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Effect of $KMnO_4$ treatment of granular activated carbon on the removal of natural organic matter

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ABSTRACT

In drinking water the amount of natural organic matter (NOM), measured as dissolved organic carbon (DOC), should be maintained at a low enough concentration to increase the stability of chlorine and minimise the disinfection by-products. This work focuses on the methods to enhance the performance of granular activated carbon (GAC) by modifying the surface of GAC by pre-treatment with potassium permanganate ($KMnO_4$) at two loading (0.1 and 1% w/w $KMnO_4$/GAC). The batch DOC adsorption experimental results at two solid to liquid ratios (5 g GAC/L; 0.5 g GAC/L) indicated that $KMnO_4$ treatment did neither improve NOM removal nor change the NOM composition in the treated water. There was also no evidence in change of GAC pore structure due to $KMnO_4$ pre-treatment. Therefore, there is no significant benefit of treating GAC with $KMnO_4$ for physical removal of NOM under the tested conditions.

Keywords: Natural organic matter; Granular activated carbon; Dissolved organic carbon, Potassium permanganate

1. Introduction

Natural organic matter (NOM) is a key parameter in all surface water and groundwater sources. The NOM content of water is measured as dissolved organic carbon (DOC). The presence of NOM negatively impacts the treatment processes and affects water quality by causing colour, taste, and odour problems, promoting microbial regrowth [1,2] and causing corrosion in distribution systems [3,4]. The removal of NOM has become increasingly important due to its potential for formation of carcinogenic disinfection by-products (DBPs) resulting from the reaction of NOM with disinfectants [5,6].

NOM levels in natural water sources have been increasing in the past few decades [5,7]. This resulted in increased disinfectant dose and coagulant dose requirement and has negative impacts on water quality and operation of treatment plants [8]. As with the sustained increase in NOM in water sources, the efficiency of current water treatment processes (especially the coagulation/flocculation processes implemented with the primary aim of turbidity removal) removes only about 10%–30% NOM. Further, the degree of NOM removal is dependent on the type of NOM, coagulant dose, and pH – usually a lower pH (~5) and higher coagulant doses (~30–60 mg $FeCl_3$/L or higher alum doses) are needed to achieve >50% removal [9]. Thus, to achieve a higher NOM removal, coagulant dose has to be increased and pH lowered. This results in the higher salinity, higher chemical requirement, and a higher sludge disposal cost. At times, especially when algal toxins are an issue or when endocrine disrupting compounds are to be removed, additional treatments are needed [10]. Therefore, optimisation of the existing water treatment processes or addition of a new one is needed to

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sufficiently reduce NOM concentration and keep the water safe for public consumption.

The treatment of water with activated carbon (AC) is an effective method for removing DOC, colour, taste, odour causing compounds, reducing bacterial regrowth potential, and removing precursors of DBPs [11,12]. High porosity with a broad range of pore sizes and substantial surface area makes AC an effective adsorbent [13,14]. Thus, the organic substances and contaminants can adhere to the large surface area of AC. The AC is available in two forms as powdered activated carbon (PAC) and granular activated carbon (GAC) depending on its particle size.

The GAC has some advantages such as it can be used in continuous flow column systems, and it can be regenerated [13]. GAC has been proven to be an effective adsorbent for removing NOM from water [12,15], but the physical adsorption of NOM lasts only for a short service time ~2 months for many waters, but it depends on the water quality and empty bed contact time (EBCT) employed during operation. Inferior water quality and lower EBCT will quickly saturate the surface and thus result in shorter than 2 months service time [10]. The improvement of the adsorption capacity of GAC by modifying its surface could be beneficial.

Potassium permanganate ($KMnO_4$) is often used as an oxidant in water treatment process to oxidise compounds in water directly [16,17]. The $KMnO_4$ alone can react with organic matter [18], can oxidise iron and, manganese [19], control taste and odour causing compounds [17], and can accelerate the degradation rate of organic chemicals such as tetrachloroethylene and trichloroethylene [20]. Herrera-Melián et al. [21] reported that the oxidative pre-treatment of water with $KMnO_4$ reduced the initial total organic carbon of water by 90% in the treated chemical waste samples [25]. At the same time, $KMnO_4$ is capable of reducing the DBPs precursors [5,22]. In addition, Chen and Yeh [23] and Wang et al. [16] showed that pre-oxidation with $KMnO_4$ promote the removal of algal cells by aggregation from water.

Moreover, in acidic–neutral and alkaline pH conditions, $KMnO_4$ can form hydrous manganese dioxide (MnO_2) as follows:

In mildly acidic pH (<7):

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_{2(s)} + 2H_2O + 1.70\ V$$

In alkaline pH (>7):

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_{2(s)} + 4OH^- + 0.59\ V$$

Further, $KMnO_4$ degrades organic matters and simultaneously reduces itself to hydrous MnO_2 [24]. The surface charge of the MnO_2 is largely determined by the pH of the solution. The charge becomes more negative as pH is increased (5–11) [25]. This hydrous MnO_2 itself (without treatment with AC) has the ability to adsorb heavy metals, humic acids (HAs), and anions [24,25]. Hence, the in situ formation of MnO_2 also could play an important role on enhancing the DOC removal from raw water. Manganese dioxide surface also works as a catalyst for absorption and consequent oxidation of Mn^{2+} which is often present in the source waters.

Depending on the nature of surface functional groups present, the surface of the AC can be acidic, basic, or neutral. Since the $KMnO_4$ is a strong oxidant it can modify the chemical characteristics, mainly functional groups, of the AC. With those modifications, organic compounds in water can be removed due to the complex formation between NOM species and functional groups on the surface of GAC [26]. Thus, adsorption properties of the AC can be modified by using $KMnO_4$ [18,27,28]. Additionally, the adsorbed $KMnO_4$ on the AC surface could oxidise the adsorbed NOM. The MnO_2 produced from reaction with NOM or other reducing agents and is supported on AC have shown effective adsorption characteristics due to its porous structure and high surface area [29].

Some previous studies used $KMnO_4$ to modify AC for the removal of certain pollutants and NOM in water. Adsorption experiments conducted by Shi et al. [28] with "$KMnO_4$ modified PAC" show that it was an effective adsorbent. They have shown that basic violet 14 dye removal has been improved from 27.9% to 99.5%. The studies conducted by Daifullah et al. [26] concluded that the $KMnO_4$-modified AC derived from steam pyrolysis of rice straw was an effective scavenger for fluoride ions in water. Wang et al. [30] showed that $KMnO_4$-modified PAC via microwave heating was an effective adsorbent on removing lead (Pb(II)) from water. These investigations suggest the synergism between AC and $KMnO_4$ could enhance the removal of contaminants (including NOM) from raw water.

Zhang et al. [18] investigated the effects of $KMnO_4$ treated PAC on the removal of NOM, i.e., $KMnO_4$ and PAC was allowed a reaction time of 1 h before addition of water containing synthetic water containing NOM of HA. They concluded that the chemical oxygen demand (COD_{Mn}) and UV_{254} reduced significantly, and $KMnO_4$ oxidation did not change the chemical and physical characteristics of the PAC surface. It is important to realise that the study measured the removal of COD_{Mn} (not NOM) by PAC after oxidising HA of higher molecular weight [31] with $KMnO_4$.

Numerous studies have focused on studying the oxidation of organic matters in water with $KMnO_4$ and the effect of $KMnO_4$ treatment of PAC on the removal of NOM. However, there is limited information on the interaction between the GAC and $KMnO_4$ on removing NOM from raw water. The objective of the present work is to assess the ability of the GAC modified with $KMnO_4$ on the removal of DOC from raw water. Special emphasis will be placed on investigating the surface, chemical and physical characteristics of GAC modified with $KMnO_4$.

2. Materials and methods

2.1. Raw water

The raw water used in this study was collected from Nepean water filtration plant, NSW, Australia. The water was collected before any treatment and used in this investigation. Water quality parameters are shown in Table 1.

2.2. Modification of GAC with $KMnO_4$

GAC with a particle size of 2.4–4.6 mm was used for all adsorption tests. The surface area, as determined from nitrogen adsorption and expressed on a dry weight basis, is 600–800 m^2/g for this product. It was made from peat bog that is kiln heated in N_2 or H_2O to carbonise all organics (C2764 Sigma-Aldrich activated charcoal [32]).

Table 1
Water quality parameters of Nepean raw water sample

Turbidity (NTU)	90
DOC (mg/L)	6.466
pH	7.4–7.7
Temperature (°C)	15–25

The surface of the GAC was modified by adding 0.1% and 1% of $KMnO_4$ by weight. Two GAC samples of 100 g were soaked in 1 L of MilliQ water containing 1 g (1%) or 0.1 g (0.1%) of $KMnO_4$ overnight until all $KMnO_4$ was absorbed to the GAC. The manganese (Mn) concentration of the remaining solution was measured using inductively coupled plasma optical emission spectrometry to ensure all Mn was absorbed to the solution. The concentration of Mn in the remaining solution treated with 1% $KMnO_4$ was 51 μg/L and treated with 0.1% was below the 5 μg/L. That indicates that >99.6% $KMnO_4$ was absorbed on the GAC.

2.3. Experimental design

Two different sets of experiments were conducted. The first set was conducted over 2-month period using clean 1 L glass bottles by adding solid (treated and untreated GAC) to liquid (Nepean raw water) (solid/liquid) 0.5 g/L ratio (0.5 g GAC/1L) and 0.1% of $KMnO_4$ (0.1% of GAC). Reactors were continuously mixed using a magnetic stirrer. Water samples (20 mL) were collected for measuring DOC at different intervals. This test was done both under sterile and natural conditions to understand the interferences caused by microbial activity. This was done because there is a possibility to grow microorganisms while experiment runs for a long period and when the GAC is used in water filtration plants this is unavoidable. Therefore, it is important to know the behaviour under natural conditions. Bottles, raw water samples, and GAC were autoclaved before the start of the experiment (for the experiment done under sterile conditions). The test was done under the room temperature 23°C.

Second sets of experiments were conducted in appropriately clean polyethylene terephthalate bottles kept in a shaker (150 rpm, room temperature 23°C). The test determined the adsorption at a high solid to liquid (s/l) ratio (1 g GAC/200 mL) and a high percentage of $KMnO_4$ (1% of GAC) treatment to test the relative effectiveness of GAC and $KMnO_4$ modification within relatively short duration (7 h). Water samples were collected at 1, 3, and 7 h and subjected to analysis. The raw water samples utilised for the two batch experiments had a neutral pH (pH = 7). Summary of the designed experimental sets has been given in Table 2.

2.4. Analytical methods

DOC was measured in all the samples using Shimadzu Total Organic Carbon Analyser with an experimental error for TOC of ±5%. For the DOC analysis, samples were filtered through pre-washed 0.45 μm mixed cellulose membrane filter paper.

Collected samples were filtered through 0.45 μm filter paper analysed using liquid chromatography – organic carbon detector (LC-OCD) for the characterisation of the NOM. The LC-OCD is a rapid sensitive method developed by DOC-Labor (Karlsruhe/Germany). This technique is based on size exclusion chromatography (SEC) where the organic compounds are separated according to their molecular size. The SEC is coupled with OCD, ultraviolet detector, and organic nitrogen detector [33]. The LC-OCD chromatogram is composed of five different fractions of NOM which elute from the SEC column. They are eluted in the following sequence with decreasing molecular weight: biopolymers (including extracellular polymeric substances, i.e., proteins and polysaccharides), humic substances (HS), building blocks (break down products of HS), low molecular weight (LMW) acids, and LMW neutrals (i.e., LMW alcohols, aldehydes, and ketones) [33,34].

Table 2
Summary of the designed experiments

Experiment	Condition	Duration	GAC/ water (g/L)	$KMnO_4$/ GAC (%)
No. 1	Sterile	2 months	0.5	0.1
	Sterile		0.5	–
	Unsterile (natural)		0.5	0.1
	Unsterile (natural)		0.5	–
No. 2	Unsterile (natural)	7 d	5.0	1
			5.0	–

At the end of the batch test, the microstructure of the GAC (both treated and untreated) was inspected by the X-ray scanning electron microscope to identify physical and chemical characteristics changes of the surface.

Continuous volumetric nitrogen gas adsorption was used to measure the surface configuration and physical characteristics of pores of GAC. The nitrogen adsorption isotherms were analysed using a Micrometrics ASAP 2020 analyser. In this experiment, the total GAC surface area, pore volume, and pore size distribution characteristics were tested.

3. Result and discussion

3.1. Effect of $KMnO_4$ treatment on long-term adsorption of NOM

Under sterilised conditions, DOC removal was not significantly different in both $KMnO_4$ treated (0.1%) and untreated GAC at a dose of 0.5 g/L (Fig. 1(a)). $KMnO_4$ can oxidise a wide range of inorganic and organic substance [35]. If $KMnO_4$ maintained its form on the surface of GAC during batch tests, it should have oxidised the NOM. There was 0.075 mg $KMnO_4$/NOM with this ratio it would be expected that exist to oxidised organic groups such as –OH, double bond may be oxidised possibly to ketones and aldehydes, or acids. It is not expected that a significant amount of carbon dioxide. More polar compounds containing –COOH and –OH groups are less prone to surface adsorption on GAC [36]. These two produce the opposite effect on the overall removal of NOM.

In addition, $KMnO_4$ could be reduced to MnO_2 by carbon even before NOM containing water was fed by the following redox reactions during the treatment of AC (represented as C).

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$$

$$2C + 4OH^- \rightarrow CO_2 \text{ (or CO)} + 2H_2O + 4e^-$$

If MnO_2 layer is formed on the surface of AC, it should have also provided an additional adsorbing surface. This should enhance the removal of NOM. However, the removal has not been different between $KMnO_4$ treated and untreated surface (Fig. 1(a)). There could be three explanations: (1) the enhancement on removal (by MnO_2 layer and conversion to CO_2) would have been overwhelmed by the conversion of organic matter to polar compounds; (2) the organic matter is not converted by the $KMnO_4$ because all $KMnO_4$ has been reduced during treatment; and (3) MnO_2 layer is not sufficient enough to enhance the organic matter adsorption.

At the used $KMnO_4$ and NOM ratio it is unlikely that has oxidised the organic matter to more polar compounds and CO_2, then allowing microbes to be present can enhance the organic matter removal in $KMnO_4$ treated case. Aditionally, in real water treatment plants, water always contains microbes and GAC, whether treated with $KMnO_4$ or not, will be colonised by microbes. Results under unsterilised (natural) conditions show that $KMnO_4$ treatment did not have any significant effect on the removal of NOM although microbes have significantly reduced the DOC compared with sterilised condition (Fig. 1(b)). These results, therefore, point out that there is little oxidation of NOM by $KMnO_4$. If any oxidation of NOM to be pronounced it would happen within the first few hours and possibly $KMnO_4$ (0.1%) is not sufficient to enhance the $KMnO_4$ oxidation. Therefore, the next set of experiments was conducted as a short term with a higher percentage (1%) of $KMnO_4$ treatment.

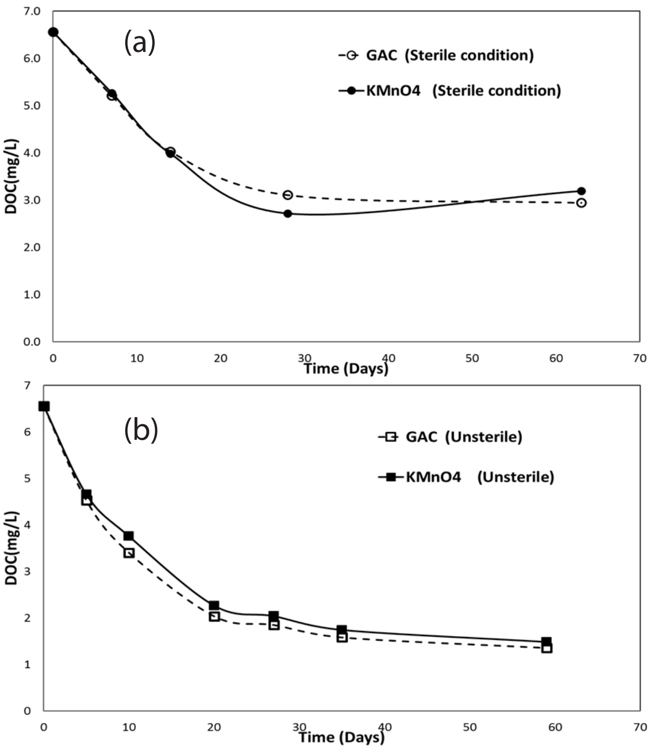

Fig. 1. (a) The DOC removal during the long-term experiment under sterile conditions 5 g GAC/L and 0.1% $KMnO_4$, in Nepean storage water. (b) The DOC removal during the long-term experiment under unsterile conditions.

3.2. Short-term behaviour under higher (1% of GAC) percentage of $KMnO_4$

Under unsterilised conditions, the treatment of GAC with a higher amount of $KMnO_4$ (1%) did not significantly improve the short-term DOC removal compared with untreated GAC (Fig. 2).

Much faster adsorption in 5 g GAC/L experiments can be explained by adsorption close to the external surface. Further, for the second experiment water was mixed using shaker (with 150 rpm). Mixing with magnetic stirrer which was used for the first experiment was much slower than the shaker.

3.3. Change in NOM composition

The effect of $KMnO_4$ on change of NOM composition was analysed using LC-OCD. Reduction of biopolymers, HS, building blocks and LMW acids was monitored. Fig. 3 (GAC) and Fig. 4 ($KMnO_4$ treated GAC) show response signals from the organic substance. It shows a very similar reduction in both cases. The least difference in between NOM characteristics by $KMnO_4$ treatment (Figs. 3 and 4) or removal of DOC (Fig. 2) shows that the oxidation effect or the difference in removal capability is minimal.

3.4. The surface characteristics of GAC

As shown in Table 3, the surface area and the pore characteristics were almost same in the GAC and $KMnO_4$ treated GAC.

These results are contradictory to the conclusion drawn on COD_{Mn} removal when $KMnO_4$ (up to 2 mg/L) was dosed into various PAC concentrations (0–30 mg/L) followed by (after 1 h) HA addition [18]. There are many reasons why this conclusion does not apply to our results: (1) In their experiments, the percentage of $KMnO_4$ on PAC ranged from 1.7% to 20% and the time allowed to coat the PAC was 1 h; whereas in our experiment we coated the surface for 1 d and applied a lower dose (0.1%–1%); (2) The molecular weight distribution of HA [31] is very much different from that of Nepean water used in this study (Fig. 2). The HA has a molecular weight distribution between 2 and 10 kDa; whereas Nepean had the average

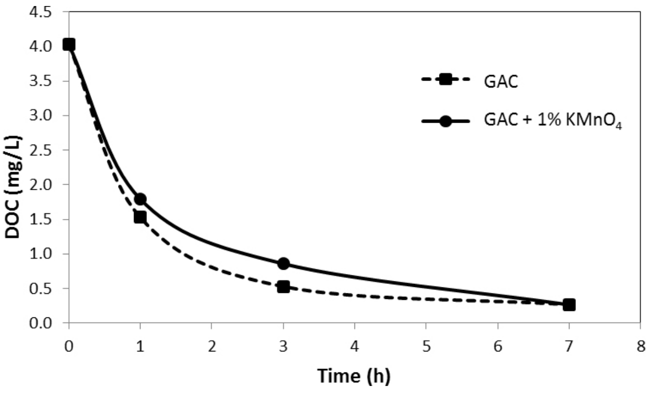

Fig. 2. The DOC removal profile during the first experiment (solid:liquid ratio = 5 g GAC/L of water).

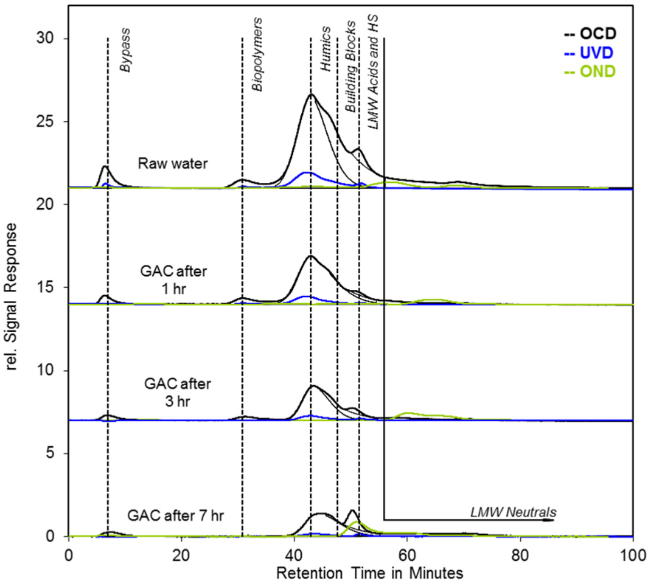

Fig. 3. LC-OCD chromatogram of samples treated with GAC (second set of experiment 5 g/L) with responses for organic carbon detection (OCD), UV-detection at 254 nm (UVD) and organic nitrogen detection (OND).

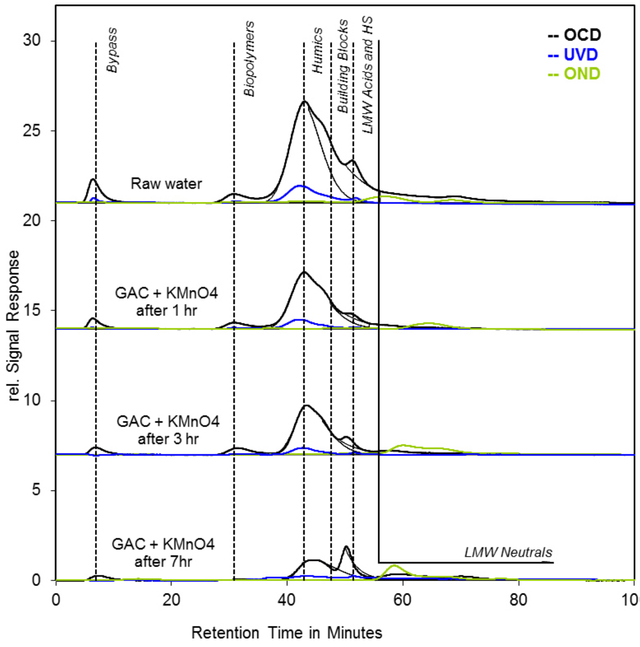

Fig. 4. LC-OCD chromatogram of samples treated with 1% $KMnO_4$ treated GAC (second set of experiment 5 g/L) with responses for organic carbon detection (OCD), UV-detection at 254 nm (UVD) and organic nitrogen detection (OND).

Table 3
The surface area and the pore volume analysis results of GAC and $KMnO_4$ treated GAC

Parameter	GAC[a]	1% $KMnO_4$ + GAC[a]
BET surface area (m^2/g)	691.6	701.4
Single point adsorption total pore volume of pores <4,370 Å diameter at P/P_o = 0.995 (cm^3/g)	0.56	0.54

[a] Samples taken from the first set of experiment.

molecular weight of 0.621 kDa. (3) It could also be noted, in [18], that it is adsorption behaviour was almost same for many PAC-containing samples irrespective of $KMnO_4$ addition. Only $KMnO_4$ containing samples showed a good correlation to added $KMnO_4$. This is supportive of our finding that $KMnO_4$ treatment of AC alone cannot alter the removal of NOM.

Collectively, these results and that of Zhang et al. [18] show that using $KMnO_4$ to coat or treat AC may not be an effective way to enhance the removal of NOM. It should also be noted that for PAC the experimental setup adopted by Zhang et al. [18] was correct, but for GAC the column has to be set up and hence it is not possible to continuously dose $KMnO_4$.

4. Conclusion

In the literature, it is usually claimed that an addition of $KMnO_4$ into PAC containing water for 1 h followed by HA addition can help enhancing the organic compounds removal from water. The experiments with $KMnO_4$ treated GAC and virgin GAC to adsorb NOM from surface water showed that physical removal by the GAC is least affected and NOM remaining after adsorption displayed similar characteristics. Both treated and untreated GAC reduced biopolymers, humics, building blocks, and LMW acids and HS in the same way. Therefore, $KMnO_4$ treatment of GAC did not improve DOC removal under tested conditions.

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