husk was washed three times with double distilled water. Excess distilled water was used to remove the soluble materials present in the rice husk bringing from the field, boiled to remove color and other fine impurities may be found in the rice husk, and then dried at 105°C for 24 hours and the adsorbent thus processed was used in its original piece size. The surface area of RH was measured by BET (Brunauer – Emmett – Teller nitrogen adsorption technique). Characteristics of RH were presented in Table 1. When the RH was heated at 105°C in an oven, most of the water had been removed from the rice husk while the second major mass loss of about 45-65% was attributed to the breakdown of cellulose constituent char, which is a carbonaceous residue.

Table1: Characterization properties of Rice Husk

Chemical Composition	
Compound	Composition wt %
SiO ₂	90.7
Al ₂ O ₃	0.13
Fe ₂ O ₃	0.06
TiO ₂	0.015
CaO	0.61
MgO	0.25
Na ₂ O	0.09
K ₂ O	2.64
P ₂ O ₅	0.73
LOI	4.71
S.A (m ² /g)	17.5

2.1.2 Stock solutions

In order to avoid interference with other elements in wastewater, the experiments in this study were carried out using simulated synthetic aqueous solution (SSAS) of different humic acid. 1000 mg/l stock solution of humic acid was prepared by dissolving known weight of humic acid in one liter of double distilled water, all solutions using in the experiments were prepared by diluting the stock solution with double distilled water to the desired

concentrations for the experimental work of this investigation. The humic acid concentrations were measured using spectrophotometer thermo – genesys 10 UV, USA.

2.2 Sorption unit

Fixed bed column of continuous mode experiments were conducted in order to test humic acid removal by treated SSAS of above humic acid each one alone at desired concentration with the various bed heights of the adsorbent media (RH) using different flow rates of SSAS of humic acid at various pH. The pH value was adjusted using 0.1 N NaOH and 0.1 N HCl solutions. A schematic representation of the sorption unit is shown in Figure1 where the flow direction is downward by gravity. The sorption unit consists of two glass container of SSAS of humic acid one for inlet and another for outlet each of (1 liter) capacity. Glass column has 2.54 cm ID and 100 cm height.

The sorption column packed with adsorbent media to a height of (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 cm) supported from the top and the bottom by glass hollow cylinder layer, each cylinder have (0.5 cm ID, 0.1 cm thickness and 1 cm long). Before starting the runs, the packed bed sorption column was rinsed by double distilled water down flow through the column. The RH is packed in the column to the desired depth, and fed to it as slurry by mixing the media RH with distilled water in order to avoid the formation of air bubbles inside the media. After the packed bed sorption column was accommodation and putting the required amount of adsorbent media, the adsorption process started by allowing the humic acid SSAS of required concentration and pH down flow through the sorption column from the inlet container by gravity at a precise flow rate in an experiment which is adjusted by the valve as shown in Figure 1.

To determination the best operational conditions, the experiments were carried out at a temperature between (20 –55°C), various pH values which are (1–8) and initial feed concentrations of SSAS of different humic acid which are between (1–100) mg/l each one alone and at different flow rates which are between (5–100) ml/min for humic acid initial feed concentration. Outlet samples after treatment in each experiment were collected every

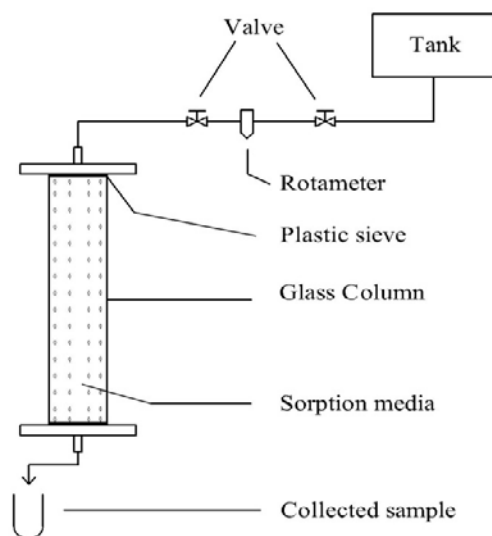


Fig. 1: The experimental adsorption unit

10 minutes from the bottom of packed column and the unadsorbed concentration of humic acid ion in SSAS was analyzed by spectrophotometer.

2.3 Reusability of Rice Husk

In order to check the reusability of sorbent media, treated RH with different humic acid was firstly dried at 105°C after that tested again in sorption unit at the conditions of experiment gives the best percent removal of humic acid from SSAS aforementioned. The capacity of the sorbent was found to be decreased until be constant at destined percent removal after different times repeated use. The destined percent removal and number of repeated uses were dependent on humic acid; thus seven times of use of sorbent was seen to be feasible.

3. Results and Discussion

The ability of RH to remove humic acid from SSAS in fixed bed column of continuous mode at various parameters which are pH's of SSAS of humic acid (pH), height bed of adsorbent media RH (h), flow rates of SSAS (F), SSAS temperature (T_{feed}) and time of treatment (t) was investigated. The experiments were achieved by varying all above parameters for different initial concentrations (C_0) of SSAS of humic acid. Thus, the results obtained are explained below.

3.1 Effect of Initial Concentration

The results showed that using adsorbent material, the percent removal of humic acid was decreased when the initial concentration (C_0) of SSAS of humic acid was increased at constant other variables as shown in Figure 2. This can be explained by the fact that the initial concentration of humic acid had a restricted effect on humic acid removal capacity; simultaneously the adsorbent media had a limited number of active sites, which would have become saturated at a certain concentration. This was lead to the increase in the number of humic acid molecules competing for the available functions groups on the surface of adsorbent material. Since the solution of lower concentration has a small amount of humic acid than the solution of higher concentration of it, so the percent removal was decreased with increasing initial concentration of humic acid. For adsorbent media, higher percent removal were 98.24 % for humic acid at initial humic acid concentration of 1 mg/l, so adsorbent material was found to be efficient to humic acid removal from SSAS and wastewater.

3.2 Effect of pH

The results showed that using adsorbent material, the percent removal of humic acid was increased when the pH of SSAS of humic acid was decreased at constant other variables as shown in Figure 3. This Increase can be explained as follows: humic acid is predominately negatively charged. Therefore, decreasing the pH renders the negatively charged humic acid molecules more neutral. A negatively charged molecule attracts ions of opposite charge (hydrogen ions in this case) to its surface from the surrounding water and becomes more neutral. A neutral molecule is inherently less soluble in water than a charged molecule (water is highly polar solvent) and, therefore, more adsorbable. In addition, at low water pH, humic acid is more coiled due to less negative-charge repulsion allowing for greater access to RH pours. In other words, the adsorption process become more favourable as water pH decreased [4].

3.3 Effect of Adsorbent Media Bed Height

The results elucidated that when the adsorbent media bed height was increased, the percent removal of humic acid was increased too at constant other variables as shown in Figure 4. The increased of bed height (h) meaning increased in the amount of adsorbent media (RH), thus increasing the surface area of adsorbent material, hence increased the

number of active sites in the adsorbent material surface i.e. increased the availability of binding sites for adsorption and consequently increase humic acid removal capacity on RH. This lead to increase the ability of adsorbent media to adsorb greater amount of humic acid from SSAS at different initial concentrations and ultimately the percent removal of humic acid increased.

3.4 Effect of Flow Rate

The results illustrated that when the flow rate of SSAS of humic acid was increased, the percent removal of humic acid was decreased at constant other variables as shown in Figure 5. This may be due to the fact that when the flow of SSAS of humic acid increasing, the velocity of solution in the column packed with the adsorbent media (RH) was increasing too, so the solution spend shorter time than that spend in the column while at low flow rate, the SSAS of humic acid resides in the column for longer time, and therefore undergoes more treatment with the adsorbent media, thus the adsorbent media uptake low amount of humic acid from SSAS of humic acid for high flow rate, therefore the percent removal of humic acid was decreased when the flow rate was increased.

3.5 Effect of Feed Temperature

The results demonstrated that when the temperature of feed which was SSAS of humic acid was increased, the percent removal of humic acid was increased too at constant other variables as shown in Figure 6. The effect of temperature is fairly common and increasing the mobility of the acidic ion. Furthermore, increasing temperatures may produce a swelling effect within the internal structure of the adsorbent media enabling humic acid ions to penetrate further. It was indicated that humic acid adsorption capacity increased with increasing feed temperature from 5 to 55° C. This effect may be due to the fact that at higher temperature an increase in active sites occurs due to bond rupture.

3.6 Effect of Treatment Time

The results demonstrated that when the treatment time of SSAS of humic acid increased the percent removal of humic acid increased at constant other variables as shown in Figure 7. This may be due to the fact that when the time of treatment of SSAS of humic acid increasing and the velocity of SSAS in the column packed with the adsorbent material was remaining constant, the solution spend longer time than that spend it when the time of treatment decreased, so the adsorbent material uptake more amount of humic acid from SSAS, therefore the percent removal of humic acid from SSAS was increased.

4 Statistical Model

A statistical model was carried out on the experimental results obtained from this study. Regression Analysis and π Theorem was adopted to maintain a relation between the percent removal of humic acid and the feed temperature, flow rate, pressure, pH of feed solution, initial concentration of humic acid, adsorbent media (RH) bed height, treatment time and column diameter. These relations are shown in Equation 1 below, which has a correlation coefficient (R^2) 0.974.

5 Utilization of Rice Husk

Huge amount of RH were lingered after using it in removal of humic acid from SSAS as explained above. Utilization from these RH uses can be achieved by using it as a fertilizer for tomato crop as follows: RH waste which was adsorbed humic acid from SSAS at different operating conditions were segregated and classified according to its contain of humic acid and utilization from these remaining samples as a raw material in synthesis of a fertilizer for tomato crop.

The samples give different ratios of humic acid to RH. The ratios were between (0.05 to 0.1 wt %) for humic acid. RH lingered with different ratios were firstly crashed to make powder, dissolved the powder in water completely and then irrigated tomato crop by this solution. Tomato crop results show bloomed and gave higher weight crop (15wt %) than tomato irrigated with fresh water.

It's known that humic acid Increases yields of crops, vegetables and fruits, Produces superior turf, healthy and deep roots, Enhances uptake of fertilizers, Creates vegetation in saline and poor soils, and Promotes ecological balance and it can do that by enhancing soil structure and fertility through the addition of vital organic matter in the soil, by efficient transfer of fertilizer nutrients and

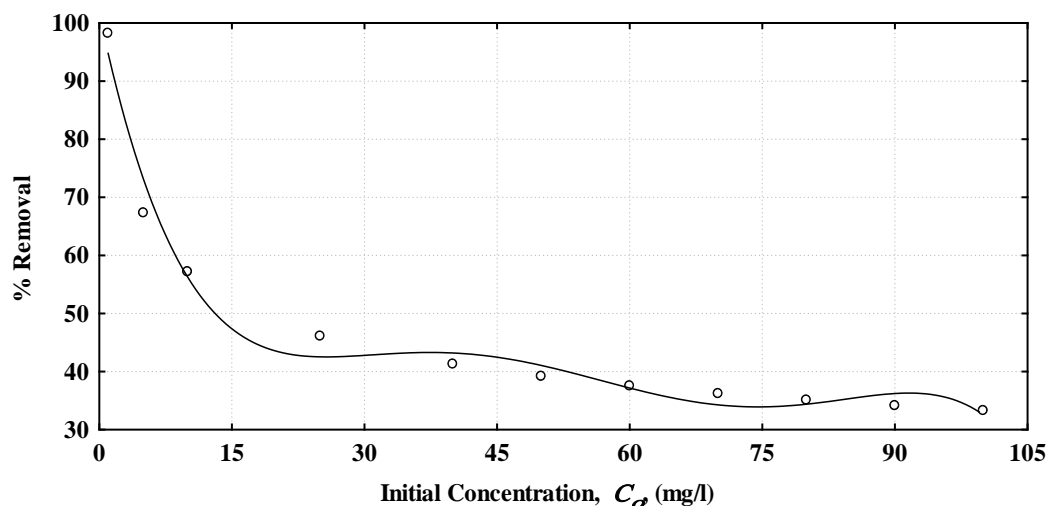


Fig. 2: Effect of initial concentration (C_0) on the percent removal humic acid @ $T_f=55^\circ\text{C}$, $h_b = 1\text{ m}$, $\text{pH}=1$, $t=60$ min. and $F=5\text{ ml/min}$.

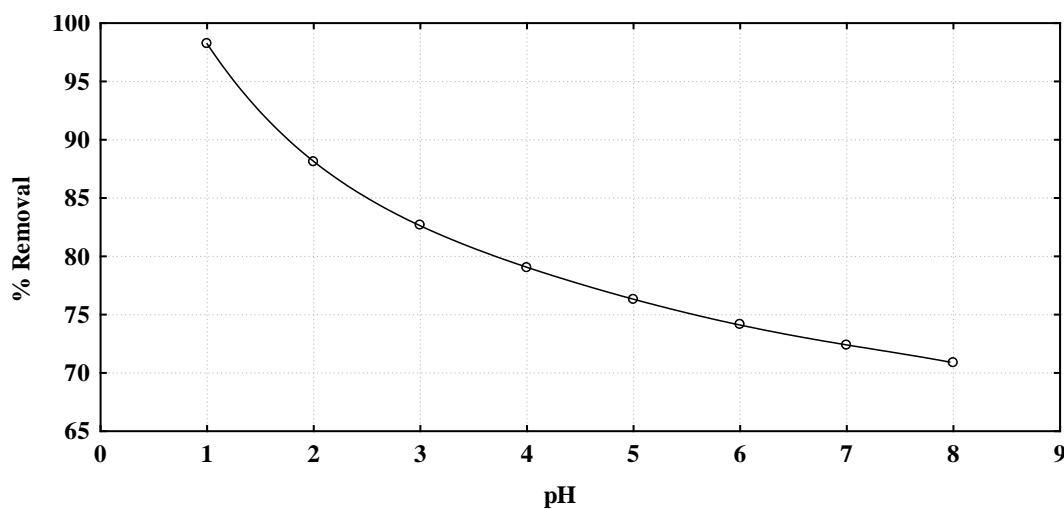


Fig. 3: Effect of pH on the percent removal of humic acid @ $C_0= 1\text{ mg/l}$, $T_f=55^\circ\text{C}$, $h_b = 1\text{ m}$, $t=60$ min. and $F=5\text{ ml/min}$.

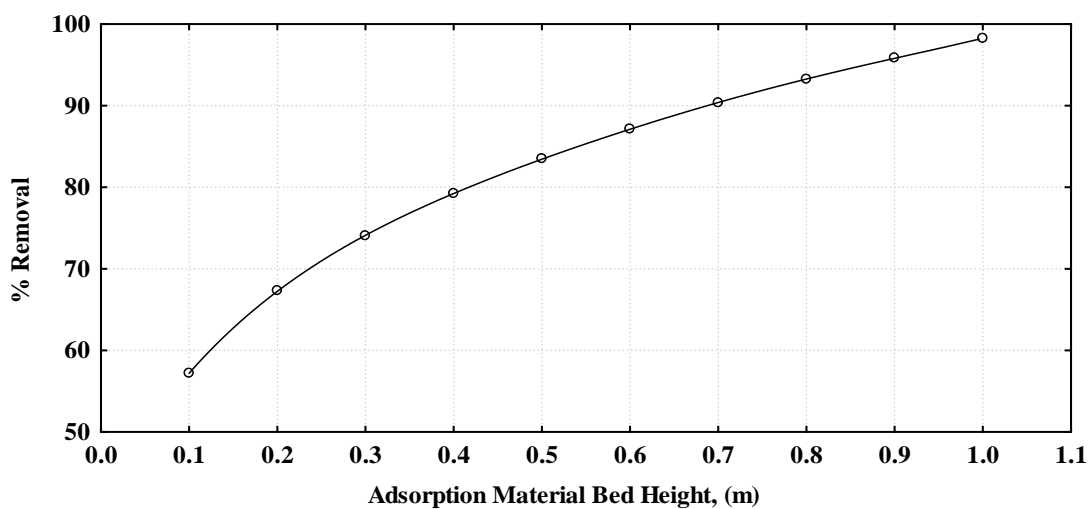


Fig. 4: Effect of adsorbent media bed height (h_b) on the percent removal humic acid @ $C_0= 1\text{ mg/l}$, $\text{pH}=1$, $T_f=55^\circ\text{C}$, $t=60$ min. and $F=5\text{ ml/min}$.

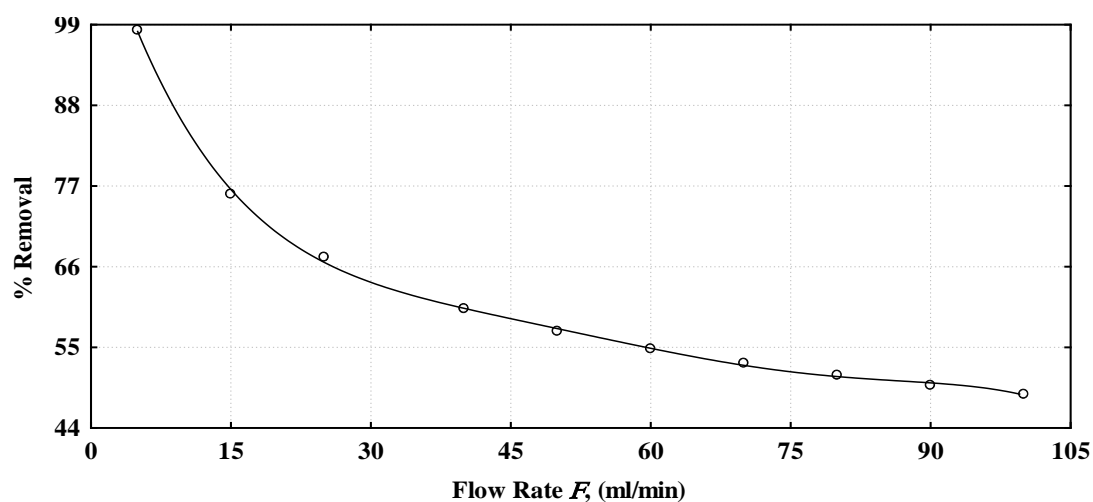


Fig. 5: Effect of aqueous solution flow rate (F) on the percent removal of humic acid @ $C_o = 1$ mg/l, pH=1, $T_f = 55^\circ\text{C}$, $h_b = 1$ m and $t = 60$ min.

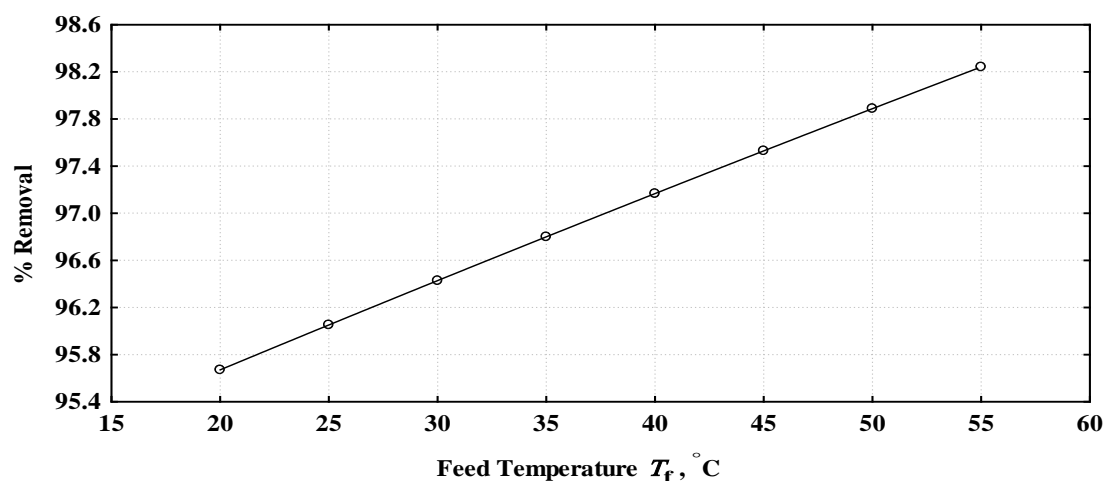


Fig. 6: Effect of feed temperature (T_f) on the percent removal of humic acid @ $C_o = 1$ mg/l, pH=1, $h_b = 1$ m, $t = 60$ min. and $F = 5$ ml/min.

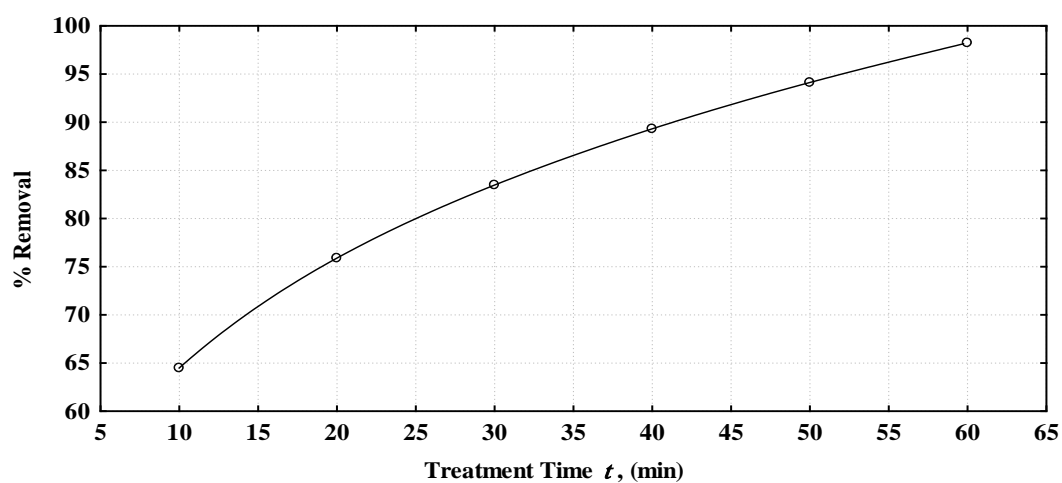


Fig. 7: Effect of treatment time (t) on the percent removal of humic acid @ $C_o = 1$ mg/l, $T_f = 55^\circ\text{C}$, pH=1, $h_b = 1$ m, and $F = 5$ ml/min.

$$\% R = 9.278 \times 10^{-6} \left(\frac{T_f \cdot P \cdot h_b \cdot C_{P_{sol}} \cdot t}{F \cdot d \cdot C_o \cdot g} \right)^{0.235} \left(\frac{1}{pH} \right)^{0.157} \dots (1)$$

Where % R is Percent Removal of Humic Acid from SSAS, T_f is feed temperature, (K), P is pressure, (Pa), h_b is adsorbent material bed height, (m), $C_{P_{sol}}$ is heatcapacity of aqueous solution, (J/g K), F is aqueoussolution flow rate, (m^3/s), d is internal diameter of sorption column, (m), C_o is initial concentration of Humic Acid, (g/m^3), t is treatment time, (s), g is acceleration due to gravity, (m/s^2).

micronutrients because of the high chelation and cation exchange proportion of the active humic acid component, increasing moisture holding capacity of soil, increasing microbial activity in the soil; and enhancing plant cell biomass. Humic acid effect in different ways on plant growth; it can effect physically through Increase water holding capacity, Increases aeration of soils, Improves soil workability, Helps resist drought, Improves seed bed, Makes soil more friable or crumbly, Reduces soil erosion and it can effect chemically by Chelates nutrients for uptake by plants, Possesses high ion-exchange capacity, Increases buffering properties of soils, and Increases percentage of total Nitrogen in soils; while humic acid can effect biologically through accelerates plant cell division and promotes growth, Increases germination of seeds and viability, Increases root respiration and formation, Stimulates growth and proliferation of soil microorganisms, and Aids in photosynthesis.

6 Conclusion

The following conclusions can be drawn:

- 1) RH showed a good ability to remove humic acid from SSAS using fixed bed adsorption unit. So, it could be recommended for removal of humic acid from wastewater in Iraq instead of other material because it is valid, cheaper, economical, easy and simplicity for using, and has a high ability to adsorb humic acid, can be used several times by costly regeneration method and can be used finally in another benefit uses.
- 2) Maximum removal of humic acid was 98.24% at initial humic acid concentration of 1 mg/l.
- 3) The percentage removal of humic acid was increased with decreasing flow rate of SSAS, pH and initial concentration of humic acid while the percentage removal was increasing with increasing of treatment time and the height of adsorbent material (RH).

- 4) It can be prepared a good fertilizer for tomato crop from the residual samples of RH that adsorb humic acid from SSAS. So we can remove the polluted waste in economic and eco-friendly method.
- 5) It can use the RH for generated electric power after using it to remove the humic acid from wastewater, thus we getting rid of two pollutants by one material in an economic and eco-friendly method.

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