Keywords: Trihalomethanes; Activated carbon; Agricultural solid wastes

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 odour causing compounds, synthetic organic chemicals (SOCs), colour forming organics, and disinfection by-product (DBP) precursors. Inorganic constituents, including some that represent a health hazard, such as perchlorate, arsenic, and some heavy metals, are also removed by adsorption [1,2]. Granular activated carbon (GAC) is used in columns or beds for gas and vapour systems, and also for processing a number of liquids. The carbon must possess sufficient mechanical strength to withstand the abrasion incident to continued use. The development of high adsorptive power is accompanied by loss of mechanical strength and density [1,3]. Therefore the activation stage cannot be too short because the carbon would lack needed adsorptive power; conversely, it cannot be too long for then the carbon would be too soft and bulky. Few materials, in their natural state, can be converted into activated carbon with high density and low attrition. Less dense material, however, can be made dense and yield a hard carbon when mixed with a binder. The binder should be a substance which when carbonized does not liquefy or expand. However, some shrinkage is desirable. The tarry by-products from woods and certain grades of anthracite and bituminous coal have been found to be good binders. To be suitable as a binder, a substance should liquefy or soften during carbonization and swell sufficiently to give a porous structure. Suitable binders include sugars, tar, pitch, and lignin [4].

Powered activated carbon (PAC) used in membrane bioreactor (MBR) employed in the treatment of bleached pulp mill effluents was evaluated. The MBR was operated with hydraulic residence time of 9.5 h and PAC concentration of 10 g/L. The addition of PAC to the MBR reduced the average concentration of chemical oxygen demand (COD) the permeate from 215 mg/L (82% removal efficiency) to 135 mg/L (88% removal efficiency), producing an effluent that can be reused on bleaching stage. Moreover, the addition of PAC to the MBR resulted in the reduction in applied pressure and provided a more stable operation during the monitoring period. This occurrence was probably due to the increase of critical flux after the addition of PAC. The fouling mechanism was investigated and the results showed that controlling the concentration of soluble microbial products (SMP) and extracellular polymeric substance (EPS) by using PAC and keeping the operational flux below critical flux is of major importance for MBR operational sustainability [5].

Low cost adsorbents from agricultural waste like rice husk was developed with various activation methods and tested for the removal of aqueous contaminants. Adsorption of a basic dye, malachite green (MG), from aqueous solution onto nitric acid treated (NRH), and peroxide treated rice husk (PRH) have been investigated. Various experiments were studied using batch adsorption technique under different conditions of pH, adsorbent dosage, initial dye concentration, and temperature. The adsorption capacities of MG by the NRH and PRH were essentially due to electrostatic forces. The NRH and PRH adsorbents had a relatively large adsorption capacity (18.1 and 26.6 mg/g). The adsorbent PRH had a higher surface charge at alkaline pH and enhanced removal of MG was obtained under alkaline conditions. Typical adsorption kinetics indicated the pseudo second-order kinetics behaviour. The adsorption isotherms obey Langmuir isotherm model.

Abstract

High chlorine dosages are used in some drinking water plants to overcome the deficiencies in the treatment to at least ensure a supply of microbiologically safe water to the population. This fact and the increment of natural organic matter (NOM) in the aquatic resources due to rainfall increases and anthropogenic activities are becoming a critical concern, due to the formation of chlorination by-products such as trihalomethanes (THM), which are carcinogenic substances. Egypt drinking water system using new treatments is essential to meet the quality guidelines. Trihalomethanes are carcinogenic by-products of disinfection that are present in drinking water. In the present research, adsorption was employed for the removal of THMs found in water supply systems. The effects of pH, contact time, adsorbents and adsorbate concentration on the adsorption system were investigated. The Langmuir and Freundlich adsorption isotherm models were used to analyse the resulting adsorption data. The kinetics of THM removal was found to follow the pseudo-second-order model rather than the Langmuir–Hinshelwood pseudo-first-order model.

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It was observed that the rate of adsorption improves with increasing temperature and the process is endothermic nature. The negative value of the change in Gibbs free energy (ΔG°) indicates that the adsorption of MG on PRH and NRH is feasible and spontaneous [6].

Currently, problems in drinking water treatment extend beyond the scope of taste and odour control. Much attention is being paid to the regulation and control of numerous organic and inorganic compounds in water. Concerns about the presence of Synthetic Organic Compounds (SOC) arose in 1960s. Beginning in the 1970s it was recognized that disinfection of water with chlorine gas or chlorine-containing compounds led to the generation of organic compounds, collectively termed Disinfection By-Products (DBPs), which were suspected of having adverse effects on health [1,2]. In this regard, Natural Organic Matter (NOM) constitutes the key group of organics acting as precursors for DBP formation. It was also shown that pre-treatment of water with ozone led to inorganic hazardous by-products such as bromates. For many decades, adsorption onto activated carbon has appeared to be one of the most reliable methods of NOM and DBP control. This type of treatment is usually conducted in GAC filters. These are usually placed after sand filtration and before disinfection, but, depending on the characteristics of the water and the object of the treatment, GAC filters may also be positioned at other locations within the treatment train [1,2].

Agricultural and food industries create various waste matters that need to be utilized and convert in value added product. Carbonaceous materials such as coconut shell, palm shell, saw dust and tropical wood are some of the most common agricultural wastes shells used to produce activated carbon. In the present study the activated carbon was prepared from two carbonaceous agriculture wastes by chemical activation using ortho-phosphoric acid (H₃PO₄) at 800 ± 5°C. Agricultural solid waste is one of the rich sources for low cost adsorbents besides industrial by-products or natural material. Due to abundant availability, agricultural waste such as orange peel poses little economic value and moreover, creates serious disposal problems. Many agricultural by-products that are available at little or no cost for example chicken feathers, cassava waste, rice husks have been reported to be capable of removing organic compounds in water. Concerns about the presence of Synthetic Organic Compounds (SOC) arose in 1960s. Beginning in the 1970s it was recognized that disinfection of water with chlorine gas or chlorine-containing compounds led to the generation of organic compounds, collectively termed Disinfection By-Products (DBPs), which were suspected of having adverse effects on health [1,2]. In this regard, Natural Organic Matter (NOM) constitutes the key group of organics acting as precursors for DBP formation. It was also shown that pre-treatment of water with ozone led to inorganic hazardous by-products such as bromates. For many decades, adsorption onto activated carbon has appeared to be one of the most reliable methods of NOM and DBP control. This type of treatment is usually conducted in GAC filters. These are usually placed after sand filtration and before disinfection, but, depending on the characteristics of the water and the object of the treatment, GAC filters may also be positioned at other locations within the treatment train [1,2].

Material and Methods

The activated carbons (commercial and synthetic) used in this study for water purification were four types:

1- The Commercial Activated Carbon (CAC): Provided by Al-Gomhoria Chemical Company; (Alexandria, Egypt).

2- Woody Activated Carbon (WAC): Wood was used as precursor for the preparation of activated carbon. The wood was cut into pieces of 2 to 3 cm in size, dried in sunlight for 2 days. The dried material was then soaked in solution of H₃PO₄ for one hour and kept at room temperature for 24 hours. Thereafter, the wood material was separated, air dried at room temperature and carbonized in muffle furnace at 320°C for 90 min. The carbon was ground to powder then the activated carbon was washed with plenty of distilled water to remove residual acid, dried, sieved into 300 to 850 μm (20-50 ASTM mesh) sizes and stored in a tight lid container for further adsorption studies [8].

3- Rice Straw Activated Carbon (RAC): Rice Straw, after collection dried at 105 ± 5°C for 6 hours and cooled to ambient temperature in desiccators and was cut into pieces of 2 to 3 cm in size, then soaked in solution of H₃PO₄ for one hour and kept at room temperature for 24 hour. The straw material was separated; air dried at room temperature and was carbonized in muffle furnace at 320°C for 90 min. The carbon was ground to powder then the activated carbon. The prepared AC from rice husk was magnified using electron microscope as shown in Figure 1 [9].

4- Activated Carbon activated by H₂O₂ (CCH): Rice Straw, after collection dried at 105 ± 5°C for 6 hours and cooled to ambient temperature in desiccators and was cut into pieces of 2 to 3 cm in size, then soaked in solution of H₂O₂ for one hour and kept at room temperature for 24 hour. The straw material was separated; air dried at room temperature and was carbonized in muffle furnace at 320°C for 90 min. The carbon was ground to powder then the activated carbon [8]. THM and TOC were determined according to APHA using GC-ECD, Agilent 5890 and TOC analyser, respectively (APHA, 2012) [8].

Results and Discussion

Total Organic Carbon (TOC)

Results presented in Tables 1-3 and Figures 2-6 showed that, as the AC dose in mg increased, the removal of TOC increased; at 10 mg dose of AC, the order of removal efficiency of TOC was

| Parameter | AC Dose(mg/L) | Commercial carbon (CAC) | Synthesized AC |
|-----------|--------------|-------------------------|---------------|
| TOC (mg/L) | Commercial | CCH | RAC | WAC |
| Removal by different type of AC | | | | |
| Average 15.80 | 2.93 | 3.65 | 3.51 | 3.80 |
| Minimum 2.00 | 1.20 | 2.20 | 1.40 | 2.40 |
| Maximum 26.00 | 5.70 | 5.90 | 5.80 | 5.20 |

Table 1: Removal of TOC using different low cost adsorbant (AC).

| Parameter | AC Dose(mg/L) | Commercial carbon (CAC) | Synthesized AC |
|-----------|--------------|-------------------------|---------------|
| TOC % by different type of AC | | | |
| Average 15.8 | 53.55 | 39.84 | 42.08 | 35.91 |
| Minimum 6.00 | 24.30 | 24.30 | 9.70 | 14.40 |
| Maximum 26.00 | 78.30 | 60.90 | 71.60 | 58.80 |

Table 2: Removal percentage of (TOC) using different low cost adsorbant (AC).
CAC > RAC > CCH > WAC, respectively. Among the four experimental carbons (CCH, CAC, RAC and WAC) the data from Table 3 indicates that in terms of adsorption of TOC organic compounds in the CAC tests, showed that, the highest performance (78.3%) followed by RAC (76.1%), CCH (60.9%), and WAC (58.8%). Activated carbon activated with hydrogen peroxide (CCH) had the highest 1/n value (0.9905) followed by WAC (0.9634), and commercial activated carbon without activation CAC (0.955) and RAC (0.9503). These values of 1/n corresponding to the respective carbons indicate that CCH has the highest rate of adsorption of the solute and RAC the least. These values of 1/n for CCH and RAC also suggest that within the chemical activation, carbon dioxide-activation improves 1/n compared to the other types of carbons. Furthermore, CCH with 1/n=1.0 (0.9905) indicates that the change observed in adsorbed solute (organic contaminants) concentration is greater than that occurred in the sorbent concentration. It is evident that, the commercial CAC were exceeded in removal of TOC composite organic compounds than that in case of prepared AC (CCH, RAC and WAC) (Figures 2 a-e) [10].

The removal of organic precursors of disinfection by-products (DBPs), i.e. natural organic matter (NOM), prior to disinfection is considered as the most effective approach to minimize the formation of DBPs. Trihalomethanes (THMs) as the main group of DBPs are categorized and considered to have the potentiality of increasing the rate of liver, kidney and central nervous system adverse effects [11]. NOM is primarily composed of humic substances, such as humic acids (HA) and fulvic acids (FA) that result from decomposition of terrestrial and aquatic biomass, but it can contain a range of organic species and microorganisms and their discharges [10]. The present results are in agreement with the finding of Carrière et al. [12]; who used powdered activated carbon in conjunction with polyaluminum chloride in TOC removal and proved that with adding only 11 mg/l of powdered activated carbon, TOC removal efficiency was improved and taste and odour agents were decreased (Figure 3).

Among the four experimental carbons, the commercial carbon CAC exceeded RAC and WAC in their adsorption performance. The physically activated carbon (steam and carbon dioxide) were superior in their adsorption to chemically activated, this could be due to the inhibition of small organics from penetrating into the micro-pores due to the presence of greater number of polar compounds on the mesopore and macropore surface of the acid activated carbons. These
data infer that the method of activation and precursors selected for the preparation of activated carbons do affect the adsorption of organic compounds and hence are factors to be considered in any adsorption process [13,14]. Also, in agreement with the present results, Abdulla [2] reported that AC removed TOC by 78%.

Pre-chlorination has potential to increase DBP levels during water treatment process. Many treatments really on pre-chlorination to solve operational problems, including turbidity, algae growth control, inorganic oxidation and microbial inactivation as well as taste and odour [1,2]. So, in the present study, AC was used to show the effect of treatment on THM without the necessity to pre-chlorination. Five characteristics of carbon are important in the adsorption of organic molecules from solution. Yenisoy-Karakas et al. [14] reviewed several articles in the literature and suggested that these factors are (1) particle size, (2) surface area, (3) chemisorbed oxygen, (4) hardness and uniformity, and (5) pore structure. These adsorptive characteristics of carbon depend upon the sourcematerial of the carbon and the activation process [14].

Although adding powdered activated carbon enhanced organic matter removal, it caused decreasing coagulant consumption. For the application of poly aluminium chloride, by increasing the amount of powdered activated carbon, TOC was decreased and the least rate of TOC achieved at 100 mg/l powdered activated carbon [14]. Activated carbon adsorption has been widely applied in removing organic matters from wastewater as it has a strong affinity for attaching organic substances even at low concentration. Having large surface area for adsorption, granular activated carbon (GAC) is one of the best adsorbents for removing various organic contaminants [2,14]. The GAC adsorption systems are therefore considered to apply for producing the effluent of high quality from sewage treatment plant which can be reused for various purposes. However, even though it has high adsorption capacity, GAC can only maintain its adsorption for a short time after its available adsorption site becomes exhausted with adsorbed organic pollutants [15].

THM

Results presented in Tables 4-6 and Figures 7-11 showed that, as the AC dose in mg increases the THM removal increased; the order of removal of THM is CAC>RAC>WAC>CCH respectively. The data presented in Table 6 the adsorption of THM organic compounds in the CAC tests, showed that the highest performance (45 %) followed

| Parameter | AC Dose(mg/L) | Commercial Carbon (CAC) | Synthesized AC |
|-----------|---------------|-------------------------|----------------|
|           |               | CCH | RAC | WAC |
| 0         | 69.0          | 54.9 | 65.7 | 64.2 |
| 2         | 57.8          | 50.8 | 57.8 | 59.7 |
| 6         | 51.0          | 50.0 | 51.1 | 57.5 |
| 10        | 44.3          | 48.6 | 44.3 | 54.8 |
| 14        | 38.6          | 45.5 | 38.6 | 53.0 |
| 18        | 35.1          | 42.8 | 35.1 | 51.7 |
| 20        | 31.5          | 38.3 | 31.5 | 47.6 |
| 22        | 31.4          | 37.3 | 31.4 | 41.9 |
| 24        | 31.2          | 37.0 | 31.2 | 42.1 |
| 26        | 27.1          | 37.1 | 27.1 | 39.6 |
| Average   | 14.36         | 40.8 | 43.6 | 40.48 | 50.66 |
| Minimum   | 2.00          | 27.10 | 37.00 | 27.10 | 39.60 |
| Maximum   | 26.00         | 57.80 | 50.80 | 57.80 | 59.70 |

Table 4: Removal of THM using different low cost adsorbent (AC).

| Parameter | AC Dose(mg/L) | Commercial Carbon (CAC) | Synthesized AC |
|-----------|---------------|-------------------------|----------------|
|           |               | CCH | RAC | WAC |
| 2         | 16.2          | 7.5  | 12.0 | 7.0  |
| 6         | 26.1          | 8.9  | 22.2 | 10.4 |
| 10        | 35.8          | 11.5 | 32.6 | 14.6 |
| 14        | 44.1          | 17.1 | 41.2 | 17.4 |
| 16        | 49.1          | 22.0 | 46.6 | 19.5 |
| 18        | 54.3          | 30.2 | 52.1 | 25.9 |
| 20        | 54.3          | 31.5 | 52.1 | 29.6 |
| 22        | 54.5          | 32.1 | 52.2 | 34.7 |
| 24        | 54.8          | 32.6 | 52.5 | 34.4 |
| 26        | 60.7          | 32.4 | 58.8 | 38.3 |

Table 5: Removal percentage of THM using different low cost adsorbent (AC).

| Parameter | AC Dose(mg/L) | Commercial Carbon (CAC) | Synthesized AC |
|-----------|---------------|-------------------------|----------------|
|           |               | CCH | RAC | WAC |
| 60.7      | 16.2          | 0.2268 | 0.7688 |
| 22.6      | 7.5           | 0.2688 | 0.8968 |
| 58.8      | 12            | 0.2265 | 0.7889 |
| 23.6      | 7             | 0.0753 | 0.9703 |

Table 6: Freundlich coefficient for the THM adsorption isotherms.
by RAC (42.2%), WAC (23.2%) and CCH (22.6%). Woody activated carbon (WAC) had the highest 1/n value (0.9703) followed by CCH (0.8968), RAC (0.7689) and CAC (0.7688). These values of 1/n corresponding to the respective carbons indicate that WAC has the highest rate of adsorption of the solute while RAC and CAC have the lowest rate. These values of 1/n for WAC and CCH also suggest that within the chemical activation carbon improves 1/n compared to the other types of carbons. Furthermore, WAC with 1/n≈1.0 (0.0.9703) indicated that the change in adsorbed solute (organic contaminants) concentration is greater than the change in the solute concentration [1]. Also, this is in agreement with Abdullah [2] who reported that AC removed 84% of THM. Moreover, Uyat et al. [16] studied the removing DBPs precursors by enhanced coagulation and powdered activated carbon (PAC) adsorption and proved that supplementing enhanced coagulation with PAC adsorption increased the removal of TOC to 76% and PAC adsorption removed mostly low molecular weight and unchanged natural organic matter (NOM) substances as indicated in Figures 7-11 [12,16].

Factors affecting AC adsorption capacity

Effect of solution pH: The pH of the solution is one of the major factors influencing the adsorption capacity of the compounds that can be ionized. In order to study the effect of the pH, several experiments were carried out with carbon CCH at a temperature of 25°C using different initial solution pH of values (2.0, 7 and 9). The pH of the solutions are maintained by means of ionic buffer solutions composed with NH₄OH, HCl, KH₂PO₄, Na₂HPO₄, NaH₂PO₄ and Citric acid. The effect of pH on the isotherms CCH for TOC is presented in Figure 12. It indicated that at very low pH (pH=2), the amount of TOC adsorbed is lower than those obtained with other pH due to the competition with H⁺ on carboxyl sites [4,7]. The effects of pH on the elimination efficiency of TOC using powdered activated carbon showed that the optimum pH range between 5.5 and 6 [2,17].

As a result, at pH 7, the rate of TOC reduction was 76%. Taking into consideration the closeness to the natural pH of water, this showed the high efficiency of powdered activated carbon in the natural pH of water. It has also shown that a considerable reduction in total organic carbon concentration is obtained in pH ranges of 5.5 to 7. This is due to the fact that TOC solubility decreased and organic matter adsorption increased in this ambient pH. The increase of pH favoured the ionization of organic matter and decreasing the pH could redound to neutralize the negative charge on the surface of powdered activated carbon using hydrogen ions as indicated in Figure 4 [2,17].

Effect of solution temperature: It is clear from the present results that the TOC adsorption decreases with increasing temperature as shown in Figure 13. This well-known effect of temperature is expected for physical adsorption that is exothermic in nature in most cases (USEPA and Hoang [11,15]. Due to this temperature dependence of adsorption capacity, the adsorption isotherms have been determined in a thermostatic bath at 25°C. Ramaraju et al. showed that, the rate of adsorption improves with increasing temperature and the process is endothermic nature [6].

Conclusion

Drinking water treatment using activated carbon (AC) is one option for treatment of drinking water problems. AC is an effective method for treating certain organic compounds, unpleasant tastes and odours, and chlorine, as well as its effective for metals, microbial contaminants, algae and other inorganic contaminants. Adsorption capacity of activated carbon had been found to be dependent on the adsorbent dosage but other variables such as adsorbate concentration, pH variation, activating reagents, temperature have their own effect on adsorption capacity. Hence this prompts the use of different model to carry out analysis of the adsorption capacity (Freundlich isotherm). Adsorption process can be well understood through isotherms resulting between adsorbate concentration in liquid and amount of adsorbate adsorbed by unit mass of adsorbent at a constant temperature. The present results obtained by the adsorption experiment were analysed by Freundlich, isotherms. TOC and THM could be effectively removed by AC adsorption from drinking water. The fitting result indicated that the adsorption of THM on RAC represents the linear consistency. External mass from TOC from tap water, contact time and mixing
were confirmed as controlling step in the sorption process. Under the prevailing conditions, the maximum RAC removal efficiency was found to be 58.8% for 65.7 µg/l THM with contact of 0.026 g of RAC.

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