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Original Research

Effective Removal of Algae from Water by Diatomite Enhanced Graphene Oxide Flocculation

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Abstract

The ability of graphene oxide (GO) to function as a flocculant capable of mediating the removal of algae and associated extracellular organic matter (EOM) from water was assessed. GO was demonstrated to mediate the dose-dependent removal of algae via flocculation, with 40 mg/L GO being sufficient to remove 100% of chlorophyll-a (*chl-a*) and 99.1% of the UV_{254}. Diatomite addition failed to enhance GO flocculation efficiency or to reduce the necessary GO dosage, although it did result in a significantly reduced settling time, with denser floc and a corresponding increase in supernatant ratio. GO-mediated algae flocculation was primarily achieved via netting and bridging mechanisms, with diatomite addition leading to the conversion of a subset of two-dimensional GO nets into three-dimensional nets containing a diatomite core. Flocculation efficiency was comparable under acidic and neutral conditions but declined significantly with rising pH when pH≥7, with just 13.8% of *chl-a* being removed at pH of 10. At pH of 5, more than 60% of EOM and 57.6% to 90.1% of the disinfection byproduct formation potentials were reduced following the GO/diatomite flocculation process, and following flocculation the solution always had a final pH of 7.4±0.4 regardless of the starting pH.

Keywords: algae, graphene oxide, flocculation, diatomite, extracellular organic matter

Introduction

Climate change and related anthropogenic activities have led to the development of increasingly severe algal blooms [1-5]. These blooms can have both direct and metabolite-mediated indirect adverse impacts on water quality, resulting in its discoloration, poor taste or odor, and contamination with algal toxins [5, 6-9]. Such blooms also negatively affect the efficiency of water treatment processes [10-12], with algal removal early during the treatment process being essential in order to minimize this impact. Potassium permanganate [13], potassium ferrate (VI) [14], chlorine [15], ozone [16] and advance oxidation process [17] have all been employed as pre-oxidants that can facilitate the enhanced removal of algae from drinking water, but these compounds can damage algal cell membranes and result in the release of algae-derived organic matter into the water supply

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[18]. As such, there is a clear value in developing an algae control strategy capable of removing algae from solution without damaging their cellular structure.

Flocculation strategies can allow for the simple and efficient separation of water and solid or colloidal particles. The most commonly utilized flocculants include polyacrylamide and alum- and iron-based inorganic flocculants. Such compounds, however, are not compatible with a large-scale water purification approach as they would lead to the accumulation of noxious monomers or metal ions that have the potential to adversely impact human health and the environment [19]. The identification of an environmentally friendly flocculant that can purify water in a cost-effective manner is therefore essential.

Owing to their unique physicochemical properties, graphene-based materials have been the focus of substantial research interest in recent years [20]. Highly oxidized graphene oxide (GO) contains a range of oxygen-based hydroxyl, carboxyl, carbonyl, and epoxy functional groups on its surface [21], making it ideally suited to adsorbing organic pollutants and heavy metals [22]. Importantly, GO is easy to synthesize in a cost-effective and large-scale manner, and it is more biocompatible than are alternative graphene-based materials [23]. Yang et al. [24] first explore the potential use of GO as a flocculant capable of removing kaolin, hematite, humic acid, and cationic light yellow 7GL from water under a range of conditions. In this context, the authors determined that GO was capable of mediating solution decontamination via sweeping and charge neutralization effects. Other researchers have shown GO to be well-suited to reducing water turbidity and removing biological contaminants from solution, making it an ideal alum alternative for water treatment efforts [25]. Despite its promising flocculation efficiency, up to 1 hour following treatment is necessary for the settling of GO-mediated flocs to occur owing to their low density. Approaches that can aid in this process by reducing this setting time will therefore improve the utility of GO as a flocculant.

Diatomite is a highly porous compound with excellent chemical stability and hydrophilicity [26], and it has received approval as a food-grade material from the US Food and Drug Administration [27]. Previous studies have explored the successful use of diatomite for the safe and effective treatment of water and wastewater supplies owing as its ability to function as an adsorbent or a flocculant [28-31]. Given its high porosity and the fact that it is denser than water, diatomite has the potential to be ideally suited to serving as a GO flocculant aid. However, to date, there have not been sufficient studies assessing the ability of diatomite to enhance GO-mediated flocculation of algae during the process of water treatment. To that end, the present study was designed to explore the utility of diatomite as a means of improving GO-mediated algae removal via flocculation.

Experimental

Materials and Methods

Graphene Oxide Preparation and Characterization

A pressurize oxidation method was used to prepare GO, as previously outlined by Bao et al. [32]. Briefly, graphite (5.0 g), $KMnO_4$ (25.0 g), and concentrated sulphuric acid (250 mL) were mixed within a teflon reactor prior to being placed in a stainless steel autoclave that was heated to 100ºC for 1.5 h. The resultant sample was then diluted in a 500 mL volume of deionized water, to which 30% H_2O_2 was gradually added until the slurry changed to a golden yellow color. At this point, HCl and deionized water were used to wash the sample until a pH of 7 was achieved, yielding humid GO that was then dried at 100ºC. Once dried, GO was characterized and a 2 mg/mL GO stock solution was prepared using Milli-Q water.

Both SEM and FTIR were used to characterize GO preparations, with an SEI Model XL30-ESEM TEM being used to assess GO surface morphology, and a Nicolet 6700 FTIR spectrometer being used to record FTIR spectra across a 500-4000 cm^{-1} scanning wave range.

Algae and Extracellular Organic Matter (EOM) Suspension Preparation

For this study, *Microcystis aeruginos*a was used as a model algae as it is a dominant cyanobacteria in many eutrophic bodies of water in China [33]. Algae were obtained from the Wuhan Institute of Hydrobiology of Chinese Academy of Sciences, and were grown using BG11 media in a 25ºC incubator. Algae were harvested during the stationary phase of growth and were spun for 10 minutes at 10,000 rpm, after which 0.7 µm cellulose acetate membranes were used to filter supernatants, with the organic compounds in this filtrate serving as EOM for the purposes of this study. Cells that were isolated via centrifugation were washed thrice prior to use, and chlorophyll-a (chl-a) concentrations in these prepared algae were measured.

Jar-Test Experiments

Prior to flocculation tests, algal suspensions were prepared by adding tap water containing algae at a concentration of 500 µg/L *chl-a*. HCl or NaOH solutions (0.1 mol/L) were used to adjust the pH of this solution as appropriate. For jar tests, 250 mL jars and a six-place programmed paddle mixer (Model TA6, Wuhan Hengling Technology Co., Ltd.) were utilized at room temperature. A known GO stock solution was combined with algae-spiked water samples, after which flocculation was performed via 2 minutes of rapid mixing (350 rpm), 15 minutes of slow mixing (50 rpm), and a 30 min settling phase. For diatomite experiments, 200 mg/L of diatomite was added prior to GO addition.

Analytical Methods

Following the settling phase, supernatant samples were collected and used for analyses of pH, *chl-a*, DOC, and UV_{254}. A827 pH meter (Metrohm, Switzerland) was used for pH analyses, while a TOC-L CPH (Shimadzu, Japan) was used for DOC analyses, and a T6 spectrophotometer (Persee, China) was used to assess UV_{254}. For *chl-a* measurements, samples were passed through a 0.45 µm filter after which 10 mL of absolute ethanol was used for chlorophyll extraction. Optical density (OD) was then measured at 630, 647, 664, and 750 nm with a T6 spectrophotometer, and the following equation was used to calculate *chl-a* concentration:

$$C(\mu g/L)=\frac{\left(11.64\times\left(D_{664}-D_{750}\right)-2.16\times\left(D_{647}-D_{750}\right)+0.10\times\left(D_{630}-D_{750}\right)\right)\times 10}{V}$$

With C representing the concentration of *chl-a*, D_{630}, D_{647}, D_{664}, and D_{750} representing the OD at 630, 647, 664 and 750 nm, respectively, and V(L) representing the sample volume.

The DBPFPs of the samples the GO/diatomite flocculation process were analysed. Samples were adjusted to pH 7.0±0.2 with 0.1 M HCl or NaOH. Then, approximately 45 mg/L NaOCl was added and the resulting solutions were incubated in dark at 20ºC for 24 h. Sodium thiosulfate was used to neutralize residual chlorine. THMs, haloacetonitriles (HANs) and chloral hydrate (CH) were measured cording to our previous work [34]. Haloacetic Acids were measured with EPA Method 552.3 by gas chromatograph with an electron capture detector (Clarus 680, PerkinElmer, USA).

Results and Discussion

GO Characterization

SEM images revealed the GO preparations in this study to exhibit a partially transparent reticulate structure with some surface folding (Fig. 1). An XPS analysis demonstrated this GO to be primarily composed of carbon and oxygen, with a C/O atomic ratio of 62%/38%, slightly higher than that reported previously [32,35]. In the FTIR spectra, C-OH, epoxy C-O, C=C, and C=O groups were evident (Fig. 2), confirming the introduction of many oxygen-containing groups into GO [27, 36-37].

The Impact of GO Concentration on Algae Removal

The removal of algae from water across a range of GO doses (0 - 60 mg/L) was investigated. As can be seen from Fig. 3, the GO flocculation was able to successfully remove algae from solution, with *chl-a* and UV_{254} removal efficiencies from <3% to 100% and 99.1%, with GO concentrations increased from 0 to 40 mg/L. No additional efficiency was achieved at doses >40 mg/L, although floc density did increase further, with supernatant ratios following a 30 min settling period of 45%, 65%, and 71% at GO concentration of 10, 40, and 60 mg/L, respectively.

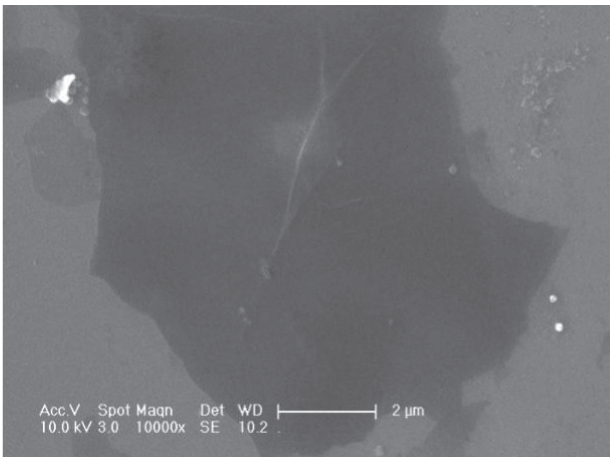

Fig. 1. SEM image of GO.

Despite its excellent flocculation efficiency in this context, the resultant floc was of fairly low density such that even slight agitation resulted in its resuspension. The use of a flocculant aid is thus necessary to improve the utility of GO as a flocculant.

The Impact of Diatomite on Flocculation

We found that despite its porous structure and ability to adsorb certain pollutants, diatomite was not able to directly mediate algae removal (Fig. 4), consistent with previous findings [38]. GO and GO/diatomite treatments

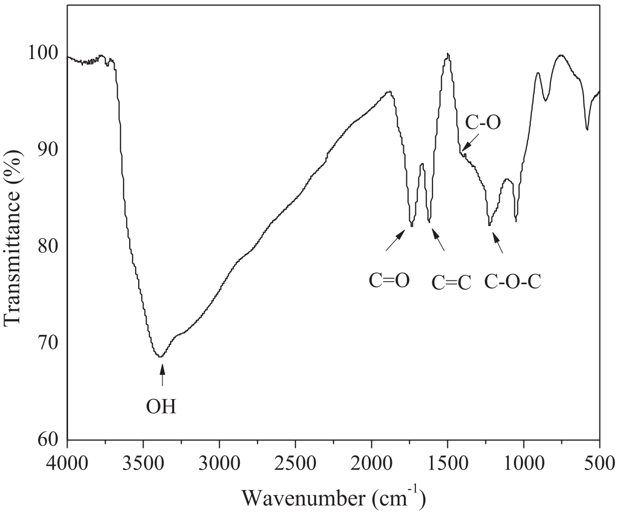

Fig. 2. FTIR spectra of GO.

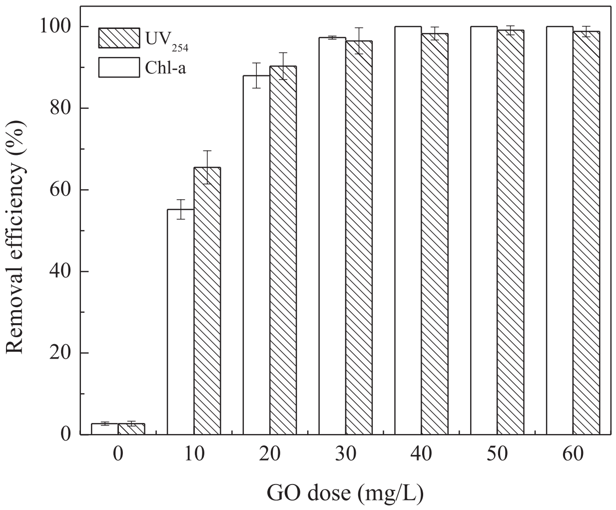

Fig. 3. Effect of GO concentration on algae removal (algae concentration: 2-5×10^6 cell/mL).

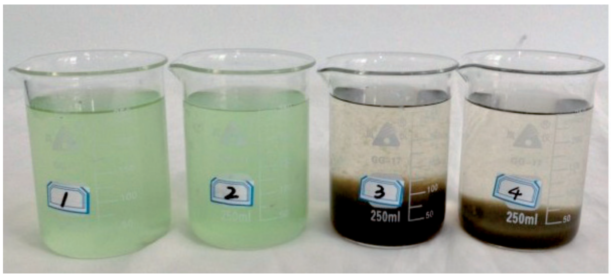

Fig. 4. Effect of different treatments on algae removal.

Table 1. Comparison of the algae removal efficiency by GO and GO/diatomite flocculation.

Concentration of *Chl-a*	Concentration of GO	Removal efficiency by GO	Removal efficiency by GO/diatomite
(μg/L)	(mg/L)	(%)	(%)
52	40	100	100
130	40	100	100
260	40	100	100
520	40	100	100
1040	40	100	100
1300	40	96.4±3.7	95.6±2.2
2600	40	47.2±5.1	49.1±4.0
2600	60	75.1±6.7	73.7±3.5
2600	80	94.3±1.9	96.1±4.2
2600	100	100	100

Diatomite: 200 mg/L

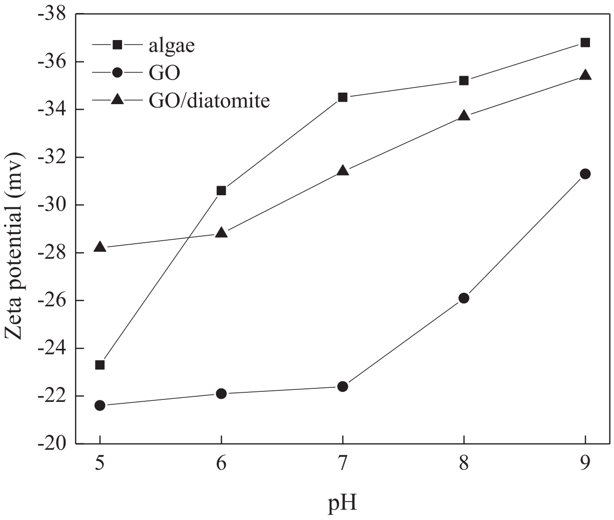

Fig. 5. Zeta potential-pH profiles of algae, GO, and GO/diatomite.

were both able to efficiently remove algae from solution via flocculation (Table 1). While the floc generated by the addition of GO alone was of low density, achieving a supernatant ratio of just 65% after a 30 min settling period, the addition of diatomite significantly improved this such that after 30 minutes a 90% supernatant ratio was achieved. Importantly, this 90% ratio was achieved after just 8 minutes, in which time GO treatment achieved a mere 35% value. In addition, supernatant turbidity values following a 30 min settling period in GO- and GO/diatomite-treated samples were 4.3 and 1.2 NTU, respectively.

The efficiency of algae removal by GO and GO/diatomite across a range of different algae concentrations is compiled in Table 1. There were no clear differences in removal efficiency values when comparing GO and GO/diatomite-treated samples, indicating that diatomite addition does not improve GO flocculation efficiency or allow for reductions in the effective GO dosage. Even so, the above results clearly demonstrate the ability of diatomite to increase floc density, thereby reducing settling times and increasing supernatant ratio values.

The Mechanistic Basis for GO-Mediated Flocculation

Yang et al. [24] utilized GO to mediate the flocculation and removal of contaminants with a range of surface charge values from water, revealing that this was achieved primarily via charge neutralization and sweeping flocculation mechanisms. To determine the mechanistic basis for flocculation in the present GO/algal system, zeta potential values for algae, GO, and GO/diatomite were measured (Fig. 5). This analysis revealed both algae and GO to have negative surface charges within tested experimental pH ranges, indicating that electrostatic neutralization is not a driver of GO and *M. aeruginosa* cell aggregation.

GO, GO/algae, GO/diatomite, and GO/diatomite/algae were assessed via SEM, revealing GO to be partially transparent with some surface folding and with a two-dimensional net- or bridge-like structure having captured the algal cells (Fig. 6). When diatomite was added these two-dimensional nets appeared to be partially converted into three-dimensional nets with a diatomite core, with *M. aeruginosa* cells similarly being captured by GO netting and bridging.

As GO contains many oxygen-containing groups, it can form strong hydrogen-bonding interactions with algal cell surface hydroxyl groups [39-40]. Hydroxyl groups within GO can also be considered to be Lewis bases, while the more electronegative oxygen groups can be considered as Lewis acids [41]. As such, Lewis acid-base interactions between GO and algae cells can occur. These interactions together with the abovementioned hydrogen bonding can overcome the charge repulsion, thereby enabling GO-mediated sweeping of algae cells.

These results clearly demonstrate that diatomite addition results in the formation of denser floc that can more readily undergo settling. Wu et al. [38] assessed how polymeric aluminum chloride (PAC) and/or diatomite addition was able to influence algae removal, revealing that diatomite addition either with or prior to PAC altered this removal efficiency. In the present study, the sequence of diatomite and GO addition did not impact the resultant algae removal (data not shown). In the previous study, PAC-mediated flocculation occurred primarily via electrostatic neutralization, with diatomite addition following PAC leading to a significant reduction in the zeta potential and more substantial higher charge repulsion between PAC and algae, thus reducing the efficiency of algae removal [38]. In contrast, electrostatic neutralization is not a significant contributor to GO-mediated algae removal, and as such, the sequence of diatomite addition did not have any apparent effect on algae removal efficiency.

The Impact of pH on Flocculation

The pH of a given solution can have a strong impact on the flocculation efficiency of any compounds added thereto. To that end, GO-mediated algal flocculation was assessed across a range of pH levels between 4 and 10. (from 4 to 10). At acidic and neutral pH values, no significant changes in algal flocculation efficiency were observed (Fig. 7). However, this efficiency declined rapidly as pH values rose when the pH was ≥7. At a pH of ≤7, almost all *chl-a* and >97.4% of the UV_{254} were removed following flocculation, whereas at a pH of 10 these values were reduced to 13.8% and 30.8%, respectively.

As discussed previously, both hydrogen-bonding and Lewis acid-base interactions allow for GO-mediated algae sweeping via overcoming charge repulsion. However, increasing pH values resulted in reductions in the zeta potential of algae and GO (Fig. 5), leading to charge repulsion. As the pH continues to rise it becomes more difficult to overcome such charge repulsion, resulting in significantly reduced removal efficiency. In addition, GO surface hydroxyl groups can react with hydroxyl radicals in alkaline solutions, leading to reductions in hydroxyl group availability for hydrogen bonding. Furthermore, in alkaline solutions GO can become deoxygenated into graphene at relatively low temperature [42-43], with these rates of deoxygenation rising with pH values. Graphene is a hydrophobic compound incapable of bridging or sweeping algal cells, thus leading to the observed marked reductions in flocculation efficiency with rising pH.

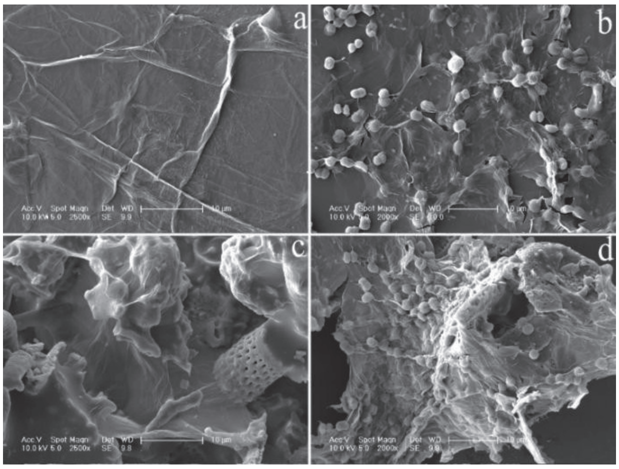

Fig. 6. SEM images of GO a), algae removal by GO flocculation b), GO/diatomite c) and algae removal by GO/diatomite flocculation d).

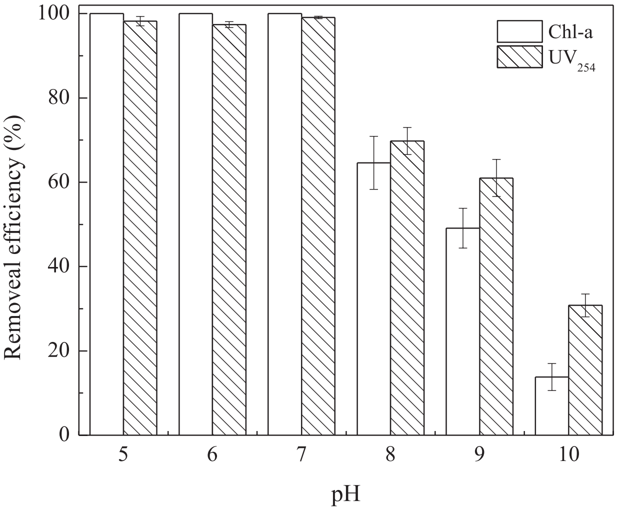

Fig. 7. The impact of pH on GO/diatomite flocculation-mediated algae removal.

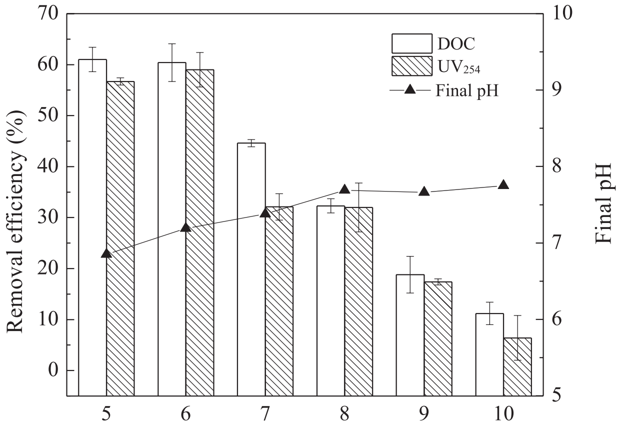

Fig. 8. The impact of pH on GO/diatomite flocculation-mediated EOM removal.

GO/Diatomite Flocculation Mediated EOM Removal

Algal cells are capable of excreting metabolites during both exponential and stationary phases of growth, leading to EOM accumulation that can drive carbonaceous or nitrogenous disinfection by-product formation during disinfection, and which is not readily removed via flocculation or pre-oxidation-enhanced flocculation [14]. Given the excellence of GO/diatomite flocculation of algal cells, we are therefore next assessed the ability of this solution to remove EOM from treated solutions.

EOM flocculation efficiency was significantly affected by pH, declining as pH values rose (Fig. 8). At a pH of 5, more than 60% of EOM and UV_{254} were removed from solution, whereas at a pH of 10 this removal efficiency was reduced to less than 10%. Interestingly, following GO-mediated flocculation, solution pH was always 7.4±0.4, irrespective of initial pH. This is likely because, under acidic conditions, strong negative GO surface charges are able to adsorb hydrogen ions, thereby leading to an increase in pH, whereas under alkaline conditions acid-base neutralization can occur between hydroxyl radicals and GO surface oxygen-containing groups, thereby reducing concentrations of hydroxyl radicals and reducing the pH of the solution accordingly.

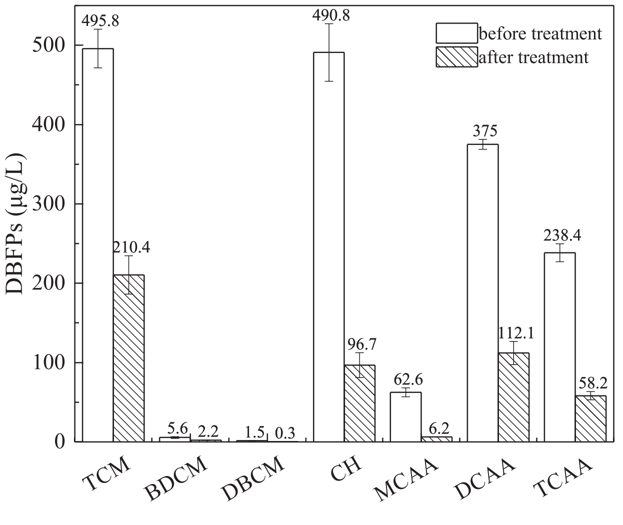

Fig. 9. The impact of GO/diatomite flocculation on disinfection byproduct formation potential.

EOM is also an important disinfection byproduct precursor, and the disinfection byproduct formation potentials (DBFPs) was always used to evaluate the precursor of disinfection byproduct removal efficiency. As shown in Fig. 9, the GO/diatomite flocculation could effectively remove the DBPs precursors of EOM, the removal efficiency ranged from 57.6% to 90.1%. which means the GO/diatomite flocculation process can effectively decrease the disinfection byproducts formation duding the following disinfection process.

Conclusions

In conclusion, the results of this study clearly demonstrate that GO can be effectively utilized as a flocculant in order to remove algae from water samples. A 40 mg/L GO concentration was sufficient to completely remove *chl-a* from solution via netting and bridging flocculation mechanisms. The floc generated by this process, however, was not very dense, and as a result, the supernatant ratio following a 30 min settling period remained at only 65%. While the addition of diatomite did not directly impact algae removal from water samples, it did result in the conversion of a subset of GO nets from two- to three-dimensional structures containing a diatomite core. This in turn significantly enhanced the ability of these samples to settle, with a markedly enhanced (90%) supernatant ratio after just 8 minutes of settling. Under neutral or acidic conditions, the efficiency of GO as an algal/EOM flocculant was not significantly affected, although it fell rapidly with rising pH when pH≥7. Following GO flocculation, the solution always maintained a pH of 7.4±0.4, regardless of the initial pH value. 57.6% to 90.1% of the disinfection byproduct formation potentials can be reduced by GO/diatomite flocculation process.

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Conflict of Interest

The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

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