Dehydrochlorination of adsorbed 1,1,2,2-tetrachloroethane on graphene
oxide-based materials' surface: comparison with dissolved form in
aqueous environment

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Abstract: Dehydrochlorination of 1,1,2,2-tetrachloroethane (TeCA) in graphene oxide (GO)-based materials-water two-phase system can be enhanced strongly. However, the dehydrochlorination kinetic of adsorbed TeCA on GO-based materials' surface is still unclear. Thus, in this study the dehydrochlorination kinetics of adsorbed TeCA on GO based-materials' surface was compared to the kinetics of dissolved TeCA in aqueous solution. The results showed that the dehydrochlorination kinetic constants of adsorbed TeCA on GO-based materials' surface (k_{s_F}) were much greater than those of dissolved TeCA in aqueous solution (k_a) due to the deprotonated surface oxygen-containing functional groups (e.g. $-\text{COO}^-$, and $-\text{O}^-$) served as conjugated bases to catalyze the reaction. In particular, at pH 8.0 and 9.0, the k_{s_F} values for GO (20 mg/L) were approximately 3 orders magnitude greater than k_a values. Furthermore, the k_{s_F} values of adsorbed TeCA for the low concentration of GO (20 mg/L) were always greater than that for the high concentration of GO (100 mg/L). The primary mechanism was that GO was apt to aggregate at high concentration, which enhanced the steric hindrance between O-containing functional groups and TeCA molecular. Consequently, the interfacial effects of GO-based materials at their low concentration could strongly enhance the transformation of adsorbed TeCA in aqueous environment.

Key words: Dehydrochlorination; Adsorbed 1,1,2,2-tetrachloroethane; Graphene oxide-based materials; Catalysis; Deprotonated surface O-containing functional groups

Introduction

Recently, graphene oxide (GO)-based materials have received much attention. Due to their remarkable electronic, mechanical, and chemical properties, GO-based materials have wide applications and may act as catalysts [1-2], adsorbents [3], transistors [4], sensors [5-6], supercapacitors [7]. Large-scale production and use have inevitably released these nanomaterials into the environment, increasing the potential for interaction with other environmental contaminants and then changing the environmental fates of these contaminants [8-11]. Many researchers have reported that GO-based materials can affect the transformation of organic contaminants in environment and even have potential to facilitate the degradation of some organic contaminants [1, 12-15].

The hydrolysis of organic contaminants is one of the most important abiotic transformation reactions in environment [16-17]. Hydrolysis reactions are often acid-catalyzed or base-catalyzed [18-19]. As a common water contaminant, TeCA can be hydrolyzed in neutral and alkaline aqueous environment [16]. In our previous studies [20-21], we found that functionalized multi-walled carbon nanotubes (MWCNTs) and activated carbons can catalyze the hydrolytic dehydrochlorination of 1,1,2,2-tetrachloroethane (TeCA) in neutral and alkaline environment, in that the deprotonated surface O-containing functional groups (e.g. carboxyl, and phenolic groups) serve as conjugated bases to catalyze the reaction. Mackenzie et al. [22-23] and Kopinke et al. [24] also reported that activated carbons can catalyze hydrolysis of TeCA and γ -hexachlorocyclohexane as well as the reductive dechlorination of trichloroethylene (TCE). Compared to carbon nanotubes and activated carbons, GO-based materials are richer in surface O-containing functional groups [25-26]. Li et al. reported that the GO-based materials can also enhance the hydrolysis of TeCA [27].

The pseudo first-order kinetics model has been introduced to demonstrate the hydrolytic dehydrochlorination of TeCA in MWCNTs/GO-water two-phase system [21, 27]. Our previous studies [21, 27] indicated that the pseudo-first order kinetic constant of TeCA dehydrochlorination in hydroxylated or carboxylated MWCNT (O-content: 3.0% ~ 5.9%)-water two-phase system was 1.2~2.0 times greater than that of TeCA dehydrochlorination in homogeneous aqueous solution [21]. The pseudo-first order kinetic constant of TeCA dehydrochlorination in GO-based materials

(O-content: 17.3% ~ 39.1%)-water two-phase system was 1.38~2.67 times greater than that of TeCA dehydrochlorination in homogeneous aqueous solution [27]. These phenomena are attributed to the deprotonated surface O-containing functional groups that can effectively enhance the catalytic effect of carbonaceous materials on hydrolytic dehydrochlorination of TeCA [21, 27]. However, it is noted that though the O-content of GO-based materials are 2.93~13.0 times of that of functionalized MWCNTs, the pseudo-first order kinetic constants of TeCA dehydrochlorination in GO-based materials-water system are approximate to that in functionalized MWCNTs-water systems [21, 27], which indicates that there may be other factors controlling the hydrolytic dehydrochlorination of TeCA in MWCNTs/GO-water system except for the deprotonated surface O-containing functional groups. In fact, the transformation of TeCA in carbonaceous materials-water two-phase system is controlled by a complex process, dehydrochlorination of dissolved TeCA in aqueous solution and adsorbed TeCA on carbonaceous surface can occur simultaneously [21]. And the later occurs only when TeCA molecular is adsorbed on carbonaceous surface, due to the catalytic effect of the deprotonated O-containing functional groups on the surface of MWCNTs/GO [20-21, 27]. Thus, the adsorption affinity of carbonaceous material also plays an important role in the process of TeCA dehydrochlorination [20-21]. The pseudo first-order kinetics model can accurately describe TeCA dehydrochlorination in carbonaceous materials-water two-phase system, but it does not differentiate the dehydrochlorination of adsorbed TeCA on GO-based materials surface from dehydrochlorination of TeCA in two-phase system [21-22, 27]. Overall, an in depth study the dehydrochlorination of adsorbed TeCA on GO surface rather than the dehydrochlorination of TeCA in GO-water two-phase system is more important to give insight into the catalytic mechanism of GO-based materials. Furthermore, high concentration of nanoparticles in aqueous solution can enhance its aggregation [28-30]. The same may be true for GO-based materials. Thus an important research aim was the study of if the aggregation of GO at its high concentration can affect the dehydrochlorination of adsorbed TeCA.

The main objectives of this study were to distinguish the difference of dehydrochlorination between dissolved and adsorbed TeCA in GO-based materials-water two-phase system, and to deeply understand the dehydrochlorination mechanism of adsorbed TeCA on GO-based materials' surface. The Freundlich-isotherm-based two-phase kinetic model and the

Langmuir-isotherm-based two-phase kinetic model were introduced to analyze the catalytic effect of GO-based materials on dehydrochlorination of TeCA. Moreover, the effect of GO at a high concentration on dehydrochlorination of adsorbed TeCA was also investigated in this study. The results of this study will be very useful for further understanding the interplay of the surface O-containing functional groups and adsorbed TeCA molecular on GO-based materials.

Materials and methods

Materials

Both graphene oxide (GO) (>99%) and reduced graphene oxide (RGO) (>99%) were purchased from Nano Materials Tech Co. (Tianjin, China). Based on the information provided by the supplier, GO was synthesized using a modified Hummers method, and RGO was obtained by reducing GO with hydrazine hydrate. Powdery graphite (purity was greater than 99.9%, and particle size was less than 45 μm) was purchased from Sigma Aldrich Co. (Shanghai, China). Oxidized graphite was obtained by oxidizing the powdery graphite with sulfuric acid, hydrogen peroxide and potassium permanganate [31], the details of oxidized procedure are provided in the supplementary material.

The Brunauer–Emmett–Teller (BET) specific surface area of the carbon-based materials was determined by multipoint N_2 adsorption–desorption using a Micromeritics ASAP2010 accelerated surface area and porosimetry system (Micromeritics Co., USA). Fourier-transform infrared (FTIR) analysis was performed using a Bruker TENSOR 27 apparatus (Bruker Optics Inc., Germany). Surface elemental analysis was performed with an X-ray photoelectron spectroscopy (XPS) (PHI-5000Versa Probe, Japan). Raman spectra were recorded with a Renishew inVia Raman spectrometer (RM2000, UK). Selected physicochemical properties of the carbonaceous materials are summarized in Table 1 and Fig. 1.

TeCA (>99%) and TCE (>99%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Stock solutions of TeCA and TCE were prepared in methanol, and stored at $-20\text{ }^\circ\text{C}$. All the solvents were high-performance liquid chromatography grade or above.

Reaction of TeCA in homogeneous aqueous solution and in the presence of GO/RGO

Reaction kinetic experiments were conducted both in homogeneous aqueous solution (i.e., electrolyte solution in the absence of GO, RGO, graphite, and oxidized graphite) and in the

presence of GO/RGO/graphite/oxidized graphite (graphite and oxidized graphite were used as the comparative experiments). Approximately 250 mL of an electrolyte (containing 0.05 M $\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$ as the pH buffer, and 0.01M NaN_3 as the bio-inhibitor) was added to each of a series of 250 mL amber glass bottles. The pH of the solution was adjusted with HNO_3 or NaOH . For the experiments involving GO/RGO/graphite/oxidized graphite, a certain amount of GO/RGO/graphite/oxidized graphite was added to the bottle before adding the aqueous solution, and the mixture was sonicated in a water bath for 5 h and then placed on an orbital shaker (7 rpm) for 24 h. Then, 50 μL of a TeCA stock solution (in methanol) was injected into the solution with a micro-syringe, to give an initial TeCA concentration of 1.0 mg/L. Next, the bottle was filled with the buffer solution, sealed immediately, and left on an orbital shaker (7 rpm) operated at a constant temperature of 25 °C. At predetermined time intervals, 1.0 mL of the solution was withdrawn, transferred to a clean glass vial containing a pH 3 buffer solution (0.05 M KH_2PO_4 ; pH adjusted with HNO_3) to terminate the reaction. The solution was extracted with hexane (3:1, v:v). The hexane extract was filtrated through a 0.22 mm membrane filter and then analyzed to determine the mass of TeCA, as well as the mass of TCE (the only organic reaction product). The mass of TeCA adsorbed to GO/RGO/graphite/oxidized graphite was less than 2% of the total mass and was not monitored. The pH of the solution was also monitored during the sampling and was found to be essentially unchanged in all the experiments. Each kinetic experiment was run in duplicate. Mass balance (Fig. S2~S5) was within the range of 91~101% for all the experiments.

Adsorption experiments of TeCA to GO/RGO

Adsorption isotherms of TeCA to GO and RGO were obtained using the procedures developed previously [10]. Briefly, a 5 g/L GO or RGO suspension (pH 5.0) was added to a series of 8 mL amber glass vials; a low pH was used to ensure that hydrolysis of TeCA would not occur. Next, a stock solution of TeCA (in methanol) was added to the vials, and the vials were capped and placed on an orbital shaker (7 rpm) for 5 d. Afterward, a piece of glass fiber was added to each vial and allowed to equilibrate for 5 d. Then, the fibers were taken out, wiped with wet tissues, and extracted with hexane to analyze the concentrations of TeCA on the fibers. The concentrations of freely dissolved TeCA were calculated based on the concentrations on the fibers and the sorption coefficient of TeCA to the fiber (K_{fibers} , 1.22×10^3 L/kg as determined in our previous study [21]).

The concentrations of TeCA adsorbed to GO/RGO were calculated based on mass balance.

Prior to initiating an adsorption experiment of TeCA to graphite/oxidized graphite, approximately 1.0 g graphite/oxidized graphite was transferred to a 40 mL amber glass vial and was pre-wetted for 24 h with approximately 40 mL of a pH 5.0 buffer. Afterward, a stock solution of TeCA (in methanol) was added to the vial using a micro-syringe. The vial was then filled to leave minimal headspace and was left on an orbital shaker (7 rpm) operated at a constant temperature of 25 °C for 7 d. Then, the vial was removed from the shaker and was centrifuged at 3000 g for 10 min to allow complete settlement of adsorbents. Then, a certain volume of the supernatant was withdrawn and extracted with hexane. The hexane extract was filtered through a 0.22 mm membrane (Anpel Scientific Instrument, Shanghai, China) to analyze the aqueous phase concentration. And the solid adsorbents were transferred to a 20 mL glass vial and extracted with acetone to analyze the concentration on adsorbent. Each isotherm contained six individual data points and each data point was run in triplicate. All the adsorption isotherms were displayed in Fig. S6.

Analysis of Reaction Kinetics Data

The first-order kinetic model was used when comparing the reaction kinetics in different experiments [16, 32]:

$$C / C_0 = \exp (-k_{\text{obs}} \cdot t) \quad (1)$$

Where C_0 (mg/L) is the initial TeCA concentration; C (mg/L) is the TeCA concentration at a given time t (h); and k_{obs} (h^{-1}) is the apparent first-order kinetic constant for the dehydrochlorination reaction of TeCA.

In order to compare the reaction kinetics of adsorbed TeCA on surface of carbonaceous materials and dissolved TeCA in aqueous solution, the Freundlich-isotherm-based two-phase kinetic model and Langmuir-isotherm-based two-phase kinetic model were used in this study. The two-phase reaction models are applicable for carbonaceous materials with low adsorption capacity (the mass of TeCA in the adsorbed phase was typically less than 2% of the total mass of TeCA in the system). The details of these two models derivation were presented in our previous study [21].

The Freundlich-isotherm-based two-phase kinetic model can be expressed as:

$$C = \left\{ \left(C_0^{1-n} + \frac{k_{s_F} \cdot K_F \cdot C_{CM}}{k_a} \right) \cdot e^{\left[\frac{k_a \cdot (n-1) \cdot t}{1} \right]} - \frac{k_{s_F} \cdot K_F \cdot C_{CM}}{k_a} \right\}^{\frac{1}{1-n}} \quad (2)$$

The Langmuir-isotherm-based two-phase kinetic model can be expressed as:

$$\ln \left[\left(\frac{C_0}{C} \right)^{\frac{A}{k_a \cdot A + k_{s_L} \cdot q_{max} \cdot C_{CM}}} \left(\frac{k_a \cdot C + k_a \cdot A + k_{s_L} \cdot q_{max} \cdot C_{CM}}{k_a \cdot C_0 + k_a \cdot A + k_{s_L} \cdot q_{max} \cdot C_{CM}} \right)^{\frac{A}{k_a \cdot A + k_{s_L} \cdot q_{max} \cdot C_{CM}} - \frac{1}{k_a}} \right] = t \quad (3)$$

In equation (2) and (3), the meanings of C and t are same to equation (1); q (mg/g) is the concentration of TeCA adsorbed to carbonaceous materials; k_a (h^{-1}) is first-order reaction kinetic constants for the transformation of dissolved TeCA; k_{s_F} (h^{-1}) and k_{s_L} (h^{-1}) are the reaction kinetic constants of adsorbed TeCA calculating from the Freundlich-isotherm-based two-phase kinetic model and the Langmuir-isotherm-based two-phase kinetic model, respectively; and C_{CM} (g/L) is the concentration of carbonaceous materials in the reaction system; K_F ($\text{mg}^{1-n} \text{L}^n \text{g}^{-1}$) is the Freundlich affinity coefficient; n is the Freundlich linearity index; q_{max} (mg/g) is the maximum adsorption capacity; and A (mg/L) is the Langmuir adsorption constant.

Results and discussions

Characteristics of GO, RGO, graphite, and oxidized graphite

The surface O-containing functional groups of GO, RGO, graphite, and oxidized graphite were examined by FTIR. As shown in Fig. 1a, the vibration and deformation bands of O–H locate at 3380 cm^{-1} , the stretching vibration band C=O of carbonyl, carboxyl, and lactone locate at 1735 cm^{-1} , the stretching vibration bands of C=C locate at 1624 cm^{-1} , and the stretching vibration bands C–O of epoxy and alkoxy locate at 1225 and 1060 cm^{-1} , respectively [33-34]. Compared to GO, the spectrum of RGO, shows the decrease of the salient bands at 1225 cm^{-1} and at 1735 cm^{-1} , indicating the loss of epoxy groups and carbonyl groups. Fig.1b demonstrates that prior to oxidation there is no characteristic peak detected on graphite. After the oxidation many O-containing functionalized groups were generated, including O–H at 3380 cm^{-1} , C=O at 1735 cm^{-1} , C–O at 1225 and 1060 cm^{-1} , respectively. The Raman spectra (Fig.S1) shows that GO and oxidized graphite have the I_D/I_G values greater than RGO and graphite (Table 1). Because the D band is usually related to the vibration of carbon atoms with dangling bonds and ascribed to the edge of carbon network [35], the increase of I_D/I_G values indicates the restoration of disorder

carbon atoms and the increased content of surface heterogeneous atoms. The results of FTIR and Raman spectra suggested that GO and oxidized graphite had greater surface heterogeneity than RGO and graphite.

The surface chemical properties of GO, RGO, graphite, and oxidized graphite were characterized further by XPS. The XPS results (Table 1) show the four carbonaceous materials have different C/O ratios. In Fig. 1 c, d, e, the spectrum of GO, RGO, and oxidized graphite can be deconvoluted into three different peaks that correspond to carbon atoms assuming different binding statuses. The peaks of C1s centered at the binding energies of 284.6, 286.4, and 287.8 eV are assigned to the carbon atoms of C=C/C-C in aromatic rings, C-O (epoxy and alkoxy), and C=O (carbonyl, carboxyl and lactone), respectively [20, 36]. The peaks of RGO, in comparison with that of GO, shows the decrease of C-O and C=O [30, 36-37]. Due to the very low content of oxygen on graphite surface, the C1s XPS peak of graphite is not able to be deconvoluted. However, after the oxidation, the C1s XPS peak of oxidized graphite can be well deconvoluted, and the content of C-O (epoxy and alkoxy) and C=O are nearly closed to GO. The results of XPS are generally consistent with the FTIR data. As shown in Table 1, the surface area of the four materials follows the order: RGO (241 m²/g) > GO (207 m²/g) > oxidized graphite (97.1 m²/g) > graphite (5.58 m²/g).

Reaction kinetics of TeCA in GO-based materials-water two-phase system

The dehydrochlorination of dissolved TeCA in homogeneous aqueous solution agrees with the pseudo first-order kinetic model, and the pseudo first-order kinetic constant (k_{obs}) is positively correlated with the concentration of OH⁻ [16, 31]. As shown in Table 2, the k_{obs} values at pH 7.0, 8.0 and 9.0 are $0.370 \times 10^{-3} \text{ h}^{-1}$, $3.75 \times 10^{-3} \text{ h}^{-1}$, and $34.5 \times 10^{-3} \text{ h}^{-1}$, respectively.

The pseudo first-order kinetic constants k_{obs} of TeCA dehydrochlorination in GO/RGO-water system at pH 7.0, 8.0, and 9.0 were also shown in Table 2. The k_{obs} values of TeCA dehydrochlorination in 20 mg/L GO-water system are $0.39 \times 10^{-3} \text{ h}^{-1}$, $6.3 \times 10^{-3} \text{ h}^{-1}$, and $62.1 \times 10^{-3} \text{ h}^{-1}$ at pH 7.0, 8.0, and 9.0, respectively. The k_{obs} values of TeCA dehydrochlorination in 20 mg/L RGO-water system are $0.39 \times 10^{-3} \text{ h}^{-1}$, $7.1 \times 10^{-3} \text{ h}^{-1}$, and $46.8 \times 10^{-3} \text{ h}^{-1}$ at pH 7.0, 8.0, and 9.0, respectively. In comparison to the homogeneous solution, both GO and RGO are able to consistently facilitate the dehydrochlorination of TeCA in two-phase system at given pH 7.0, 8.0

and 9.0 (Fig. S7 and S8). The catalytic effects of GO and RGO are mainly due to the deprotonated surface O-containing functionalized groups (e.g. $-\text{COOH}$ and $-\text{OH}$ groups) serve as conjugate bases (e.g. $-\text{COO}^-$ and $-\text{O}^-$ groups) that can effectively facilitate the dehydrochlorination of TeCA in neutral and alkaline solutions [21-22, 27]. In order to further confirm the catalytic effect of surface O-containing functional groups on the dehydrochlorination of TeCA, graphite (without surface O-containing functionalized groups) and oxidized graphite (with an abundance of surface O-containing functional groups) were used to conduct the experiment of TeCA dehydrochlorination at pH 8.0 and 9.0. The k_{obs} values of TeCA dehydrochlorination in graphite-water system are approximately equal to that in homogeneous solution, while the k_{obs} values of TeCA dehydrochlorination in oxidized graphite-water system are far greater than that in homogeneous solution (Table 2 and Fig. S9). These results were consistent with our previous study [21, 27] and further confirmed that the surface O-containing functionalized groups of carbonaceous materials could facilitate the dehydrochlorination of TeCA in alkaline environment.

The role of the adsorption affinity of GO-based materials

The surface oxygen content of GO (31.4 wt. %) is about two times greater than that of RGO (17.3 wt. %) (Table 1), especially, the contents of C–O and O–C=O groups (the main catalytic groups for TeCA dehydrochlorination) on GO surface are far greater than that on RGO surface (Fig. 1c and 1d). However, the catalytic effects of GO and RGO were not proportional to their surface oxygen content. For example, as shown in Table 2, the dehydrochlorination rate of TeCA in 20 mg/L GO-water system (k_{obs} : $6.30 \times 10^{-3} \text{ h}^{-1}$) is slightly lower than that in 20 mg/L RGO-water system (k_{obs} : $7.01 \times 10^{-3} \text{ h}^{-1}$) at pH 8.0. The phenomenon indicates that there may be other factors (e.g. adsorption affinities of GO and RGO) affect the dehydrochlorination of TeCA except for the surface O-containing functional groups [27]. Only TeCA is adsorbed on GO or RGO surface, the deprotonated O-containing functional groups can touch the TeCA molecular and enhance its dehydrochlorination [27]. The adsorption affinities of GO (20 mg/L) and RGO (20 mg/L) for TeCA at different pH values were compared in Fig. 2. The adsorption capacity of RGO for TeCA was always nearly one order magnitude greater than that of GO. Thus, even though the content of O-containing functional groups on the surface of GO was greater than RGO, the overall catalytic effect of GO was counterbalanced by its weaker adsorption affinities for TeCA. Furthermore, the

adsorption capacities of graphite are approximately equal to that of oxidized graphite for TeCA at pH 8.0 and 9.0 (Fig. 2), however, the k_{obs} values of oxidized graphite are greater than those of graphite (Table 2), which indicates that oxidized graphite with abundant O-containing functional groups exhibits a stronger catalytic effect on the dehydrochlorination of TeCA than graphite without O-containing functional groups. These results confirmed that the adsorption affinities and the surface O-containing functional groups of GO-based materials were both important in promoting the dehydrochlorination of TeCA in GO-based materials-water two-phase system.

Comparison of reaction kinetics of adsorbed TeCA with that of dissolved TeCA

The transformation of TeCA in GO-based materials-water two-phase system includes the dehydrochlorination of dissolved TeCA in aqueous solution and the dehydrochlorination of adsorbed TeCA on carbonaceous surface. In order to deeply understand the dehydrochlorination of adsorbed TeCA on carbonaceous surface, the Freundlich-isotherm-based two-phase kinetic model and the Langmuir-isotherm-based two-phase kinetic model were used to obtain the reaction kinetic constants for the transformation of adsorbed TeCA [21]. The fitting parameters of adsorption isotherms were shown in Fig. S6. The figures display that the fitting curves of Freundlich isotherm can cover the adsorption data of the four carbonaceous materials better than that of Langmuir isotherm. Therefore, the Freundlich-isotherm-based two-phase kinetic model was selected to analyze the data of reaction kinetics of TeCA in GO-based materials-water system.

As shown in Table 2, the k_{s_F} values of adsorbed TeCA on GO and RGO surface are always greater than k_{a} values of dissolved TeCA in solution at any pH values. In particular, at pH 8.0 and 9.0, the k_{s_F} values of GO is 2~3 orders magnitude greater than k_{a} values, the k_{s_F} values of RGO is 1~2 orders magnitude greater than k_{a} values. The results indicate that transformation rate of adsorbed TeCA is far faster than that of dissolved TeCA. The $k_{\text{s}_F}/k_{\text{a}}$ values of GO (20 mg/L) and RGO (20 mg/L) are 71 and 4.6, respectively, at pH 7.0, 711 and 67, respectively, at pH 8.0, and 782 and 25.6, respectively, at pH 9.0, which indicates that GO and RGO can exhibit strong catalytic effect on the dehydrochlorination of TeCA at higher pH values (8.0 and 9.0) and the catalytic effect on the dehydrochlorination of TeCA of RGO is weaker than that of GO. The results indicate the catalytic effect of GO-based materials increased with increasing solution pH values, that is because dehydrochlorination of adsorbed TeCA is depended on the content of surface acidic

functionalities such as carboxyl and phenolic hydroxyl groups, and the deprotonated degrees of these acidic functionalities increased with increasing solution pH values. Strelko et al. reported that the pK_a values of carboxyl groups on carbonaceous materials ranged from 3 to 6 [38], however, oxidized carbons may contain a complex mixture of acidic functionalities and the pK_a values of carboxyl groups can be up to 8 [39]. The pK_a value of phenolic hydroxyl groups on carbonaceous materials is likely around 9~10 [39]. The lactone groups on carbonaceous materials can hydrolyze to form the deprotonated carboxyl and phenolic hydroxyl groups as the pH greater than 8.0 [40]. Thus, at high pH values (8.0 and 9.0), more conjugate bases are formed and therefore the catalytic effect of carbonaceous materials become stronger. A closer look at the changes of k_a and k_{s_F} values with solution pH (Fig. 3) indicates that increasing pH by approximately one unit results in an increase of k_a value by a factor of 10. The k_{s_F} values of GO are always greater than that of RGO, which are consistent with their surface O-containing functional groups contents. Moreover, with so few surface O-containing functional groups graphite has no catalytic effect on the dehydrochlorination of TeCA. In contrast, oxidized graphite has abundant surface O-containing functional groups and thus the k_{s_F} values of oxidized graphite are 116 and 77.8 times of k_a values at pH 8.0 and 9.0, respectively. The results strongly confirmed the catalytic effect of surface O-containing functional groups on dehydrochlorination of adsorbed TeCA.

Influence of high concentration of GO in aqueous solution

High concentration of nano particles in aqueous solution likely enhances their aggregation [29-30], a high concentration of GO (100 mg/L) was thus used to investigate the impact of aggregation of GO on the dehydrochlorination of TeCA. Generally, the transformation rate of reactant is positively related to the concentration of catalyst. For example, the rate of dehydrochlorination of dissolved TeCA increased with the increasing $[OH^-]$ in homogeneous solution [16, 32]. The dehydrochlorination of TeCA in GO-water system also displays the same trend—the pseudo first-order kinetic constants (k_{obs}) increased with the increasing concentration of GO. The k_{obs} values of TeCA dehydrochlorination in GO-water system follow the orders: 100 mg/L ($0.47 \times 10^{-3} \text{ h}^{-1}$) > 20 mg/L ($0.39 \times 10^{-3} \text{ h}^{-1}$), 100 mg/L ($7.12 \times 10^{-3} \text{ h}^{-1}$) > 20 mg/L ($6.30 \times 10^{-3} \text{ h}^{-1}$), and 100 mg/L ($66.0 \times 10^{-3} \text{ h}^{-1}$) > 20 mg/L ($62.1 \times 10^{-3} \text{ h}^{-1}$) at pH 7.0, 8.0 and 9.0, respectively

(Table 2, and Fig. S7 and S8). However, it is notable that the variation trend of k_{s_F} values is very different from that of k_{obs} values with variable GO concentration. The k_{s_F} values of adsorbed TeCA dehydrochlorination on GO follow the orders: 20 mg/L (0.026 h^{-1}) > 100 mg/L ($0.021\times 10^{-3}\text{ h}^{-1}$), 20 mg/L (2.66 h^{-1}) > 100 mg/L (0.674 h^{-1}), and 20 mg/L (27 h^{-1}) > 100 mg/L (6.17 h^{-1}) at pH 7.0, 8.0, and 9.0, respectively (Table 2). The increase of nanoparticles concentration can enhance their aggregation—the aggregation rate and aggregates size can increase with the increasing concentration of nanoparticles [28-29]. Thus, GO was apt to aggregate with its increasing concentration, and more O-containing functional groups were sequestered in the inside of the GO aggregate, which could enhance the steric hindrance between O-containing functional groups and TeCA molecular. Consequently, the increasing GO concentration caused a low transformation rate of adsorbed TeCA.

Conclusion

Due to low environmental concentrations, the potential effects of GO-based materials on the transformation of environmental organic contaminants are often neglected. Here we found that once TeCA molecular was adsorbed onto GO/RGO surface, the hydrolytic dehydrochlorination of adsorbed TeCA became strongly enhanced due to the deprotonated surface O-functional groups (e.g. carboxyl, and phenolic groups) of GO/RGO served as conjugated bases to catalyze the reaction. In particular, at high pH 8.0 and 9.0, the k_{s_F} values for adsorbed TeCA on GO and RGO (20 mg/L) were 1~3 order magnitude greater than k_a values for dissolved TeCA in homogeneous solution. Furthermore, the rate of dehydrochlorination of adsorbed TeCA was always faster at low concentrations of GO compared to high concentrations of GO. An important environmental implication of this study is that when GO-based materials were released into environment, the interfacial effect of GO-based materials at their low environmental concentration was able to significantly facilitate the transformation of adsorbed TeCA in aqueous environment.

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495

496 *Tables and figures*497 **Table 1.** Selected physicochemical properties of GO-based materials and graphite-based materials

Carbonaceous materials	SA^a (m^2/g)	O^b (wt. %)	C^b (wt. %)	N^b (wt. %)	C/O^b ratio	I_D/I_G^c
GO	207	31.4	67.3	1.30	2.14	1.38
RGO	241	17.3	78.4	4.3	4.53	0.98
graphite	5.58	4.30	95.0	0.53	22.1	0
oxidized graphite	97.1	33.5	67.5	-	2.01	1.41

498 ^a surface area measured using the Brunauer–Emmett–Teller (BET) method.499 ^b Analyzed with X-ray photoelectron spectroscopy.500 ^c Analyzed with Raman spectrometry.

501

502 **Table 2.** Protocols of reaction experiments in homogeneous aqueous solution and in the presence of GO-based materials and graphite-based materials.

exp. no.	Carbonaceous materials	C_{CM} (mg/L)	pH	pseudo-first order kinetic model		Freundlich-isotherm-based two-phase kinetic model			Langmuir-isotherm-based two-phase kinetic model		
				$k_{obs}^{b, c}$ (h ⁻¹)	R^2	$k_{s_F}^b$ (h ⁻¹)	k_{s_F}/k_a	R^2	$k_{s_L}^b$ (h ⁻¹)	k_{s_L}/k_a	R^2
1a	- ^a		7.0	0.37×10^{-3}	0.9863	-	-	-	-	-	-
1b	GO	20	7.0	0.39×10^{-3}	0.9864	0.026	71	0.9864	0.041	110	0.9871
1c	GO	100	7.0	0.47×10^{-3}	0.9929	0.021	56	0.9929	0.031	84	0.9933
1d	RGO	20	7.0	0.39×10^{-3}	0.9856	0.0017	4.6	0.9857	0.0018	4.8	0.9878
2a	- ^a		8.0	3.75×10^{-3}	0.9895	-	-	-	-	-	-
2b	GO	20	8.0	6.30×10^{-3}	0.9944	2.66	711	0.9958	4.51	1202	0.9895
2c	GO	100	8.0	7.12×10^{-3}	0.9948	0.674	179	0.9954	1.12	288	0.9862
2d	RGO	20	8.0	7.10×10^{-3}	0.9905	0.252	67	0.9905	0.258	69	0.9908
3a	- ^a		9.0	34.5×10^{-3}	0.9995	-	-	-	-	-	-
3b	GO	20	9.0	62.1×10^{-3}	0.9934	27	782	0.9894	28.5	826	0.9899
3c	GO	100	9.0	66.0×10^{-3}	0.995	6.17	178	0.9926	8.67	251	0.9906
3d	RGO	20	9.0	46.8×10^{-3}	0.9724	0.883	25.6	0.9715	0.551	16	0.9935
4a	graphite	400	8.0	4.50×10^{-3}	0.9809	-	-	-	-	-	-
4b	graphite	400	9.0	34.3×10^{-3}	0.9838	-	-	-	-	-	-
4c	oxidized graphite	400	8.0	6.60×10^{-3}	0.9878	0.4375	116	0.9877	0.376	100	0.9928
4d	oxidized graphite	400	9.0	51.9×10^{-3}	0.9723	2.6875	77.8	0.9721	1.97	57.1	0.9961

503 ^a No carbonaceous materials added (i.e., experiments conducted in homogeneous aqueous solution in the absence of carbonaceous materials).

504 ^b Values obtained by fitting reaction kinetic data using eqs 1, 2, or 3.

505 ^c For the experiments conducted in homogeneous aqueous solution (i.e., in the absence of carbonaceous materials), $k_{obs} = k_a$.

Fig. 1. Fourier-transform infrared (FTIR) spectra of (a) GO and RGO, and (b) oxidized graphite and pristine graphite; X-ray photoelectron spectra of C1s core levels of (c) GO, (d) RGO, and (e) oxidized graphite.

Fig. 2. Comparison of adsorption affinities of the four materials (GO, RGO, graphite, and oxidized graphite) within the concentration ranges covered in the reaction kinetics experiments. The q values were calculated using the C_w values observed in the reaction experiments and K_F and n values obtained in the isotherm experiments (Table S1).

Fig. 3. Changes of kinetic constants of dissolved 1,1,2,2-tetrachloroethane (k_a) and kinetic constants of the GO or RGO-adsorbed 1,1,2,2-tetrachloroethane (k_{s_F}) with pH.