Adsorption of Humic acid on Powdered Activated Carbon (PAC)

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Abstract

Removal capacity and rate of Humic Acid (HA) onto powdered activated carbon (PAC) were studied at constant room temperature which is 24-25^{o}C by using tap water as a solvent. If enough PAC is added to solution, maximum HA removal efficiency of PAC which is more than 99% is observed, and adsorption uptake was found almost 22.5 mg HA/g PAC for 90% removal of HA. And also, almost 90% of HA adsorption/removal onto PAC was observed at first 40-50 minutes. After that time period, change in adsorption rate does not have big variation.

Keywords: Humic Acid (HA) removal, powdered activated carbon (PAC) and Adsorption, isotherm, removal rate.

1. Introduction

Adsorption is a mass transfer operation in which substances present in a liquid phase are adsorbed or accumulated on a solid phase and thus removed from the liquid. Adsorption processes are used in drinking water treatment for the removal of taste-and odor-causing compounds, synthetic organic chemicals (SOCs), color-forming organics, and disinfection byproduct (DBP) precursors. Inorganic constituents, including some that represent a health hazard, such as perchlorate, arsenic, and some heavy metals, are also removed by adsorption.

The primary adsorbent materials used in the adsorption process for drinking water treatment are powdered activated carbon (PAC) and GAC. Powdered activated carbon is added directly to water and can be applied at various locations within a water treatment plant and is usually removed by sedimentation or filtration.

1.1. Adsorption Phenomena

The constituent that undergoes adsorption is referred to as the *adsorbate*, and the solid onto which the constituent is adsorbed is referred to as the *adsorbent.* During the adsorption process, dissolved species are transported into the porous solid adsorbent granule by diffusion and are then adsorbed onto the extensive inner surface of the adsorbent. Dissolved species are concentrated on the solid surface by chemical reaction (chemisorption) or physical attraction (physical adsorption) to the surface.

Physical adsorption is a rapid process caused by nonspecific binding mechanisms such as van derwaals forces and is similar to vapor condensation or liquid precipitation. Physical adsorption is reversible, that is, the adsorbate desorbs in response to a decrease in solution concentration. Physical adsorption is the most common mechanism by which adsorbates are removed in water treatment.

Interest in adsorption as a process for removal of organics from drinking water was heightened because the public became increasingly concerned about water sources that were contaminated by industrial wastes, agricultural chemicals, and municipal discharges. Another major concern was the formation of DBPs during chlorination of water containing background organic matter (referred to as DBP precursors). It has been found that activated carbon can be effective in removing some of the DBP precursors.

Porous adsorbents can have a large internal surface area (400 to 1500 m^2/g) and pore volume (0.1 to 0.8 mL/g) and as a result can have an adsorption capacity as high as 0.2 g of adsorbate per gram of adsorbent, depending on the adsorbate concentration and type.

1.2. Powdered Activated Carbon

With a small particle size PAC can be added to water at various locations in the water treatment process to provide time for adsorption to take place and then remove the PAC by sedimentation and/or filtration.

Powdered activated carbon is primarily used in the treatment of taste and odor compounds and the treatment of low concentrations of pesticides and other organic micro pollutants. The convenience of PAC is that it can be employed periodically (when needed) in a conventional water treatment plant with minimum capital costs. For example, PAC can be used during summer months for surface water sources containing taste and odor compounds resulting from algal blooms. It can also be employed to remove chemical pollution (pesticides and herbicides) carried in spring runoff.

1.3. Development of Isotherms to Describe Adsorption

The affinity of the adsorbate for an adsorbent is quantified using adsorption isotherms, which are used to describe the amount of adsorbate that can be adsorbed onto an adsorbent at equilibrium and at a constant temperature, For most applications in water treatment, the amount of adsorbate adsorbed is usually a function of the aqueous--phase concentration and this relationship is commonly called an isotherm.

2. Materials and methods

2.1. Materials

The commercially available powdered activated carbon (PAC) supplied by Aldrich was used as the adsorbent for this study. PAC was dried at 110^{o}C for 24h, cooled and stored prior to use. Humic acid (HA) was obtained as a commercial reagent grade solid in powdered form (Husky industries). Stock solutions were prepared from 1g of dry HA product initially dissolved in 1L of pure water, stirred on a hot stirrer plate for 30 min at 80 ^{o}C and filtered using 0.45 µm membranes

2.2. Experimental procedure

A jar test apparatus (Phipps and Bird stirrer, 120 V AC, 50 – 60 Hz) was used which had the facility to preset the stirring intensity (rpm). For each test, 500 mL of solution was used within a 1L beaker and adsorption onto PAC involved rapid mixing at 150 rpm for 120 sec, followed by slow stirring at 50 rpm for 90 min. For removal efficiency test, samples were taken at the end of 90 min using a sampler and filtered by 0.45 µm membranes. For time contact test, samples were taken at desired time intervals and filtered accordingly. The UV absorbances of the samples were measured immediately at a wavelength of 254 nm (Spectronic Genesys 2 of Spectronic instruments)

3. Results and Discussions

3.1. HA removal efficiency onto PAC

According to results at table 3.1, if we increase PAC dosage HA removal increases, but extreme dosages are just consuming more PAC. By using the formula below,

removal = **(Co-CA)/Co*100** Eq (1)

for removal of 10, 25, 50, 100 mg/L HA from solution, required PAC dosages are 0.2, 0.6, 1 and 2 g were observed respectively, for calculated 90 % removal of HA, and there is linear relation between PAC dosage and HA removal which can be seen at figure 3.1.

HA C_o(mg/L)	Residual C_A(mg/L)	PAC (g)	C_o, initial (UV)	C_A (UV)	Removal rate(%)	q_A, mg adsorbate/g adsorbent
10	0.984615385	0.2	0.325	0.032	90.15384615	22.53846154
10	2.769230769	0.5	0.325	0.09	---	---
10	0.030769231	0.8	0.325	0.001	99.69230769	6.230769231
25	15.48619448	0.1	0.833	0.516	38.05522209	47.56902761
25	11.01440576	0.2	0.833	0.367	55.94237695	34.96398559
25	1.830732293	0.4	0.833	0.061	---	---
25	2.400960384	0.6	0.833	0.08	90.39615846	18.83253301
25	0.570228091	0.8	0.833	0.019	97.71908764	15.26860744
50	30.81264108	0.1	1.772	1.092	38.37471783	95.93679458
50	29.5993228	0.2	1.772	1.049	40.8013544	51.001693

50	16.73250564	0.5	1.772	0.593	66.53498871	33.26749436
50	4.571106095	1	1.772	0.162	90.85778781	22.71444695
100	58.92156863	0.2	3.06	1.803	41.07843137	102.6960784
100	47.25490196	0.4	3.06	1.446	52.74509804	65.93137255
100	32.45098039	0.8	3.06	0.993	67.54901961	42.21813725
100	17.48366013	1.5	3.06	0.535	82.51633987	27.50544662
100	10.13071895	2	3.06	0.31	89.86928105	22.46732026

Table 3.1 Removal efficiency of HA by PAC

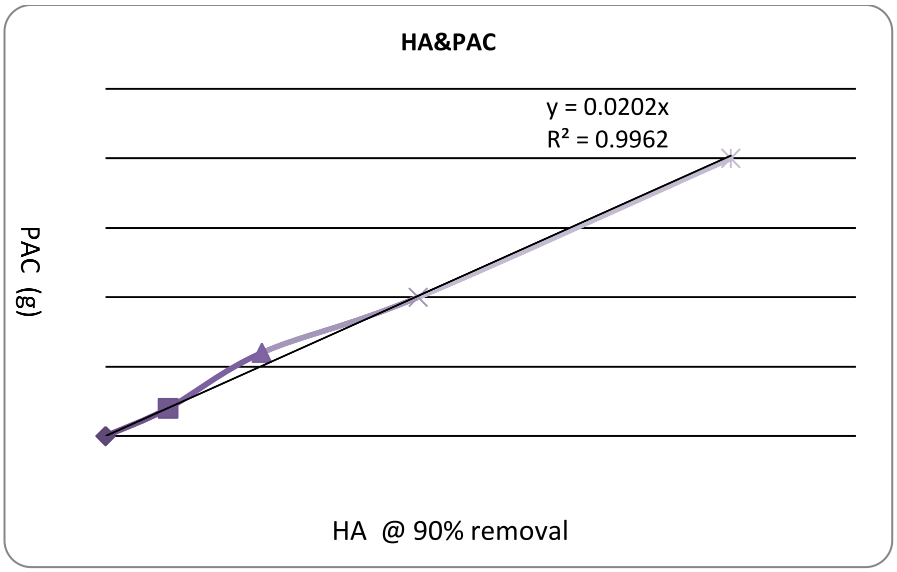

Figure 3.1 90 % HA removal dosages of PAC

3.2. HA removal change with time

By using HA and PAC dosages which is required for 90 percent HA removal, after 2 minute rapid mixing and 50 rpm 40-50 minute slow mixing, removal rates are approaching almost 85-90 percent can be seen at figure 3.2 below. After 40-50 minutes, change in removal rate does not have big difference. It means contact time is very important for HA adsorption onto PAC and it can be said that for the adsorption of HA onto PAC initial contact time is more important.

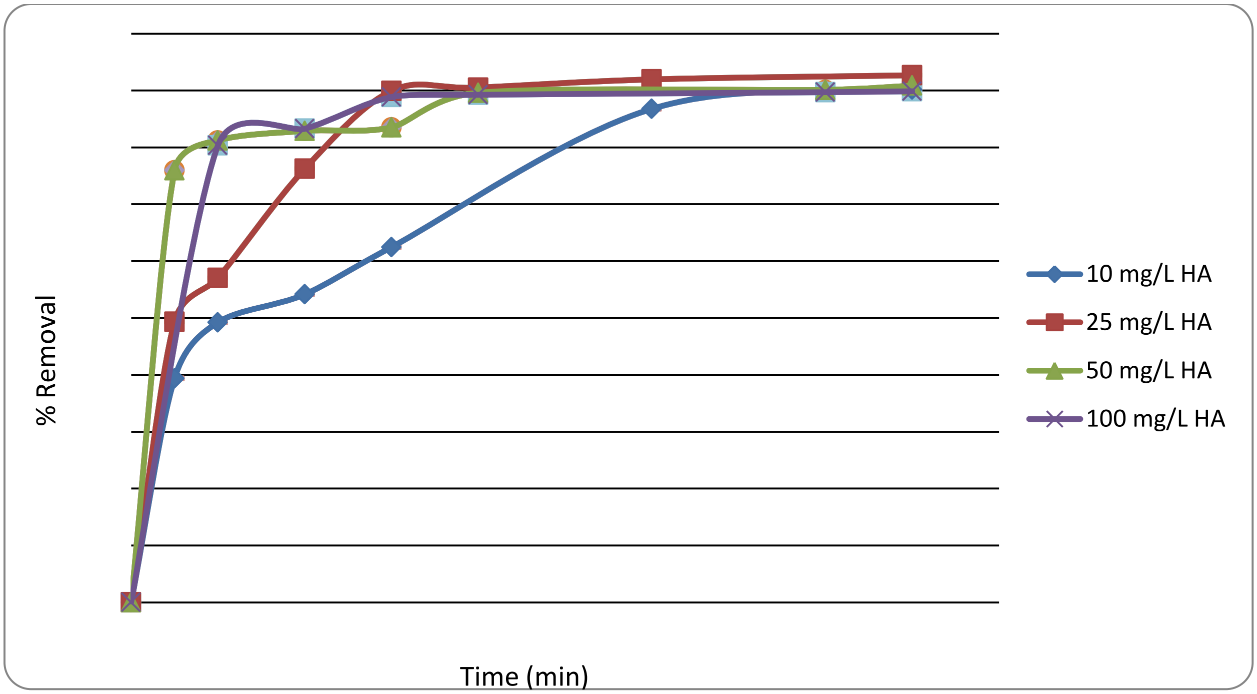

Figure 3.2 Removal rate change of HA with time

3.2 Effective Removal Isotherm and change by time

Adsorption isotherm can be calculated by using the equation which is below.

$$\mathbf{q_A = (V/M)(C_o - C_A)} \quad \text{Eq(2)}$$

q_A = eadsorbent-phase concentration of adsorbate, mg adsorbate./g adsorbent

V = Volume of aqueous phase added to the bottle

M = Mass of adsorbent, g

C_o = initial aqueous--phase concentration of adsorbate, mg/ L

C_A = aqueous-phase concentration of adsorbate, mg/L

Like the removal efficiency, By using HA and PAC dosages which is required for 90 percent HA removal, after 2 minute rapid mixing and 50 rpm 40-50 minute slow mixing, adsorption isotherm approaching almost 22 mg adsorbate/g adsorbent can be seen at figure 3.3 and table 3.1. After 40-45 minutes, increase in adsorption isotherm does not have big difference. It means contact time is very important for HA adsorption onto PAC.

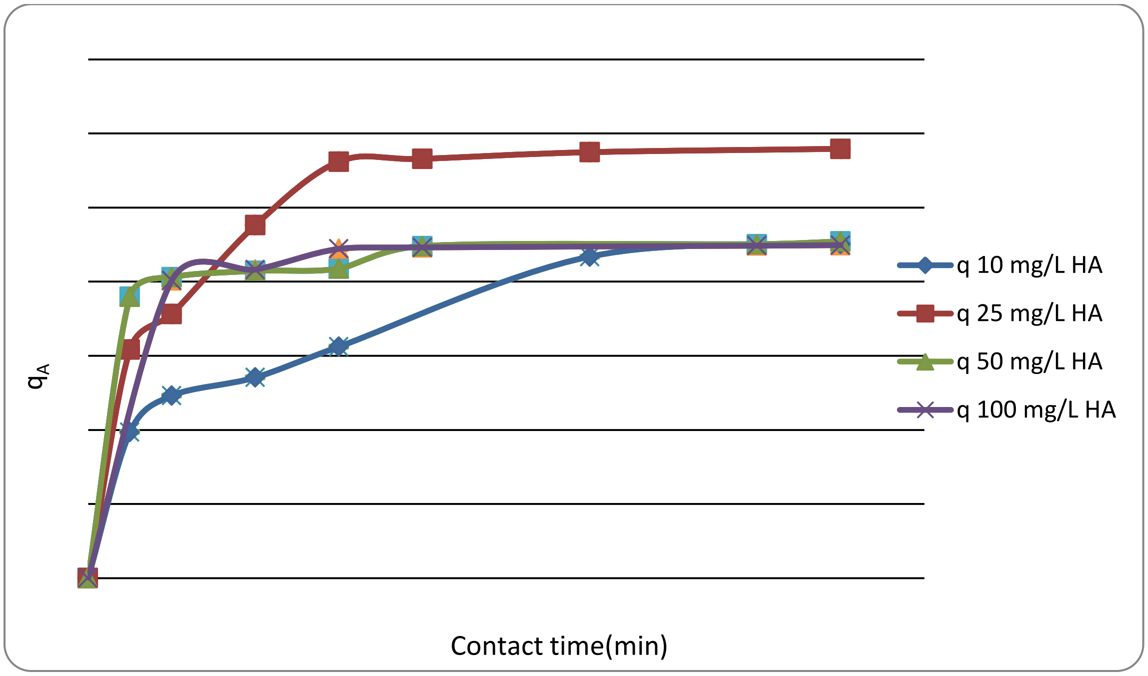

Figure 3.3 Adsorption isotherm change of HA with time

4. Conclusion

The present study shows that the PAC can be used as an effective and favorable adsorbent for the removal of HA from aqueous solution. According to our results, if enough PAC is added to solution, maximum HA removal efficiency can be reached, and adsorption uptake can be found as mg HA/g PAC. At this study is was found almost 22.5 mg adsorbate/g adsorbent for % 90 removal of HA. The adsorption reached top within 40-45 min at the experimental conditions in all the cases. The r-shaped adsorption isotherm indicates that there is a high affinity of contact time with adsorption rate.

The fitting result indicated that the adsorption of HA on PAC represents the linear consistency. External mass from DOC from tap water, contact time and mixing were confirmed as the rate-controlling step in the sorption process. Under the prevailing conditions, the maximum PAC removal efficiency was found to be 99.7% for 10 mg HA with contact of 0.8 g of PAC.

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