

## Article

# Estimating the Reducing Power of Carbon Nanotubes and Granular Activated Carbon Using Various Compounds

Heesoo Woo <sup>1</sup> , Ilho Kim <sup>2</sup> and Saerom Park <sup>2,\*</sup>

<sup>1</sup> Center for Water Resource Cycle Research, Korea Institute of Science and Technology, Seoul 02792, Korea; ruis@kist.re.kr

<sup>2</sup> Department of Land, Water and Environment Research, Korea Institute of Civil Engineering and Building Technology, Goyang-si 10223, Korea; ihkim@kict.re.kr

\* Correspondence: srpark@kict.re.kr; Tel.: +82-31-910-0628

**Abstract:** Determining the degree of the reducing power of multi-walled carbon nanotubes (MWCNTs) and granular activated carbon (GAC) enables their effective application in various fields. In this study, we estimate the reducing power of carbon nanotubes (CNTs) and GAC by measuring the reduction degree of various compounds with different reduction potentials. MWCNTs and GAC materials can reduce Cr(VI), Fe(III) and  $\text{PMo}_{12}\text{O}_{40}^{3-}$ , where the reduction potentials range from +1.33 V to +0.65 V. However, no reduced forms of  $\text{PW}_{12}\text{O}_{40}^{3-}$  and  $\text{SiW}_{12}\text{O}_{40}^{4-}$  compounds were detected, indicating that the reducing power of MWCNTs and GAC is insufficient for reduction potentials in the range +0.218 V to +0.054 V. MWCNTs exhibit a short reduction time (5 min), whereas GAC exhibits a gradually increasing reduction degree of all the compounds assessed until the end of the reaction. This indicates a higher reduction degree than that of MWCNTs systems. Acidic initial pH values favor reduction, and the reduction degree increases as the pH becomes lower than 4.0. Moreover, large quantities of MWCNTs and GAC increase the concentrations of the reduced compounds.



**Citation:** Woo, H.; Kim, I.; Park, S. Estimating the Reducing Power of Carbon Nanotubes and Granular Activated Carbon Using Various Compounds. *Water* **2021**, *13*, 1959. <https://doi.org/10.3390/w13141959>

Academic Editors: Maria João Rosa and Rui M. C. Viegas

Received: 2 June 2021

Accepted: 14 July 2021

Published: 16 July 2021

**Publisher's Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

**Keywords:** multi-wall carbon nanotubes; granular activated carbon; reduction; adsorption; chromium; iron; polyoxometalate

## 1. Introduction

Carbon-based materials and their derivatives have been widely studied and used in various applications, due to their excellent adsorption ability, good conductivity, thermal and chemical stability and low cost [1,2]. Particularly, the use of carbon-based materials in water purification has received much attention in pollutant removal via adsorption, redox and catalytic reactions [3]. Among numerous carbon-based materials, granular activated carbon (GAC) and carbon nanotubes (CNTs) have been known as promising materials to remove inorganic [4,5] and organic compounds [6,7], due to their faster kinetics and higher reactivity than other common adsorbents. Moreover, GACs and CNTs can be regenerated and reused easily [8]. GAC materials are synthesized from raw materials such as fruit seeds, coconut shell, wood and lignin, and have high adsorption capacity in pollutant removal, owing to their very large inner surface area (800~1200 m<sup>2</sup>/g) induced by pore structures. The performance is determined by the internal pore structure, size and physico-chemical properties [9]. Another efficient material, cylindrical hollow CNTs, are different in that they have tubular morphologies with graphene layers [10]. Owing to this unique structure, they possess superior physical and chemical properties, such as large specific surface area, electrochemical stability and mechanical and electric properties, leading to many applications [7,11]. These CNTs can be divided into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) according to the number of layers. Removal of pollutants such as copper, silver, lead and nickel using pristine GAC and CNTs materials via adsorption has been studied extensively [12–14].

Recently, the use of functionalized GAC and CNTs produced via oxidative/acidic treatment or addition of metals has also received considerable attention as adsorbents, electron donors and electron-transfer mediators [15–20]. Modification of GAC and CNTs via acid treatment improves the adsorption of heavy metals, by inducing electrostatic attraction between the metallic ions and newly introduced functional groups such as –OH, –C=O and –COOH on their surfaces [21–23]. Such modified CNTs and GAC can also serve as catalysts or reductants that mineralize the target contaminants [24]. Some studies have previously verified their role as electron donors, exhibiting metal reduction [25–27] under certain conditions. However, systematic studies on estimating the reducing power are lacking. Estimating the reducing power of GAC and CNTs may provide insights into their applicability in redox reactions. To address this issue, we evaluated the reducing power of GAC and CNTs using various compounds with different reduction potentials (i.e., Cr(VI) ( $E^0 = +1.33$  V), Fe(III) ( $E^0 = +0.77$  V) and  $\text{PMo}_{12}\text{O}_{40}^{3-}$  ( $E^0 = +0.65$  V),  $\text{PW}_{12}\text{O}_{40}^{3-}$  ( $E^0 = +0.218$  V) and  $\text{SiW}_{12}\text{O}_{40}^{4-}$  ( $E^0 = +0.054$  V)) in this study, and estimated their reduction potentials (Figure 1) [28–30]. Chromium commonly requires the removal and/or reduction of Cr(VI) to Cr(III) in water treatment due to its toxicity and Fe(III) was selected owing to its easy-accessibility [31,32]. For other polyoxometalates, given that they have unique chemical structure, polynuclear metal-oxo clusters with discrete and chemically modifiable structures, the intention of choosing these compounds was to investigate if CNTs and GAC are able to reduce them regardless of their unique chemical structures [33]. In addition, the effect of several experimental factors such as the initial pH and dosage of GAC and CNTs on the reducing power were investigated.

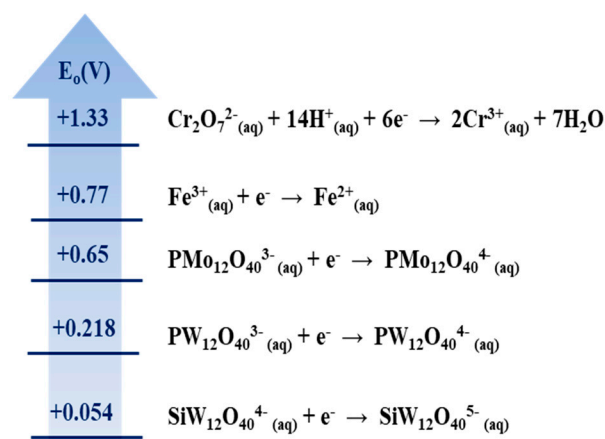


**Figure 1.** Reduction potential of various compounds used in this study.

## 2. Materials and Methods

### 2.1. Reagents

Analytical-reagent-grade chemicals were used without further purification, except for carbonaceous materials. The chemicals used in this study include MWCNTs (Comocat or Hanhwa), SWCNTs (Nanolab), GAC (Daejung), iron(II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Sigma-Aldrich), iron(III) perchlorate hydrate ( $\text{Fe}(\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ , Sigma-Aldrich), phosphotungstic acid ( $\text{HNa}_2\text{PW}_{12}\text{O}_{40}$ , Fluka), tungstosilicic acid ( $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ , Fluka), phosphomolybdic acid ( $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ , Fluka), sodium dichromate dihydrate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ , Sigma-Aldrich, St. Louis, MI, USA), chromium trichloride hexahydrate ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , Sigma-Aldrich), 1,10-phenanthroline (Sigma-Aldrich), ammonium acetate ( $\text{CH}_3\text{COONH}_4$ , Sigma-Aldrich), sodium acetate ( $\text{CH}_3\text{COONa}$ , Sigma-Aldrich), acetic acid ( $\text{CH}_3\text{COOH}$ , Sigma-Aldrich), 1,5-diphenylcarbazide (Sigma-Aldrich), acetone (J.T. Baker), potassium permanganate ( $\text{KMnO}_4$ , Sigma-Aldrich), hydrochloric acid ( $\text{HCl}$ , Sigma-Aldrich), sulfuric acid ( $\text{H}_2\text{SO}_4$ , Sigma-Aldrich), perchloric acid ( $\text{HClO}_4$ , Sigma-Aldrich) and sodium hydroxide ( $\text{NaOH}$ , Sigma-Aldrich). All solutions were prepared using deionized water obtained from a Milli-Q ultrapure water-purification system ( $>18.2$  M $\Omega$ ·cm, Millipore, Burlington,

MA, USA), and stored at 4 °C prior to use. All the carbonaceous materials used in this study were immersed in 1 M HCl for approximately 2 min, and then filtered and washed with deionized water and dried in the oven at 333.15 K for 10 h prior to use.

## 2.2. Experimental Setup and Procedure

All experiments on redox reactions of carbonaceous materials were conducted in 100 mL-Erlenmeyer flasks under continuous N<sub>2</sub> purging to maintain an anaerobic condition. Each flask contained a 100 mL reaction solution prepared from an aliquot of a predetermined amount of stock solution in desired concentrations (0.1–1.0 mM). The initial pH was adjusted using 1 M HClO<sub>4</sub> or 1 M NaOH solutions. To initiate the redox reactions, a designated amount of carbonaceous materials was added to the solution to achieve the concentration of 0.1–2.0 g/L, and the suspension underwent vigorous magnet-mixing. In addition, 1 mL of suspension was withdrawn at each sampling and immediately filtered using a 0.45 µm PTFE syringe. The suspension was then analyzed to measure the concentrations of dissolved Fe(II), Cr(III) and Cr(VI), and reduced polyoxometalates (POM) anions.

## 2.3. Analytical Methods

The Brunauer-Emmett-Teller surface area, pore volume, and average pore size of carbonaceous materials were determined by adsorbing N<sub>2</sub> gas molecules at 77 K using an ASAP 2420 system (Micromeritics Instrument). The concentration of dissolved Fe(II) (Supplementary Materials) was determined using the 1,10-phenanthroline method [34]. In addition, Cr(VI) was analyzed by the 1,5-diphenylcarbazide method [35]. The concentration of total chromium (Cr(III) plus Cr(VI)) in the solution was measured when necessary, according to the method for the Cr(VI) measurement described above. However, in this case, the remaining Cr(III) was intentionally oxidized to Cr(VI) by adding several drops of 10 mM KMnO<sub>4</sub> oxidant to the sample. The concentration of Cr(III) was determined from the difference between the concentrations of total chromium (Cr(III), Cr(VI)) and Cr(VI). The details of Fe(II) and Cr(VI) measurements are described in Section 1 of the (supporting information, SI). The reduced POM (PW<sub>12</sub>O<sub>40</sub><sup>4−</sup>, SiW<sub>12</sub>O<sub>40</sub><sup>5−</sup> and PMo<sub>12</sub>O<sub>40</sub><sup>4−</sup>) were monitored by measuring the UV/visual absorption spectra at 730 nm using a UV–vis spectrophotometer (S-3100, Sinco). All experiments were conducted in duplicate or triplicate, and the means with standard deviations were taken as the results.

## 3. Results and Discussion

### 3.1. Estimating the Reducing Power of CNTs and GAC Using Various Compounds

To compare the reducing power of CNTs, two MWCNTs (Hanwha and Comocat) and an SWCNT (nano-lab) were applied in the reduction of Fe(III) to Fe(II) (Figure 2). By comparing the two differently manufactured MWCNTs (Hanwha vs. Comocat), no significant difference in the Fe(II) concentration was observed in 20 min of reaction. At a longer reaction time (60 min), MWCNT-Hanwha showed gradually increasing Fe(II) concentration up to 0.1 mM and no significant change was observed in the Fe(II) concentration for MWCNT-Comocat. In the comparison of the reducing capacity of MWCNTs with that of SWCNTs, a small discrepancy was observed in the reduction degree of Fe(III) until 20 min, whereas SWCNTs measured the less and more Fe(II) concentrations at 60 min than the systems of MWCNT-Hanwha and MWCNT-Comocat, respectively (Figure 2). Considering that MWCNTs are less toxic and more cost-effective than SWCNTs [36,37], we used the MWCNT-Comocat as a representative CNT for the reduction of other compounds.

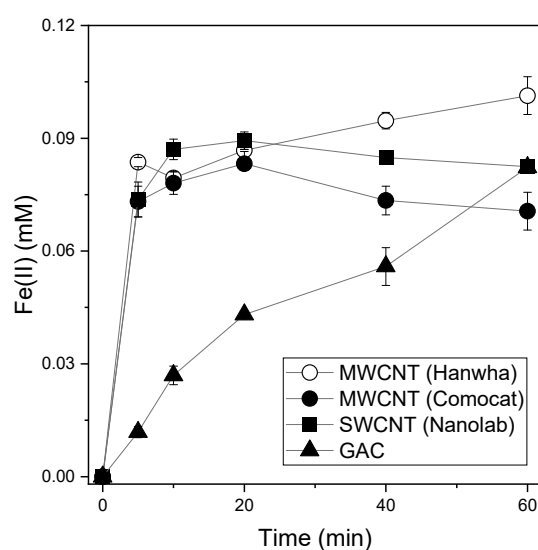


**Figure 2.** Reduction of Fe(III) to Fe(II) by GAC and various CNTs at acidic pH conditions ( $[\text{Fe(III)}]_0 = 0.2 \text{ mM}$ ,  $[\text{CNT}]_0 = [\text{GAC}]_0 = 1 \text{ g/L}$ ,  $\text{pH}_0 = 3$ , anaerobic condition, [reaction time = 60 min]).

The reducing power of MWCNTs and GAC was estimated and compared by measuring the concentration of the reduced forms of all the assessed compounds. In addition, the reduction degree (%) of the compounds was quantified using Equation (1) at reaction times of 5 min and 60 min, which are representative of early and longer reaction times, respectively. For the  $\text{PMo}_{12}\text{O}_{40}^{3-}$  compound, the reduction degree was estimated by comparing the degree of absorbance measured at the initial and sampling times.

$$\frac{\text{concentration/absorbance of the reduced forms measured}}{\text{initial concentration/absorbance of the target compound}} \times 100\% = \text{reduction degree}(\%) \quad (1)$$

MWCNTs and GAC materials were able to reduce compounds having reduction potentials  $E^0 = +1.33 \text{ V}$  ( $\text{Cr(VI)} \rightarrow \text{Cr(III)}$ ) to  $E^0 = +0.65 \text{ V}$  ( $\text{PMo}_{12}\text{O}_{40}^{3-} \rightarrow \text{PMo}_{12}\text{O}_{40}^{4-}$ ). However, the reduced forms of  $\text{PW}_{12}\text{O}_{40}^{3-}$  and  $\text{SiW}_{12}\text{O}_{40}^{4-}$  were not detected in both systems, indicating that MWCNTs and GAC could not reduce compounds with reduction potentials less than  $+0.218 \text{ V}$  (Figures S1 and S2 in SI). By comparing the reducing power of MWCNTs and GAC at the early stage (5 min reaction time), MWCNTs showed a higher reduction degree (%) than that of GAC for Fe(III) and  $\text{PMo}_{12}\text{O}_{40}^{3-}$ . However, no difference in the reduction degree (%) for Cr(VI) was observed between MWCNTs and GAC systems (Figure 3a). However, at the long reaction time (60 min), GAC showed higher reducing capability than that of MWCNTs, showing 70%, 40% and 30% reduction of Cr(VI), Fe(III) and  $\text{PMo}_{12}\text{O}_{40}^{3-}$ , respectively (Figure 3b). Thus, it can be said that while MWCNTs exhibit strong reducing power in short periods, GAC requires longer reaction times to exhibit a continuous increase in the reducing power. The reducing power of GAC is mostly higher than that of MWCNTs at the final reaction time (Figure 1, Figures S1 and S2). Even though GAC possesses a higher specific surface area than MWCNTs (Table 1), it contains numerous inaccessible micropores in aggregated form, which requires the diffusion of target compounds into the internal porous structure [38–40]. In contrast with GAC materials, MWCNTs exhibit a high available surface area for the target compounds on both their external surfaces and loose bundles/aggregate forms [40,41]. Therefore, MWCNTs may be advantageous for fast redox reactions, whereas GAC requires diffusion and contact time for the adsorption and reduction of the compounds due to the unique porous structure. This hypothesis is also supported by the results of chromium adsorption ( $\text{Cr}_{\text{total}} = \text{Cr(VI)} + \text{Cr(III)}$ ) (Figure 4). MWCNTs showed the fastest adsorption of  $\text{Cr}_{\text{total}}$  in 5 min, and no significant change of the  $\text{Cr}_{\text{total}}$  adsorption degree until 60 min was observed. GAC exhibited steadily increasing  $\text{Cr}_{\text{total}}$  adsorption degree during the whole reaction time (Figure 4). Interestingly, even though GAC showed a higher reduction degree of

Cr(VI) than that of MWCNTs, a lesser adsorption degree of  $\text{Cr}_{\text{total}}$  was observed in the GAC system than the MWCNT systems, even at a long reaction time (60 min). Likely, not all of the adsorbed Cr(VI) onto the MWCNTs is reduced, and thus, a portion of the adsorbed Cr(VI) may remain as an adsorption phase without reduction. However, this requires further verification.

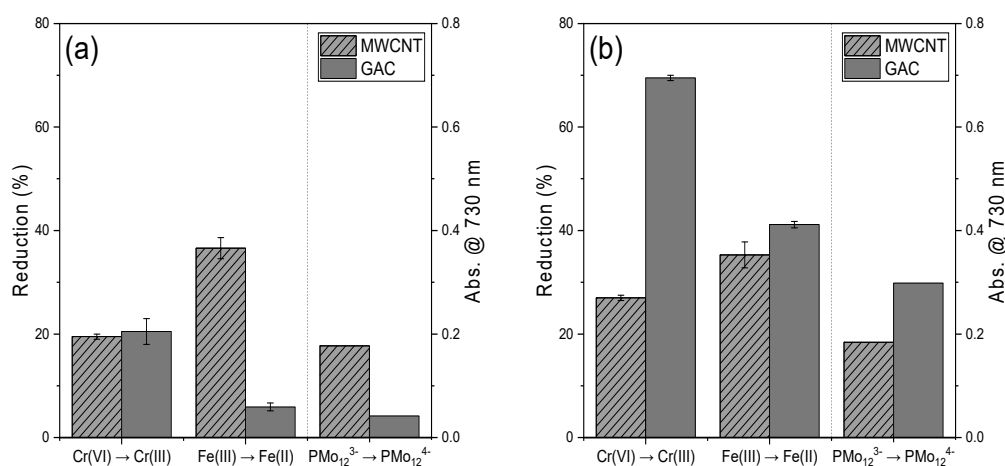


**Figure 3.** Reduction % of Cr(VI), Fe(III) and UV absorbance appearance at 730 nm with reduction of  $\text{PMo}_{12}\text{O}_{40}^{3-}$  by MWCNT and GAC at acidic pH condition, respectively, (a) at 5 min and (b) at 60 min ( $[\text{Fe(III)}]_0 = 0.2 \text{ mM}$ ,  $[\text{Cr(VI)}]_0 = 0.1 \text{ mM}$ ,  $[\text{PMo}_{12}\text{O}_{40}^{3-}]_0 = 1.0 \text{ mM}$ ,  $[\text{CNT}]_0 = [\text{GAC}]_0 = 2.0 \text{ g/L}$ ,  $\text{pH}_0 = 3$ , anaerobic condition, [reaction time = 6 and 60 min]).

**Table 1.** Detailed characteristics of MWCNTs and GAC.

| Carbon-Based Materials | BET Specific Surface Area ( $\text{m}^2/\text{g}$ ) | Pore Volume ( $\text{m}^3/\text{g}$ ) | Average Pore Size (nm) |
|------------------------|-----------------------------------------------------|---------------------------------------|------------------------|
| MWCNTs                 | 236.25                                              | 1.92                                  | 32.53 (Mesoporous)     |
| GAC                    | 648.24                                              | 0.26                                  | 1.63 (Microporous)     |

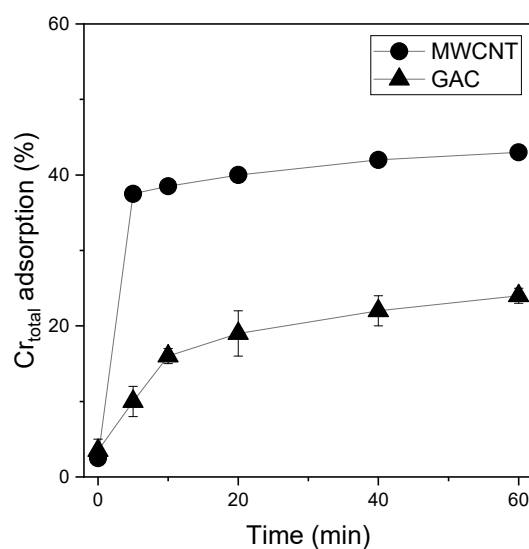


**Figure 4.** Adsorption of  $\text{Cr}_{\text{total}}$  onto the surface of MWCNT and GAC, respectively, at acidic pH condition ( $[\text{Cr(VI)}]_0 = 0.1 \text{ mM}$ ,  $[\text{MWCNT-Comocat}]_0 = [\text{GAC}]_0 = 2.0 \text{ g/L}$ ,  $[\text{pH}_0 = 2.5]$ , anaerobic condition).

In Figure 3a, we consider that Cr(VI) tends to be relatively readily reduced among the compounds assessed due to its high reduction potential ( $E^\circ = +1.33 \text{ V}$ ). GAC can reduce

Cr(VI) to Cr(III) in a short time (5 min), equivalent to that of MWCNTs and showing no difference in the Cr(VI) reduction degree between MWCNTs and GAC. In addition, at long reaction time (60 min), GAC showed about 2.5 and 1.5 times higher reduction degree (%) for Cr(VI) and  $\text{PMo}_{12}\text{O}_{40}^{3-}$  than MWCNTs, respectively. The MWCNTs exhibited approximately 1.1 times higher reduction degree of Fe(III) than that of GAC showed (Figure 3b). It is hypothesized that the dissolved Fe(III) ions may be beneficial for adsorption to on the reactive surface area and/or the pore structure of MWCNTs, due to its smaller molar mass (molar mass: 55.845 g/mol) than other compounds ( $\text{Cr}_2\text{O}_7^{2-}$ , molar mass: 386.92 g/mol and  $\text{PMo}_{12}\text{O}_{40}^{3-}$ , molar mass: 1822.470 g/mol). This leads to the increasing reduction degree, which is almost equivalent to that of GAC [41,42].

### 3.2. Effect of Initial pH on the Reducing Power of MWCNTs and GAC

The generated concentrations of the reduced forms such as Cr(III), Fe(II) and  $\text{PMo}_{12}\text{O}_{40}^{4-}$  were measured at various pH conditions from pH 2 to pH 7 (Figure 5). In the range of pH values 5–7, the reduced forms of the compounds were not detected in both the MWCNTs and GAC systems. For the MWCNT systems, significantly increasing concentrations of the reduced compounds were observed as the pH decreased from pH 4 to 2. However, GAC did not show the reduction of Cr(VI), Fe(III) and  $\text{PMo}_{12}\text{O}_{40}^{3-}$  in this pH range (Figure 5). This indicates that the reducing power of MWCNTs was more sensitively influenced by the pH condition than that of GAC systems.

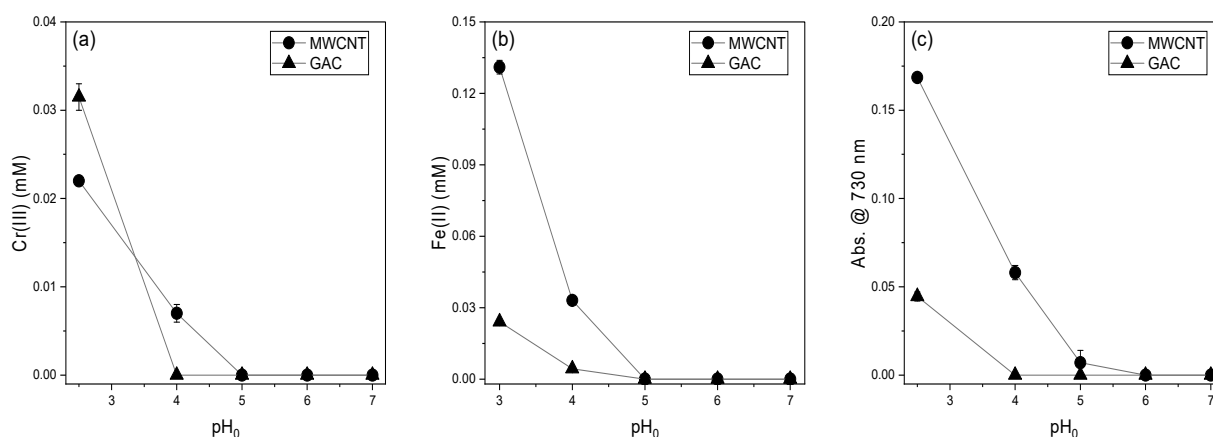


**Figure 5.** Reduction of (a) Cr(VI), (b) Fe(III) and (c)  $\text{PMo}_{12}\text{O}_{40}^{3-}$  at different initial pH conditions ( $[\text{Cr(VI)}]_0 = [\text{Fe(III)}]_0 = [\text{PMo}_{12}\text{O}_{40}^{3-}]_0 = 0.1 \text{ mM}$ ,  $[\text{MWCNT-Comocat}]_0 = [\text{GAC}]_0 = 2.0 \text{ g/L}$ ,  $[\text{pH}_0] = 2.5\text{--}7$ , anaerobic condition, [reaction time = 5 min for Fe(III), 60 min for Cr(VI), 120 min for  $\text{PMo}_{12}\text{O}_{40}^{3-}$ ]).

There are two possible reasons why the acidic initial pH condition is favorable for the reduction reactions in both the MWCNTs and GAC systems. Considering that most metals exist in soluble forms such as  $\text{Fe}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{HCrO}_4^-$  and  $\text{Cr}^{3+}$  or  $\text{Cr}(\text{H}_2\text{O})_6^{3+}$  at decreasing pH conditions ( $<\text{pH } 4$ ), increasing pH conditions can generate insoluble metal-hydroxide precipitates such as  $\text{Fe}(\text{OH})_n^{3-n}$  and  $\text{Cr}(\text{OH})_x$ . We hypothesized that soluble forms of metals may be more beneficial to adsorption and reduction reactions in the MWCNTs and GAC systems [43,44]. The other possible reason is that the reduction reaction may consume protons according to the corresponding redox reaction equations, such as in the chromium compound (Figure 1) [45]. In case of POM compounds, it is known that a single electron transfer occurs under neutral pH conditions, and two electrons are transferred under highly acidic pH conditions. Thus, acidic conditions can increase the driving force to trigger reduction reactions [46,47].

### 3.3. Effect of MWCNTs and GAC Dosage on the Reducing Power

Regarding the effect of the dosing amount of MWCNTs and GAC on the reducing power, increasing amounts of carbonaceous materials resulted in high concentrations of

the reduced forms of all compounds (Figure 6). However, GAC materials did not induce the reduction of  $\text{PMo}_{12}\text{O}_{40}^{3-}$  until 1.0 g/L of GAC was applied. Then, increasing reducing power was observed at 2.0 g/L of GAC concentration. Given that it is relatively difficult to reduce  $\text{PMo}_{12}\text{O}_{40}^{3-}$  due to its low reduction potential, it is likely that the reducing power of GAC at 1.0 g/L concentration might not have been enough to initiate the reduction of  $\text{PMo}_{12}\text{O}_{40}^{3-}$ . In contrast with  $\text{PMo}_{12}\text{O}_{40}^{3-}$ , no difference in the Cr(III) concentration measured between MWCNTs and GAC systems was observed up to doses of 0.5 g/L (Figure 6). This is also related to the reduction tendency of the target compound, which means that the amount of reductants such as MWCNTs and GAC is not a limiting factor to determine the reduction degree in the presence of easily reduced compounds with high reduction potential.

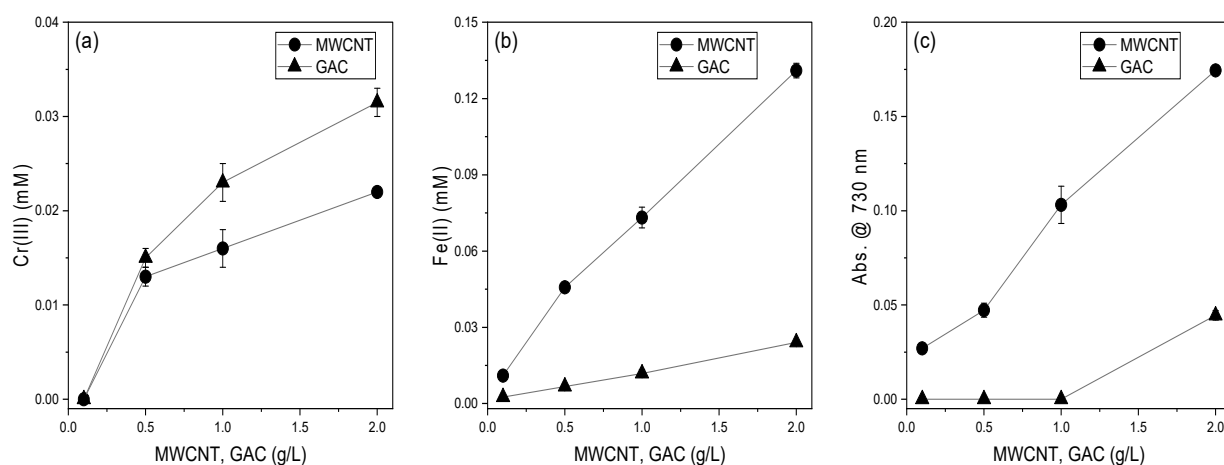


**Figure 6.** Reduction of (a) Cr(VI), (b) Fe(III) and (c)  $\text{PMo}_{12}\text{O}_{40}^{3-}$  at different dosage of MWCNT and GAC applied ( $[\text{Cr(VI)}]_0 = [\text{Fe(III)}]_0 = [\text{PMo}_{12}\text{O}_{40}^{3-}]_0 = 0.1 \text{ mM}$ ,  $[\text{MWCNT-Comocat}]_0 = [\text{GAC}]_0 = 0.1, 0.5, 1.0, 2.0 \text{ g/L}$ ,  $[\text{pH}_0 = 2.5\text{--}3]$ , anaerobic condition, [reaction time = 5 min for Fe(III), 60 min for Cr(VI), 120 min for  $\text{PMo}_{12}\text{O}_{40}^{3-}$ ]).

#### 4. Conclusions

In this study, the reducing capability of CNTs (MWCNTs) and GAC was indirectly determined using the reduction degree of five compounds with different reduction potentials. Our findings show that both MWCNTs and GAC were able to reduce Cr(VI), Fe(III) and  $\text{PMo}_{12}\text{O}_{40}^{3-}$ , where the reduction potentials range from +1.33 V to +0.65 V. However, they failed to reduce  $\text{PW}_{12}\text{O}_{40}^{3-}$  and  $\text{SiW}_{12}\text{O}_{40}^{4-}$  with reduction potentials +0.218 V and +0.054 V, respectively. This is likely that the difference on the reduction potentials between CNTs/GAC and  $\text{PW}_{12}\text{O}_{40}^{3-}$ / $\text{SiW}_{12}\text{O}_{40}^{4-}$  was not enough to induce electron transfer. In addition, while MWCNTs exhibit potent reducing power in a short period (5 min), GAC consistently increased the reduction degree. This observation led us to hypothesize that MWCNTs have easily accessible external and internal reactive sites for target compounds, whereas GAC requires diffusion and contact time for the adsorption and reduction of the compounds, due to their unique pore structure. This hypothesis was also supported by the adsorption study of  $\text{Cr}_{\text{total}}$ , where fast saturation was observed in the MWCNTs systems (5 min) and gradually increasing adsorption of  $\text{Cr}_{\text{total}}$  was observed in the GAC systems. Moreover, acidic initial pH conditions were more favorable for the reduction reaction, and large quantities of MWCNTs and GAC induced a high reduction rate as expected.

Carbon is the most common chemical element and the materials made by carbon can be obtained in an eco-friendly and low-cost procedure [48,49]. Even though carbon-based materials such as MWCNTs and GAC may be not the best beneficial materials in terms of cost when they were used as reductants in water treatment, this study estimating the range of their reducing powers was able to provide an insight into their many applications not only as adsorbents but also as reductants and catalysts. In addition, it is expected that these easily available carbonaceous materials can function as activators in reducing

peroxymonosulfate and peroxydisulfate oxidants by generating various types. This is an issue that needs further investigation. This will be beneficial to water purification via redox reactions using carbon-based materials.

**Supplementary Materials:** The following are available online at <https://www.mdpi.com/article/10.3390/w13141959/s1>, Section 1. The methods for measuring the concentration of Fe(II) and Cr(VI) were modified from Tamura et al. (1974) and Clesceri et al. (1998), respectively; Figure S1. Reduction of Cr(VI) to Cr(III) by MWCNT and GAC at acidic pH condition ( $[\text{Cr(VI)}]_0 = 0.1 \text{ mM}$ ,  $[\text{MWCNT-Comocat}]_0 = [\text{GAC}]_0 = 2.0 \text{ g/L}$ ,  $[\text{pH}_0 = 2.5]$ , anaerobic condition, [reaction time = 60 min]). Figure S2. Time profile of  $\text{PW}_{12}\text{O}_{40}^{4-}$ ,  $\text{SiW}_{12}\text{O}_{40}^{5-}$  and  $\text{PMo}_{12}\text{O}_{40}^{4-}$  production in the presence of MWCNT and GAC systems at acidic pH condition ( $[\text{PW}_{12}\text{O}_{40}^{3-}]_0 = [\text{SiW}_{12}\text{O}_{40}^{4-}]_0 = [\text{PMo}_{12}\text{O}_{40}^{3-}]_0 = 1.0 \text{ mM}$ ,  $[\text{MWCNT-Comocat}]_0 = 2.0 \text{ g/L}$ ,  $[\text{pH}]_0 = 2.5$ , anaerobic condition, [reaction time = 120 min]).

**Author Contributions:** H.W. performed most of experiments and wrote the manuscript. I.K. conducted the literature analyses and provided the constructive discussion on this study. S.P. contributed to the concept of the study and writing-review, editing, supervision of this study. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was supported by the Korea Ministry of Environment (MOE) as “Development of ozonated micro-bubble (AOPs) combined with flexible ceramic membrane process to treat non-degradable compounds” research program (2021003040001) and “Aquatic Ecosystem Conservation Research Program” (2021003040002).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available upon request from the corresponding author.

**Acknowledgments:** Authors are very grateful for the funds [project: 2021003040001 and 2021003040002] provided by the Korea Ministry of Environment.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

- Chen, Q.; Wang, X.; Yi, P.; Zhang, P.; Zhang, L.; Wu, M.; Pan, B. Key Roles of Electron Cloud Density and Configuration in the Adsorption of Sulfonamide Antibiotics on Carbonaceous Materials: Molecular Dynamics and Quantum Chemical Investigations. *Appl. Surf. Sci.* **2021**, *536*, 147757. [\[CrossRef\]](#)
- Wei, C.; Akinwalemiwa, B.; Yu, L.; Hu, D.; Chen, G.Z. 7-Polymer Composites with Functionalized Carbon Nanotubes and Graphene. In *Polymer Composites with Functionalized Nanoparticles Synthesis, Properties, and Applications Micro and Nano. Technologies*; Elsevier: Amsterdam, The Netherlands, 2019; pp. 211–248.
- Bartoli, M.; Frediani, M.; Rosi, L. *Carbon-Based Material for Environmental Protection and Remediation*; IntechOpen: London, UK, 2020.
- Huang, Y.; Lee, X.; Macazo, F.C.; Grattieri, M.; Cai, R.; Minter, S.D. Fast and Efficient Removal of Chromium (VI) Anionic Species by a Reusable Chitosan-Modified Multi-Walled Carbon Nanotube Composite. *Chem. Eng. J.* **2018**, *339*, 259–267. [\[CrossRef\]](#)
- Ko, Y.J.; Choi, K.; Lee, S.; Cho, J.M.; Choi, H.J.; Hong, S.W.; Choi, J.W.; Mizuseki, H.; Lee, W.S. Chromate Adsorption Mechanism on Nanodiamond-Derived Onion-Like Carbon. *JHM* **2016**, *320*, 368–375. [\[CrossRef\]](#)
- Peng, J.; He, Y.; Zhou, C.; Su, S.; Lai, B. The Carbon Nanotubes-Based Materials and Their Applications for Organic Pollutant Removal: A Critical Review. *Chin. Chem. Lett.* **2020**, *32*, 1626–1636. [\[CrossRef\]](#)
- Kurwadkar, S.; Hoang, T.V.; Malwade, K.; Kanel, S.R.; Harper, W.F., Jr.; Struckhoff, G. Application of Carbon Nanotubes for Removal of Emerging Contaminants of Concern in Engineered Water and Wastewater Treatment Systems. *Nanotechnol. Environ. Eng.* **2019**, *4*, 12. [\[CrossRef\]](#)
- Larasati, A.; Fowler, G.D.; Graham, N.J.D. Chemical regeneration of granular activated carbon: Preliminary evaluation of alternative regenerant solutions. *Environ. Sci. Water Res. Technol.* **2020**, *6*, 2043–2056. [\[CrossRef\]](#)
- Sonthimer, H.; Crittenden, J.C.; Summers, R.S.; Frick, B.R.; Fettig, J.; Hörner, G.; Hubele, C.; Zimmer, G. *Activated Carbon for Water Treatment*, 2nd ed.; DVGW-Forschungstelle: Karlsruhe, Germany, 1988.
- Ajayan, P.M. Nanotubes from Carbon. *Chem. Rev.* **1999**, *99*, 1787–1800. [\[CrossRef\]](#)
- Thostenson, E.T.; Ren, Z.; Chou, T.W. Advances in the Science and Technology of Carbon Nanotubes and Their Composites: A Review. *Compos. Sci. Technol.* **2001**, *61*, 1899–1912. [\[CrossRef\]](#)
- Yu, J.G.; Zhao, X.H.; Yu, L.Y.; Jiao, F.P.; Jiang, J.H.; Chen, X.Q. Removal, Recovery and Enrichment of Metals from Aqueous Solutions Using Carbon Nanotubes. *J. Radioanal. Nucl. Chem.* **2014**, *299*, 1155–1163. [\[CrossRef\]](#)

13. Shahrokhi-Shahraki, R.; Benally, C.; El-Din, M.G.; Park, J.B. High Efficiency Removal of Heavy Metals Using Tire-Derived Activated Carbon vs Commercial Activated Carbon: Insights into the Adsorption Mechanisms. *Chemosphere* **2021**, *264*, 128455. [[CrossRef](#)]
14. Chai, W.S.; Cheun, J.Y.; Kumar, P.S.; Mubashir, M.; Majeed, Z.; Banat, F.; Ho, S.H.; Show, P.L. A Review on Conventional and Novel Materials Towards Heavy Metal Adsorption in Wastewater Treatment Application. *J. Clean. Prod.* **2021**, *296*, 126589. [[CrossRef](#)]
15. Feng, D.; Guo, D.; Zhang, Y.; Sun, S.; Zhao, Y.; Shang, Q.; Sun, H.; Wu, J.; Tan, H. Functionalized Construction of Biochar with Hierarchical Pore Structures and Surface O-/N-containing Groups for Phenol Adsorption. *Chem. Eng. J.* **2021**, *410*, 127707. [[CrossRef](#)]
16. Masjoudi, M.; Golgoli, M.; Ghobadi Nejad, Z.G.; Sadeghzadeh, S.; Borghei, S.M. Pharmaceuticals Removal by Immobilized Laccase on Polyvinylidene Fluoride Nanocomposite with Multi-Walled Carbon Nanotubes. *Chemosphere* **2021**, *263*, 128043. [[CrossRef](#)] [[PubMed](#)]
17. Li, F.; Liu, L.; Yang, Z.; Li, S. Physical and Mechanical Properties and Micro Characteristics of Fly Ash-Based Geopolymer Paste Incorporated with Waste Granulated Blast Furnace Slag (GBFS) and Functionalized Multi-Walled Carbon Nanotubes (MWCNTs). *J. Hazard. Mater.* **2021**, *401*, 123339. [[CrossRef](#)]
18. Marques, R.R.N.; Machado, B.F.; Faria, J.L.; Silva, A.M.T. Controlled Generation of Oxygen Functionalities on the Surface of Single-Walled Carbon Nanotubes by HNO<sub>3</sub> Hydrothermal Oxidation. *Carbon* **2010**, *48*, 1515–1523. [[CrossRef](#)]
19. Romanos, G.E.; Likodimos, V.; Marques, R.R.N.; Steriotis, T.A.; Papageorgiou, S.K.; Faria, J.L.; Figueiredo, J.L.; Silva, A.M.T.; Falaras, P. Controlling and Quantifying Oxygen Functionalities on Hydrothermally and Thermally Treated Single-Wall Carbon Nanotubes. *J. Phys. Chem. C* **2011**, *115*, 8534–8546. [[CrossRef](#)]
20. Likodimos, V.; Steriotis, T.A.; Papageorgiou, S.K.; Romanos, G.E.; Marques, R.R.N.; Rocha, R.P.; Faria, J.L.; Pereira, M.F.R.; Figueiredo, J.L.; Silva, A.M.T.; et al. Controlled Surface Functionalization of Multiwall Carbon Nanotubes by HNO<sub>3</sub> Hydrothermal Oxidation. *Carbon* **2014**, *69*, 311–326. [[CrossRef](#)]
21. Atieh, M.A.; Bakather, O.Y.; Tawabini, B.S.; Bukhari, A.A.; Khaled, M.; Alharthi, M.; Fettouhi, M.; Abuilaiwi, F.A. Removal of Chromium (III) from Water by Using Modified and Nonmodified Carbon Nanotubes. *J. Nanomater.* **2010**, *2010*, 232378. [[CrossRef](#)]
22. El-Sheikh, A.H.; Al-Degs, Y.S.; Sweileh, J.A.; Said, A.J. Separation and Flame Atomic Absorption Spectrometric Determination of Total Chromium and Chromium (III) in Phosphate Rock Used for Production of Fertilizer. *Talanta* **2013**, *116*, 482–487. [[CrossRef](#)]
23. Yang, S.; Wang, X.; Yang, H.; Sun, Y.; Liu, Y. Influence of the Different Oxidation Treatment on the Performance of Multi-Walled Carbon Nanotubes in the Catalytic Wet Air Oxidation of Phenol. *J. Hazard. Mater.* **2012**, *233–234*, 18–24. [[CrossRef](#)]
24. Bach, A.; Semiat, R. The Role of Activated Carbon as a Catalyst in GAC/Iron Oxide/H<sub>2</sub>O<sub>2</sub> Oxidation Process. *Desalination* **2011**, *273*, 57–63. [[CrossRef](#)]
25. Seo, J.; Lee, H.J.; Lee, H.; Kim, H.E.; Lee, J.Y.; Kim, H.S.; Lee, C. Enhanced Production of Reactive Oxidants by Fenton-Like Reactions in the Presence of Carbon Materials. *Chem. Eng. J.* **2015**, *273*, 502–508. [[CrossRef](#)]
26. Peng, J.; Xue, J.; Li, J.; Du, Z.; Wang, Z.; Gao, S. Catalytic Effect of Low Concentration Carboxylated Multi-Walled Carbon Nanotubes on the Oxidation of Disinfectants with Cl-Substituted Structure by a Fenton-Like System. *Chem. Eng. J.* **2017**, *321*, 325–334. [[CrossRef](#)]
27. Yang, Z.; Yu, A.; Shan, C.; Gao, G.; Pan, B. Enhanced Fe(III)-Mediated Fenton Oxidation of Atrazine in the Presence of Functionalized Multi-Walled Carbon Nanotubes. *Water Res.* **2018**, *137*, 37–46. [[CrossRef](#)]
28. Pope, M.T.; Varga, G.M., Jr. Heteropoly Blues. I. Reduction Stoichiometries and Reduction Potentials of Some 12-Tungstates. *Inorg. Chem.* **1966**, *5*, 1249–1254. [[CrossRef](#)]
29. Bae, E.; Lee, J.W.; Hwang, B.H.; Yeo, J.; Yoon, J.; Cha, H.J.; Choi, W. Photocatalytic Bacterial Inactivation by Polyoxometalates. *Chemosphere* **2008**, *72*, 174–181. [[CrossRef](#)]
30. Bard, A.J.; Parsons, R.; Jordan, J. *Standard Potentials in Aqueous Solution*; Marcel Dekker, Inc.: New York, NY, USA; Basel, Switzerland, 1985.
31. Wielinga, B.; Mizuba, M.M.; Hansel, C.M.; Fendorf, S. Iron promoted reduction of chromate by dissimilatory iron-reducing bacteria. *Environ. Sci. Technol.* **2001**, *35*, 522–527. [[CrossRef](#)] [[PubMed](#)]
32. Voelz, J.L.; Johnson, N.W.; Chun, C.L.; Arnold, W.A.; Penn, R.L. Quantitative dissolution of environmentally accessible iron residing in iron-rich minerals: A review. *Environ. Sci. Technol.* **2019**, *3*, 1371–1392. [[CrossRef](#)]
33. Gumerova, N.I.; Rempel, A. Polyoxometalates in solution: Speciation under spotlight. *Chem. Soc. Rev.* **2020**, *49*, 7481–7846. [[CrossRef](#)]
34. Tamura, H.; Goto, K.; Yotsuyanagi, T.; Nagayama, M. Spectrophotometric Determination of Iron(II) with 1,10-phenanthroline in the Presence of Large Amounts of Iron(III). *Talanta* **1974**, *21*, 314–318. [[CrossRef](#)]
35. Clesceri, L.S.; Greenberg, A.E.; Eaton, A.D. *Standard Methods for the Determination of Water and Wastewater*, 20th ed.; United Book Press, Inc.: Baltimore, MD, USA, 1998.
36. Zardini, H.Z.; Amiri, A.; Shanbedi, M.; Maghrebi, M.; Baniadam, M. Enhanced Antibacterial Activity of Amino Acids-Functionalized Multi Walled Carbon Nanotubes by a Simple Method. *Colloids Surf. B Biointerfaces* **2012**, *92*, 196–202. [[CrossRef](#)]
37. Kang, S.; Herzberg, M.; Rodrigues, D.F.; Elimelech, M. Antibacterial Effects of Carbon Nanotubes: Size Does Matter! *Langmuir* **2008**, *24*, 6409–6413. [[CrossRef](#)]

- 
38. Das, R.; Abd Hamid, S.B.; Ali, M.E.; Ismail, A.F.; Annuar, M.S.M.; Ramakrishna, S. Multifunctional Carbon Nanotubes in Water Treatment: The Present, Past and Future. *Desalination* **2014**, *354*, 160–179. [[CrossRef](#)]
  39. Ji, L.; Chen, W.; Duan, L.; Zhu, D. Mechanisms for Strong Adsorption of Tetracycline to Carbon Nanotubes: A Comparative Study Using Activated Carbon and Graphite as Adsorbents. *Environ. Sci. Technol.* **2009**, *43*, 2322–2327. [[CrossRef](#)] [[PubMed](#)]
  40. Sweetman, M.J.; May, S.; Mebberson, N.; Pendleton, P.; Vasilev, K.; Plush, S.E.; Hayball, J.D. Activated Carbon, Carbon Nanotubes and Graphene: Materials and Composites for Advanced Water Purification. *C* **2017**, *3*, 18. [[CrossRef](#)]
  41. Yang, K.; Xing, B.S. Adsorption of Organic Compounds by Carbon Nanomaterials in Aqueous Phase: Polanyi Theory and Its Application. *Chem. Rev.* **2010**, *110*, 5989–6008. [[CrossRef](#)] [[PubMed](#)]
  42. Comer, J.; Chen, R.; Poblete, H.; Vergara-Jaque, A.; Riviere, J.E. Predicting Adsorption Affinities of Small Molecules on Carbon Nanotubes Using Molecular Dynamics Simulation. *ACS Nano* **2015**, *9*, 11761–11774. [[CrossRef](#)]
  43. Pérez-Candela, M.; Martín-Martínez, J.M.; Torregrosa-Maciá, R. Chromium (VI) removal with activated carbons. *Water Res.* **1995**, *29*, 2174–2180. [[CrossRef](#)]
  44. Liu, P.; Ptacek, C.J.; Blowes, D.W.; Finrock, Y.Z.; Liu, Y.Y. Characterization of Chromium Species and Distribution During Cr(VI) Removal by Biochar Using Confocal Micro-Ray Fluorescence Redox Mapping and X-Ray Adsorption Spectroscopy, Environmental. *International* **2020**, *134*, 105216. [[CrossRef](#)]
  45. Lakatos, J.; Brown, S.D.; Snape, C.E. Coals as Sorbents for the Removal and Reduction of Hexavalent Chromium from Aqueous Waste Streams. *Fuel* **2002**, *81*, 691–698. [[CrossRef](#)]
  46. Benazzi, E.; Karlsson, J.; Ben M'Barek, Y.; Chabera, P.; Blanchard, S.; Alves, S.; Proust, A.; Pullerits, T.; Izzet, G.; Gibson, E.A. Acid-Triggering of Light-Induced Charge-Separation in Hybrid Organic/Inorganic Molecular Photoactive Dyads for Harnessing Solar Energy. *Inorg. Chem. Front.* **2021**, *8*, 1610–1618. [[CrossRef](#)]
  47. Ueda, T. Recent Achievements in the Analysis of the Electrochemical Properties of Polyoxometalates. *Rev. Polarogr.* **2014**, *61*, 11–19. [[CrossRef](#)]
  48. Kolodynska, D.; Krukowska, J.; Thomas, P. Comparison of sorption and desorption studies of heavy metal ions from biochar and commercial active carbon. *Chem. Eng. J.* **2017**, *307*, 353–363. [[CrossRef](#)]
  49. Gonzaga, M.I.S.; Matias, M.; Andrade, K.R.; Jesus, A.N.; Cunha, G.D.C.; Andrade, R.S. Aged Biochar Changed Copper Availability and Distribution Among Soil Fractions and Influenced Corn Seed Germination in a Copper-Contaminated Soil. *Chemosphere* **2020**, *240*, 124828. [[CrossRef](#)] [[PubMed](#)]