



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Effect of surface, structural and textural properties of graphenic materials over cooperative and synergetic adsorptions of two chloroaromatic compounds from aqueous solution

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ARTICLE INFO

Keywords:

Intercalation
Surface interactions
Graphenic materials
Infrared spectroscopy
Adsorption
Catalysis

ABSTRACT

Graphenic materials have been recently applied for adsorption processes due to their high efficiency and their easy capability of surface modification. In the present study two different graphene oxides, two reduced graphene oxides under inert atmosphere and one reduced graphene oxide under ammonia atmosphere were used as adsorbents for removing two chloroaromatic compounds from water: 2,4-dichlorophenol and 2,4-dichlorophenoxyacetic acid. Hydrogen bonds and π - π interactions have been detected by Attenuated Total Reflectance infrared spectroscopy in the solids with adsorbed species. Besides, two direct relationships between their adsorption capacities and graphenic surface, textural and structural properties were found. In order to obtain real adsorption information, some experiments with the presence of both pollutants at the same time were performed. From these mixture experiments, when graphene oxide was used as adsorbent some cooperative effects between pollutants were detected. Based on XRD results and an innovative comparison between different infrared techniques, the importance of interlayer spaces during adsorption was demonstrated. Otherwise, synergetic interactions between pollutants were revealed as the main adsorption forces when reduced graphene oxides were used, being their aromatic structures a decisive factor in their final adsorption capacity.

1. Introduction

Nowadays, the decontamination and purification of water are considered very important topics to pay attention due to the high industrial and domestic applications. Multiple pollutants are presented together in the real environment [1], where adsorption and posterior catalysis processes are defined as some of the most effective methods to separate and eliminate contaminants from the liquid phase. Carbonaceous nanomaterials (CNMs) have been intensively studied as adsorbents in aqueous solutions since they exhibit many advantages in comparison to other adsorbents [2–4]: much larger surface areas, specific distribution of porosity, different shapes and forms, etc. However, molecular surface interactions between organic compounds and CNMs control their adsorption properties [5,6], where diverse functional groups of these materials have tremendous impacts on adsorption-catalysis processes [7]. Furthermore these interactions between materials and contaminants are relevant from the catalytically point of view, in particular if the graphenic materials are used as metal free catalysts [8,9]. In this line is important to notice their application for oxidation

reactions [10,11]. Thus, the oxidative treatments of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4-dichlorophenol (2,4-DCP) at the same time in water over carbon surfaces have not been reported yet. The 2,4-D pollutant is recognized as a prior contaminant to be removed from the residual water due to its vast used as a pesticide in different countries. As consequence of its multiple uses, it can be found into superficial and subterranean water over the world. Besides, its toxicity has a lot of secondary effects into the nervous and endocrine systems [12,13]. The synthesis procedure of the 2,4-D compound is based on different modifications of the 2,4-DCP.

Graphene is one of the main promising carbonaceous materials in nanotechnology due to its unique properties such as high strength, high electrical conductivity and facile modification [14,15]. Its planar structure permits the instantaneous full access to its active sites, minimizing problems of diffusion and making it a perfect material for adsorption process [16]. In contrast to graphene, graphene oxide (GO) contains higher degree of oxygen on its surface ($-\text{COOH}$, $-\text{OH}$, $-\text{C}=\text{O}$ groups), which can significantly interact and alter chemicals adsorption [17,18] and their catalytic behaviour. Due to the existence of oxygen

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<http://dx.doi.org/10.1016/j.cattod.2017.03.048>

Received 30 November 2016; Received in revised form 12 March 2017; Accepted 24 March 2017
0920-5861/ © 2017 Published by Elsevier B.V.

functional groups into GO layers, the intercalation of contaminants between them has to be reflected, given that they can be considered as very active sites of adsorption.

The purpose of this study is to prove the efficient adsorptive and co-adsorptive properties of different graphenic materials, emphasizing their exposed active surfaces and the effect of different type of starting size of graphite (10 and 325 mesh). The presence of surface functional groups (oxygen, nitrogen) and textural properties of the graphenic materials, are also evaluated in relation with their adsorption capacities. Besides, the effect of GO interlayers as active sites of contaminants intercalation is deeply discussed by a comparison of characterization techniques.

2. Experimental

2.1. Synthesis of materials

The synthesis of graphene oxide (GO10 and GO325) was carried out following a modified Brodie method [19]. Nitric fuming acid (200 mL) was added to 10 g of graphite in a crystal flask, and potassium chlorate (80 g) was slowly incorporated during a moderate stirring at 0 °C. After 21 h of reaction, the mixture was filtered and washing with double distilled water until almost pH = 6 and finally dried in a vacuum oven at 50 °C during 24 h. Thermal reduction of GO was carried out in a sample holder (approximately 300 mg) inside a horizontal cylindrical tube placed in an oven, in order to obtain reduced graphene oxides or few layer graphene (rGO10 and rGO325). The GO was purged with N₂ (at 100 mL/min) during 1 h and then it was heated up to 100 °C (at 5 °C/min) where it was kept during another one hour. Afterwards, temperature was reached to 300 °C (at 1 °C/min). Finally, samples were heated up to 500 °C (at 10 °C/min) and then cooled down to room temperature under an inert atmosphere. In order to incorporate nitrogen functional surface groups onto the surface, GO325 was thermally reduced under ammonia atmosphere (N-rGO325). The process was performed in a vertical fluid bed reactor. After one hour of purging the sample with N₂ (100 mL/min), a mixture of gases consisting in N₂ (87 mL/min), H₂ (3.5 mL/min) and NH₃ (10 mL/min) was fed to the reactor. Temperature ramp was the same as indicated for the synthesis of rGO from GO. These samples were used without previous grinding or sizing.

2.2. Characterization of materials

X-ray analysis (XRD) were performed using a Rayflex XRD 3100 instrument provided with CuK α X-rays ($\lambda = 1.54 \text{ \AA}$) and a Ni filter. Steps of 0.05° were employed with a time of 1 s per step and a 2 θ range of 5–95°. BET surface area (S_{BET}) values were determined by N₂ adsorption–desorption isotherms at 77 K. Previous to these measurements the samples were outgassed at 150 °C for 8 h. Measurements were done in a Micrometrics ASAP-2020 automatic apparatus. X-ray photoelectron (XPS) spectra were obtained in order to know the superficial composition of different adsorbent materials by means of an ESCA-PROBE P (Omicron) spectrometer. Each sample was gently pressed into a flat and homogeneous tablet, fixed in the sample holder, which was placed into the degasification chamber for 7 h to achieve a vacuum value of nearly 10⁻⁶ Pa before analyzing. As reference to correct the binding energies, it was used the peak of C1 s (BE = 284.6). Using XPS-CASA software it was possible to determine the relative concentrations and atomic ratios. Thermogravimetric (TG) analysis data were collected using a SDTQ600 5200 TA instrument. The samples were heated under flowing helium stream and the evolved gases were analyzed by an on-line mass quadrupole. Attenuated diffusive reflectance (ATR) measurements were collected using a Bruker, Vector 22 apparatus. It was collected 256 scans with a resolution of 4 cm⁻¹. The diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded by a MCT detector from 256 scans and with a resolution of

4 cm⁻¹. Spectrums were collected using a VARIAN 670 spectrometer equipped with a diffuse reflectance accessory. Samples were thoroughly grounded and mixed with pre-dried potassium bromide to a final concentration of approximately 1% (w/w).

2.3. Adsorption measurements

To obtain adsorption isotherms, different amounts of carbonaceous materials (10–100 mg) were put in contact with a defined concentration of contaminant solution in 0.05 L vessels. The thermostatic bath with the adsorption vessel was maintained at 23.0 ± 1 °C and operated at 200 oscillations per minute. Every sample was filtered with HPLV of 45 μm prior its measurement. 2,4-D and 2,4-DCP and their concentrations were analyzed by UV spectroscopy at 283 and 278 nm respectively in a Varian CARY 1 spectrophotometer. The experiments of mixture adsorption kinetics were carried out at different initial concentrations, 50 and 150 mg/L, 50/50%volume. Based on these kinetic determinations the equilibration times (20 min–1 day) were selected to assure the constant amount of solved chloroaromatic compound. Samples were analyzed by a High Pressure Liquid Chromatograph (HPLC) with a ZORBAX-RP C18 column accomplished with a UV–vis detector. To calculate the equilibrium adsorption capacity, the following equation was applied, where, q_e is referred to the adsorption capacity (mg/mg), C_0 (mg/L) is the initial pollutant concentration, C_e (mg/L) is the equilibrium concentrations, V is the solution volume (L) and m is the mass of the adsorbent (mg).

$$q_e = \frac{(C_0 - C_e) \cdot V}{m}$$

3. Results and discussion

3.1. Material characterization

The XRD results from the different synthesized materials are summarized in Table 1. After the oxidizing treatment, GO is formed and the main peak of graphite plane (002) is changed into lower 2 θ values. In Fig. S1 (A) and (B), XRD patterns of the different materials are depicted. The peak of the plane (100) of GO325 and GO10 is located at 15.21° and 16.09, respectively.

The increase of the interlaminar distance (d) of GO is due to two different simultaneous effects: i) different oxygen functional groups were produced and covalently bonded on the basal plane, modifying the carbon sp² hybridization into sp³, ii) some oxygen functional groups and water molecules are intercalated between graphenic layers of GO [20,21]. In Fig. S1, it can be seen that after thermal exfoliation of GO, the peak of the plane (001) has mainly disappeared, indicating that its structure has changed [22]. With this disruption of long-range periodic layered structure, a new solid is obtained, so, it can be assumed that reduced graphene oxide (rGO) was produced [23,24]. In Table 1 the calculation of the average number of layers before and after thermal reduction process is also summarized. This process was more effective for rGO325 (10 layers) than rGO10 (21 layers). In the case of rGO10 (Fig. S1 (B)), it can be also observed that there is a little broad peak at 24° due to the stacking of its graphene sheets. Its “ d ” value is higher

Table 1
XRD results and S_{BET} values.

MATERIALS	2 θ (°)	d (nm)	N°. layers	S_{BET} (m ² /g)
GO10	16.09	0.55	99	5
GO325	15.21	0.58	61	8
rGO10	24.67	0.36	21	400
rGO325	24.92	0.36	10	600
N-rGO325	26.45	0.35	28	225

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