



Removal of dissolved organic carbon by functional reduced graphene oxide from organic-rich water pre-treated by electrocoagulation

Soumya Kanta Ray^{*a}, Chanchal Majumder^a and Prosenjit Saha^b

^aDepartment of Civil Engineering, Indian Institute of Engineering Science and Technology, Shibpur, Howrah-711 103, West Bengal, India

^bJIS Institute of Advanced Studies and Research (JISIASR), Kolkata-700 091, India

E-mail: ray.soumya5@gmail.com

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Dissolved organic carbon (DOC) is produced from different anthropogenic activities and microbial activities on organic matter. TOC influences the production of carcinogenic disinfection by-product (DBP) at the time of disinfection during water treatment. This TOC is extremely hydrophilic in nature and difficult to separate from water by the conventional treatment procedures. Therefore, an integrated system is introduced to control TOC where a pre-treatment by electrocoagulation (EC) followed by adsorption with a nano-adsorbent made of reduced graphene oxide (rGO) coated sand impregnated by iron was used. The pre-treatment reduced 38.19% of TOC whereas 99.3% of TOC was removed by this integrated process. The process can be introduced successfully for domestic level application with small footprint successfully.

Keywords: Dissolved organic carbon (DOC), disinfection by-product (DBP), electrocoagulation (EC), functionalized reduced graphene oxide (fRGO).

Introduction

In water bodies dissolved organic carbon (TOC) can be contributed anthropogenic activities or by decomposition of organic matter naturally. Natural organic matter (NOM) has hydrophobic tail and hydrophilic head which make it difficult to remove from water. The hydrophilic component is dissolved in water and contributes to TOC in the water system¹. The hydrophilic substances, like fulvic acids (FAs), humic acid (HA) are organic acids of dark coloured and derived from plant residue.

Structurally, they consist of aliphatic chains connected with aromatic rings². It influences the water bodies by changing the physical and chemical characteristics. They also produce different complexes reacting with heavy metals³⁻⁵. Moreover, they are very much responsive with a large range of disinfectants which are used during water and wastewater treatment and producing carcinogenic disinfection by-products (DBPs). The major constituents of DBP are trihalo-methanes and halo acetic acids. These are mutagenic, carci-

nogenic and affect harmful toxicity on the human cell line⁶⁻⁹. The DBPs are difficult to remove by conventional water treatment process¹⁰ and impair the performance of other processes like adsorption¹¹, photocatalysis¹², ion-exchange¹³, granular filtration, membrane filtration¹⁴, advanced oxidation process¹⁵. The hypothetical molecular structure of FA is given in Fig. 1.

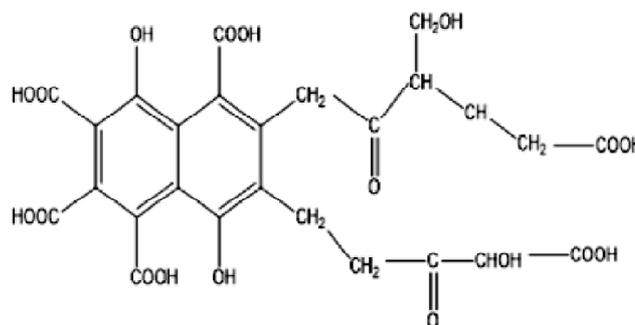


Fig. 1. Hypothetical molecular structure of fulvic acids (FA)¹⁶.

NOM is composed of large molecular weight substances and can be removed by coagulation, although the hydrophilic lower molecular weight (LMW) moieties of NOM are apparently removed less efficiently than the hydrophobic higher molecular weight (HMW) complexes^{7,17,18}. Thus, LMW and hydrophilic components control the residual organic matter after coagulation¹⁹.

Electrocoagulation (EC) is efficiently used as a pretreatment to neutralize negative charge of TOC as well as suspended colloidal particles for different water treatment systems^{20–25}. The removal of DBPs during water treatment is hindered by the major suspended colloidal particles. At the same time, EC is helpful for removal of a certain proposition of TOC from contaminated water^{26–29}.

From the last two decades nanotechnology has been gradually drawing more attention to more realistic water purification system and performing as an excellent adsorbent^{30–32}. The system can perform with the presence or absence of pretreatment like coagulation-flocculation³³. Graphene oxide (GO)³⁴ functionalized by different radicals like hydroxyl, epoxy and carboxylic acids which can be further decorated to prepare nanocomposite to be coated on sand layer for specific contaminant removal^{35–37}. In this study an effort has been taken to integrate of EC followed by fRGO adsorption system to assess the removal of TOC from water treatment.

Materials and methods

Reagents:

Fulvic acid was used as a TOC source procured from Indiamart. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) and sodium chloride (NaCl) was from Merck, Dermsdat, Germany.

Electrocoagulation setup:

In EC system sacrificial electrode material is used to deliver coagulant dose electrochemically. A 32V AC-DC converter (PSD3005, Scientific Mes-Technik Pvt. Ltd., India) was done in batch mode experiments to dose of coagulant in the laboratory in 2 L capacity borosil glass jar. Aluminum (Al) plates were operated as electrodes to dose aluminum as a coagulant. The active electrode area was retained at 8×6 cm² each and the gap between electrodes was fixed at 5 mm. Fig. 2 illustrates the experimental setup for the EC.

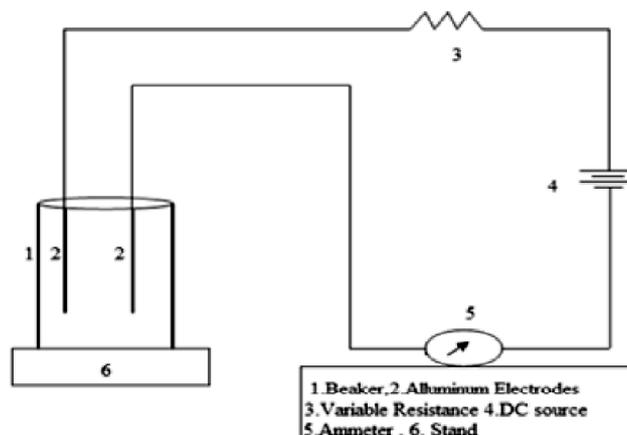


Fig. 2. Experimental setup for EC in bench scale.

The dose of fulvic acid (FA) was maintained at 5 mg/L as an equivalent TOC of 2.307 mg/L. A dose of 20 mg/L of sodium chloride (NaCl) was mixed to enhanced the electrical conductivity in the solution. The EC runs were conducted by adding 20 mg/L NaCl in the reactor to increasing conductivity of solution. TOC content of TOC was measured with TOC analyzer (Vario TOC cube, Germany). The effect of variation of a dose of coagulant was determined from the amount of aluminum dissolved into water by EC and was calculated by Faraday's law. In EC, each solution was stirred at 100 rpm for flash mixing for 1 min proceeded by 20 rpm slow mixing for 30 min at 27°C by the use of a magnetic stirrer (Tarson, India). The pH of solutions was maintained by the help of 0.25 N NaOH and 0.25 N HCl solution. The samples were passed by 0.45 μm Whatman filter paper and TOC outcome concentration of filtrate was computed. The effect of current density was measured by varying the current value through the same electrodes area. The effect of charge loading was calculated by varying the current value over time throughout the operation of EC.

Experimental

Effect of pH:

Batch studies were performed to calculate percentage removal of TOC at varying pH values. Each 1000 mL solution of 2.307 mg/L TOC was prepared for EC. The effect of pH was studied at different pH values. Six trial solutions were prepared by adjusting the pH 2, 4, 6, 8, 10, 12 respectively.

The current applied through EC system was maintained at 150 mA for 90 s for each run. The final removal percentage was reported against equilibrium pH.

Effect of volume:

The removal of TOC was influenced by the change of initial volume of samples for EC. The three trial solutions were withdrawn of volume of 500, 1000 and 1500 mL respectively. The initial pH was fixed at 7 and the TOC was maintained at 2.307 mg/L for each run of EC. The current applied was 150 mA for 90 s for each run.

Effect of initial TOC:

The removal of TOC was affected by the variation of initial concentration of TOC. Six runs were managed at a TOC concentration of 1, 2, 3, 4, 5 and 6 mg/L. The EC current and duration was constant at 0.15 amp and for 90 s respectively.

Effect of dose of coagulant:

Dose of coagulant was determined from Faraday's law of electrolysis,

$$m = \frac{itM}{zF}$$

where m = weight of coagulant (g), i = applied current (mA), t = time (s), M = molecular weight (g. mol^{-1}), z = valency of metal, F = Faraday's constant ($96485.33 \text{ C. mol}^{-1}$). Here, the applied current varied from 10, 50, 100, 150, 200 and 250 mA respectively. The time spent is 90 s for each case in 1000 mL solution at pH 7.

Effect of current density (mA/cm^2):

The current density was varied at fixed charge loading of 13.5 C/L. The different current densities studied were 1, 2.1, 4.2, 8.3, 16.7, and 33.3 mA/cm^2 respectively. The above current density values were attained by varying the electrode area from 6, 12, 18, 24, 30, 36, and 42 cm^2 respectively. The time consumed for this study was fixed at 90 s in each case. These experiments were conducted in 1000 mL solution at pH 7 and the TOC was fixed at 2.307 mg/L.

Effect of charge loading (C/L):

Charge loadings was the amount of charge per unit volume of sample. Precaution was measured that when charge loading was studied, current density was kept constant at a

value of 3.125 mA/cm^2 . The different charge loading maintained were 9.00, 13.50, 18.00, 22.50, 27.00, 31.50 C/L respectively. The different charge loading was attained by operating the EC system from 60, 90, 120, 150, 180 and 210 s respectively. The applied current was fixed at 150 mA in each case. These experiments were conducted in 1000 mL solution at pH 7 and TOC was retained at 2.307 mg/L.

Preparation of fRGO:

Hummer's method was used to prepare GO³⁸. In a batch synthesis process 5.0 g graphite powder stirred and mixed well with 2.5 g sodium nitrate (NaNO_3) within a 1.2 L borosilicate glass beaker. This mixture put within an ice bath with 120 mL 98% concentrated sulfuric acid (H_2SO_4) drop wise by a magnetic stirrer. After stirring properly, 15 g of potassium permanganate pouring into beaker very carefully and maintained the reaction temperature at 20°C by using ice bath for 5 min. Then the ice bath was separated and thoroughly maintained 35°C temperature for 30 min. Once the mixture became pasty and light brown then 150 mL of deionized (DI) water was poured drop wise and raise the temperature and stable at 98°C for 15 min into an oil bath. Then the paste becomes exfoliated and fumes get stopped. Now the paste got cooled down for 15 min in a water bath at 25°C and 450 mL DI water was added to it. The color of the paste got dark brown and 15 mL of 30% H_2O_2 was poured into solution till it became yellow. Then the suspension was centrifuged (Remi India, PR-24) at 4000 rpm with 10% HCl and DI water mixture till the pH became 7.

Then hydrazine hydrate (N_2H_4) was added while stirring was continued for 2 h to prepare a homogeneous suspension at 100°C. Thereafter *N,N*-dimethylformamide (DMF) and DI water at a ratio of 9:1 was mixed into the suspension and sonicated to reduce the GO into reduced graphene oxide (RGO) at a concentration of 20 mg/mL. Now 3 mL of RGO concentration 20 mg/mL was spread into 147 mL of DI water and 15 mg (Essay ~95%) of ferrous sulfate (FeSO_4) was added to the suspension. The suspension stirred at 500 rpm at 27°C for 1 day and 5 mL 0.1 (N) ammonium hydroxide (NH_4OH) was poured to maintain pH 8. After the suspension became brownish red the solution was heated till the water was evaporated totally. Then the brownish red material was

kept in a hot air oven at 85°C for 12 h to dry and to complete the functionalization of RGO with iron³⁹. The prepared RGO was then coated on 50 g sand ($D_{10} = 0.3$ and coefficient of uniformity (C_u) = 1.714) which was chosen as adsorbent material. The coating was completed by keeping the composite in a hot air oven at 150°C for 3 h followed by 450°C in muffle furnace for 30 min³⁹. The adsorbent thus collected and was applied in a batch adsorption after EC process. The water treatment process flow diagram is shown in Fig. 3 below.

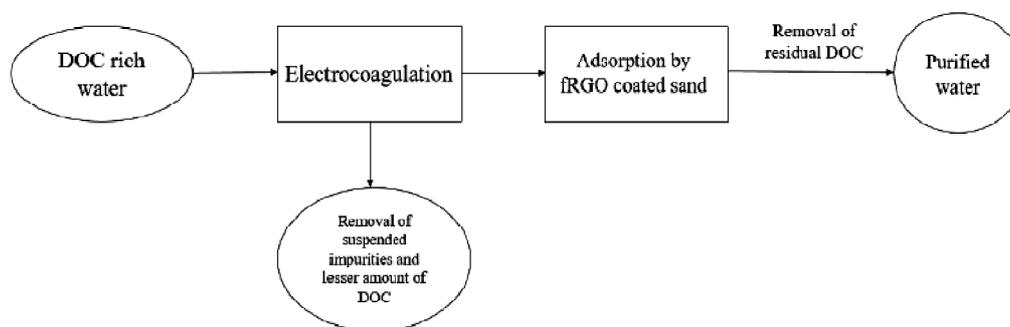


Fig. 3. Schematic diagram illustration for water treatment by integration of EC and fRGO adsorption.

Residual TOC removal:

After the pretreatment was completed by EC, the residual TOC was adsorbed by the fRGO nano composite. After the floc has been removed by the sand filter the residual part of solution was shifted to another beaker 1.2 L and fRGO nano composite coated sand particles dispersed into the solution of residual TOC. The pH was maintained to 7 with shaking speed 100 rpm at 27°C.

Results and discussion

Effect of pH:

The effect of pH on TOC removal is shown in Fig. 4.1. It is clear from the figure place between pH vales 4.5 to 5.5. It is reported that⁴⁰ pK value of humic substances is in the range of 3–5. Thus, even at adequate low pH it remains negatively charged. During EC, aluminum hydroxide $Al(OH)_3$ generated after anodic dissolution which remains positively charged. At such low pH aluminum flocks remain positively charged ($pH_{pzc} = 5.0$ for $\alpha-Al(OH)_3$ ^{40,41}). Thus, maximum removal is

found around a pH value of 4.5. Relatively lower removal (36.12%) of TOC was done by EC which is because of contiguity of pH of pzc of aluminum hydroxide and pK value of fulvic acid. Similar results were also published by other researchers^{23,24,27}.

Effect of volume of water:

The effect of volume on TOC removal was shown in Fig. 4.2.

It is cleared that with increasing the volume the removal was decreased. This is due to the fact that for a particular

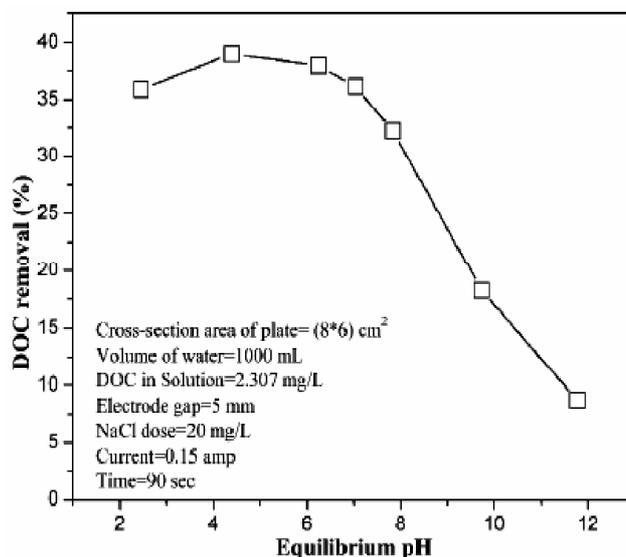


Fig. 4.1. Relation between TOC removal (%) vs equilibrium pH.

charge loading, when volume is increased coagulant dose is decreased thus removal decreased. The result of increasing

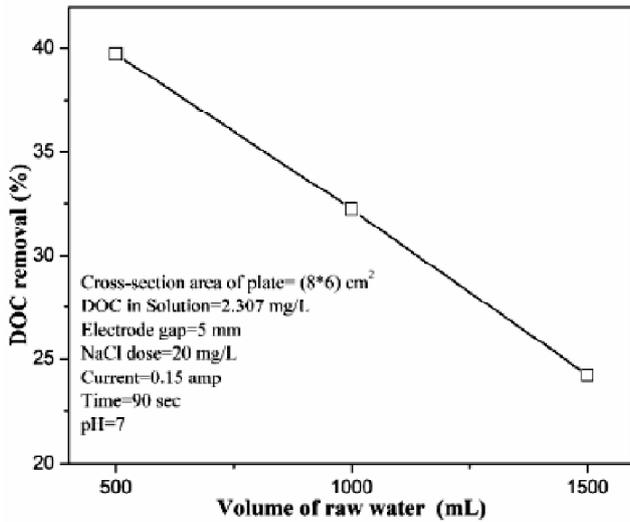


Fig. 4.2. Relation between TOC removal (%) vs volume of raw water (mL).

volume the amount of TOC increased in solution and subsequently showed that lower removal. The removal of TOC was decreased because the amount of TOC was increased in solution that hinders floc formation rate^{25,41}.

Effect of initial TOC:

The effect of initial TOC on its removal was presented in Fig. 4.3. It is evident that TOC removal was decreased when initial TOC concentration is increased. This is due to the fact that the amount of TOC became high for a particular dose of coagulant.

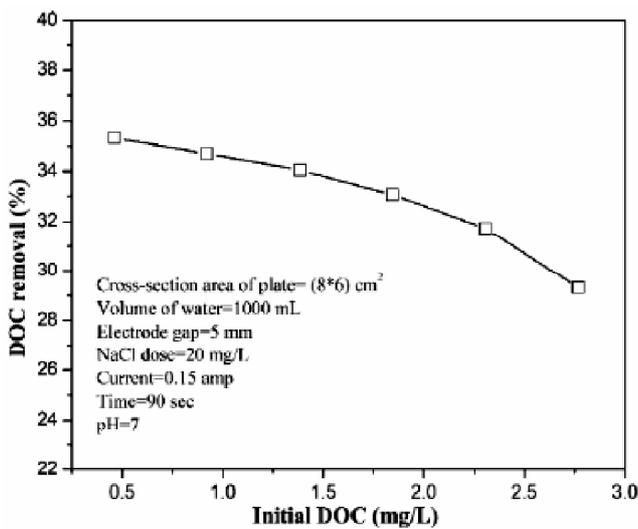


Fig. 4.3. Relation between TOC removal (%) vs initial TOC dose (mg/L).

In EC the removal rate of TOC was decreased by the increasing initial TOC in the solution. The rate of increasing amount of TOC was reduced the charge carrying capacity in the solution by decreasing conductivity^{41,42}. Fig. 4.3 illustrated below:

Effect of coagulant dose:

The effect of coagulant dose on TOC removal is shown in Fig. 4.4.

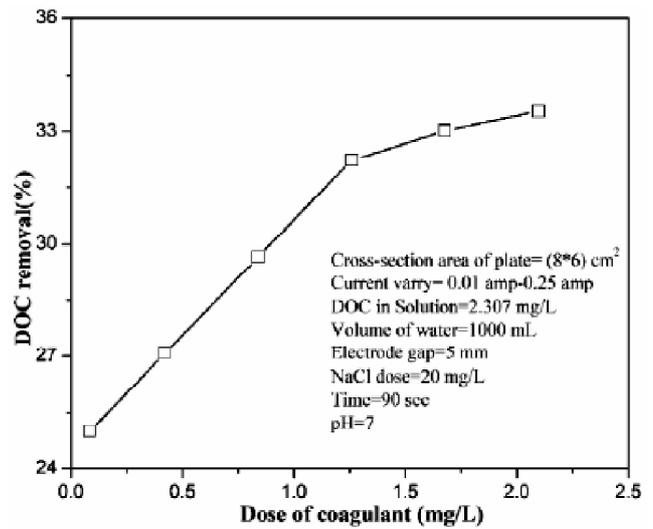


Fig. 4.4. Relation between TOC removal (%) vs dose of coagulant (mg/L).

It was clear from the Fig. 4.4 that with increasing of coagulant dose TOC removal is increased. However, after some optimum coagulant dose if EC is operated further for higher dose then the removal of TOC was decreased. This is mainly due to the fact that after optimum dose the floc became positively charged and repulsive force predominate between Al^{3+} and the floc. This repulsive force disintegrates the flocs due to charge reversal and showed a lower removal tendency^{7,43-45}. It was also found that up to a coagulant dose of 1.25 mg/L as aluminum the removal rate is rapid and thereafter removal decreased tangentially and finally 32% removal was achieved at a coagulant dose of 2 mg/L as aluminium.

Effect of current density (mA/cm²):

The effect of current density on TOC removal is shown in Fig. 4.5. In this study the effect of current density was studied keeping charge loading constant at a value of 13.5 C/L. The current density was varied by varying the electrode area. It was clear from the Fig. 3.5, that with increasing current

density the removal of TOC was decreased. To maintain a constant current of 150 mA at a fixed charge loading of 32 C/L, the voltages were increased to 3.8, 5.5, 8.9, 13.1, 17.2, 23.3 and 28.1 V respectively.

To increase the current density at desired value of the operating potential was increased. During increase of potential beyond the standard oxidation-reduction potential of aluminium (1.662) some side reactions like splitting of water takes place. Thus, some portion of energy (charges) is lost with increasing current density. Due to this loss coagulant dose reduces and subsequently the removal of TOC reduces with increasing current density^{46,47}. Thus, over voltage was in the electrocoagulation may be responsible not only for aluminum generation but also hydrolysis of water^{46,48}. For this reason, at a fixed charge loading, the TOC removal was reduced 20.86% from 38.19%^{49,50}.

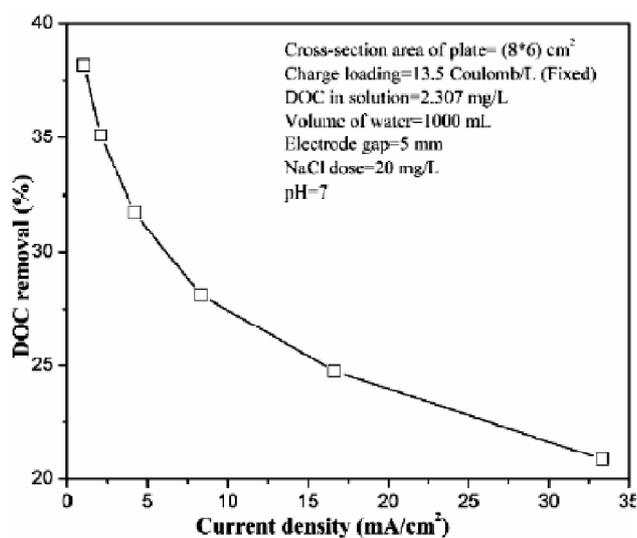


Fig. 4.5. Relation between TOC removal (%) vs current density (mA/cm²).

Effect of charge loading (C/L):

Charge loading (C/L) is defined as the amount charge per unit volume of sample. The effect of charge loading was shown in Fig. 4.6. It was clear from the Fig. 4.6 that with increasing the charge loading removal rate of TOC is increased. In this run the current density was fixed at 3.125 mA/cm² and the different charge loading was attained by varying EC operating time.

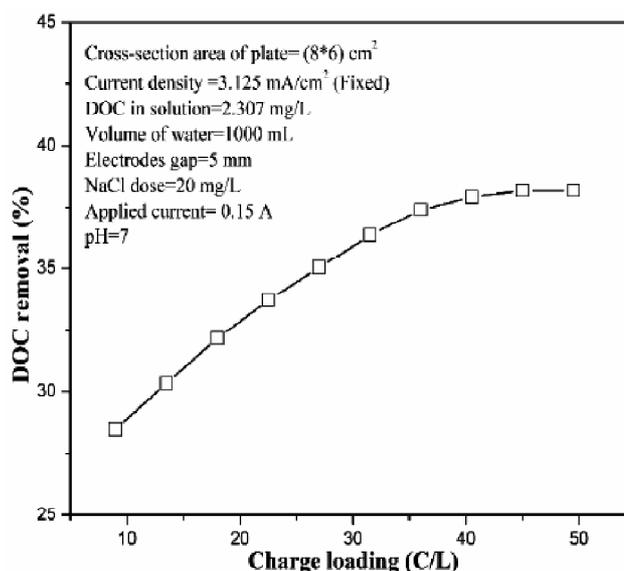


Fig. 4.6. Relation between TOC removal (%) vs charge loading (Coulomb/L).

With increasing the charge loading from 9 to 31.5 C/L, the TOC removal was increased from 28.6 to 34.05%. This is due to the fact that with increasing the charge loading more and more coagulant were released into the solution hence more and more TOC was removed which is quite natural. With increased coagulant dose, neutralization of negatively charged FA molecules takes place and initially this removal rate remains high and over time the removal rate gone down. Similar results are also reported by other researchers^{49,51}.

Kinetic study:

Kinetic study was conducted to evaluate the time dependent removal rate of TOC as showed in Fig. 4.7(a). Followed by EC, the TOC removal kinetics was tested by fRGO. Four different kinetic models namely pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion models were tested. The kinetics models tested are shown in Fig. 4.7 [(b), (c), (d) and (e)] respectively. It was found that pseudo-second order model fitted excellent over other kinetics models. The model constants and 'R²' values of the models are given in Table 1. Comparing the 'R²' values it is evident that pseudo-second order model fits the best. This was probably due to the fact that the fRGO activated with huge numbers of active ligands of Fe, which chemically adsorbed TOC from contaminated water. This study displayed the dominance of chemisorption over physisorption^{35,39,52}.

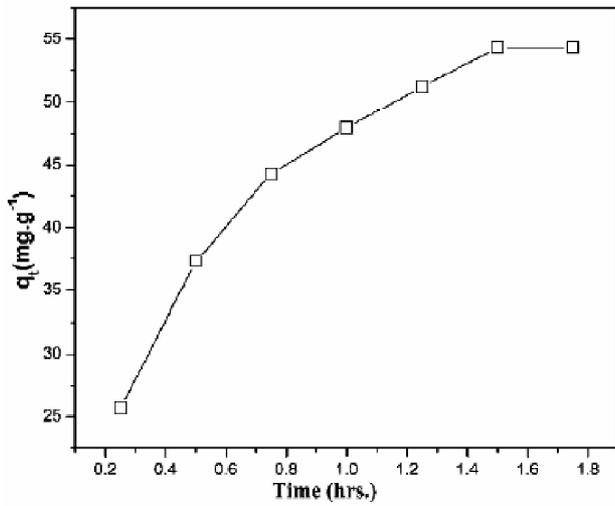


Fig. 4.7(a). Effect of contact time on TOC adsorption by the fRGO.

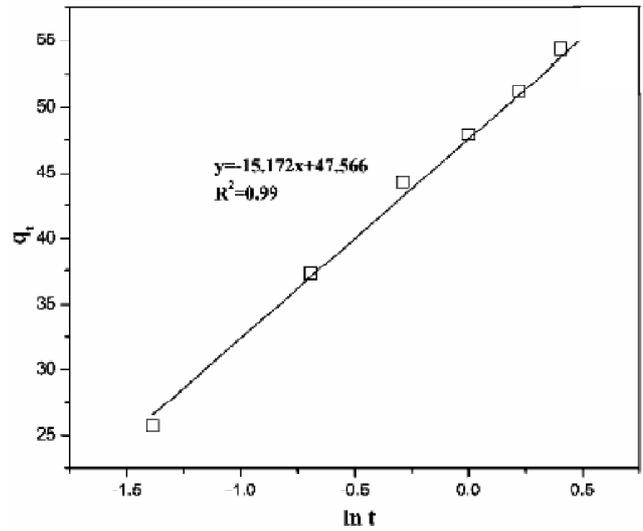


Fig. 4.7(d). Elovich kinetics.

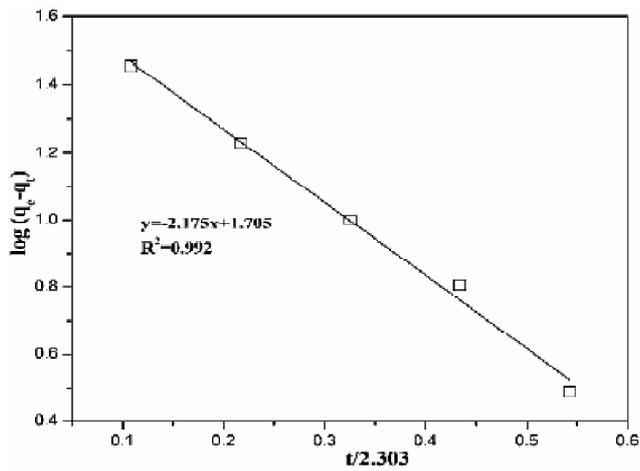


Fig. 4.7(b). Pseudo-first order kinetics.

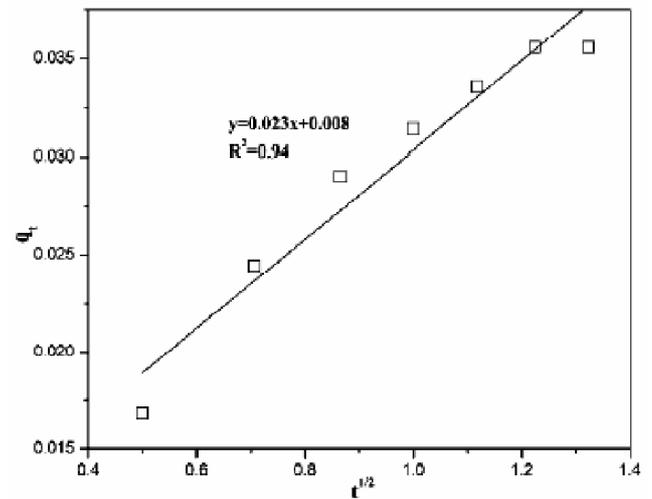


Fig. 4.7(e). Intraparticle diffusion.

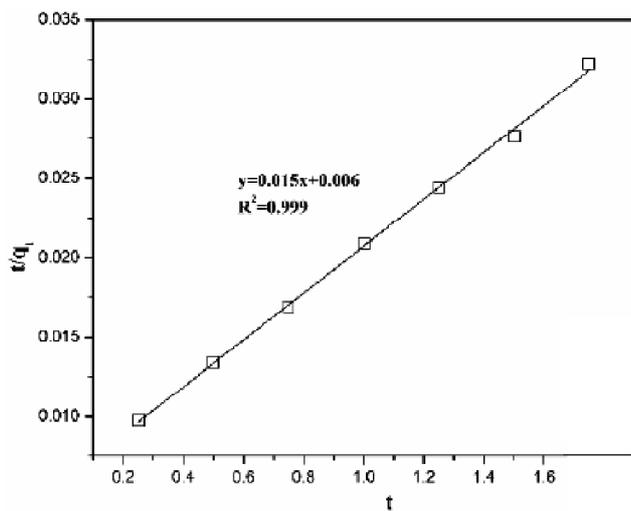


Fig. 4.7(c). Pseudo-second order kinetics.

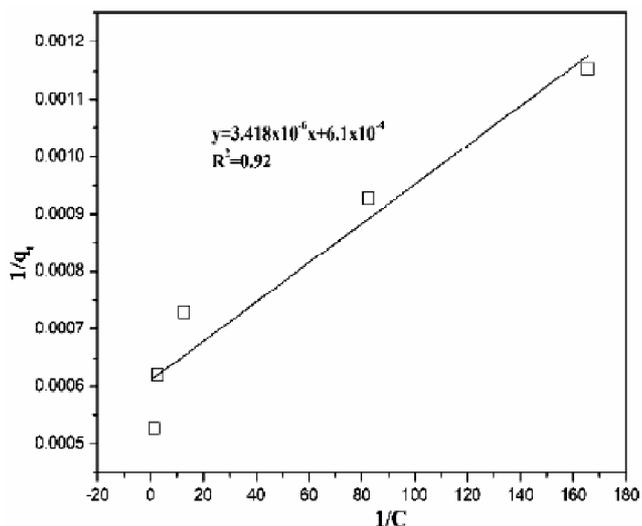
Fig. 4.7. Effect of contact time on the removal efficiency at initial concentration = 3.091 mg/L, initial concentration as per TOC = 1.426 mg/L, V = 25 mL, t = 1.5 h, temperature of 300 K.

It was observed that EC did not remove significant TOC (38.19% only) from fulvic acid solution. To improve the removal of TOC, further study was conducted in batch mode with fRGO adsorbent. Followed by EC, the residual TOC was removed by fRGO nano-composite.

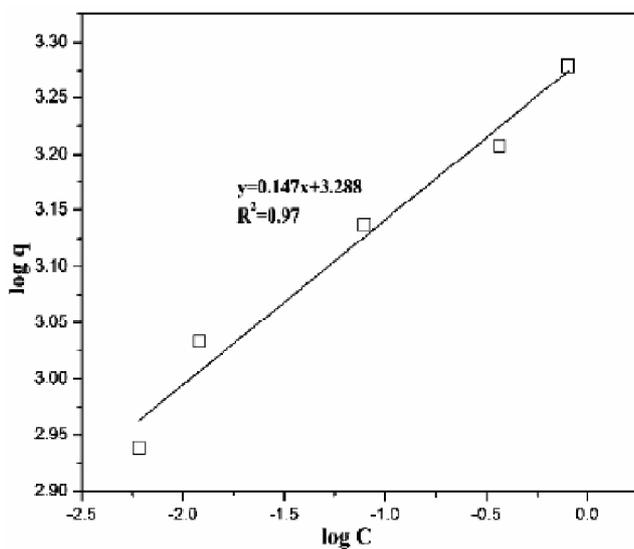
Five different dosages of fRGO were added to 25 ml of solution having 1.426 mg/L of TOC. The equilibrium adsorp-

Table 1. Correlation coefficients and constants for kinetics models are given

Nano adsorbent	Pseudo-first order model			Pseudo-second order model			Elovich model	
	q_e	K_{s1}	R^2	q_e	K_{s2}	R^2	α	β
fRGO	50.7	2.175	0.992	66.67	0.038	0.999	0.0007	-0.066



4.8(a). Langmuir isotherm.



4.8(b). Freundlich isotherm.

Fig. 4.8. Isotherms of TOC removal by fRGO (initial concentration = 3.091 mg/L, initial concentration as per TOC = 1.426 mg/L, V = 25 mL, contact time for 1.5 h, pH at 7 and temperature of 300 K.

tion capacity was reported against the mass of active fRGO nanocomposite. Two important adsorption isotherms such as Langmuir and Freundlich isotherms were tested and shown in Fig. 4.8(a, b).

It was found that compared to initial TOC, 99.3% of TOC removal was achieved within 1.5 h of contact time which corresponds to a maximum adsorption capacity of TOC of 1940.88 mg/g. This study specified that a low and intermediary concentration of TOC on the heterogeneous surface of fRGO is fulfilling a Freundlich isotherm model over the Langmuir isotherm model^{35,39,52}. Table 2 shows the details of the isotherm study.

Table 2. The factors and correlation coefficients for Langmuir and Freundlich isotherms are given for TOC removal by fRGO

Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_{max}	K_L	R^2	K_F	n	R^2
fRGO	1639.344	178.47	0.92	1940.88	6.803	0.97

Conclusions

This study showed that only EC is not effective to remove TOC from contaminated water. EC achieved only 38.19% of TOC removal over 31.5 C/L of charge loading. The study suggested that for a constant charge loading, the removal rate decreased if current density is increased. It was clear that only EC is not capable of removing TOC significantly. Followed by EC, fRGO adsorption improved the TOC removal significantly. The combined EC and fRGO adsorption can achieve 99.3% removal of TOC from contaminate water. The study suggested that pseudo-second order kinetics model fits best over other kinetics model and Freundlich isotherm model fit superior over other adsorption models. The system may be used successfully for removal of trace quantity of TOC from drinking water.

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