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$\mbox{Cu}/\mbox{Cu}_2\mbox{O-immobilized}$ cellulosic filter for enhanced iodide removal from water

Jaeyoung Seon, Yuhoon Hwang

Department of Environmental Engineering, Seoul National University of Science and Technology, Seoul 01811, Republic of Korea

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ABSTRACT

We developed a Cu/Cu₂O-immobilized filter-type adsorbent for efficient iodide anion removal. A cellulose filter (CF) was used as a support, and its surface was modified using acrylic acid to enhance copper immobilization. The modified filter (CF-AA) exhibited 10x higher copper adsorption than the unmodified filter. Cu/Cu₂O was prepared on CF-AA by using a simple hydrothermal method to obtain CF-AA-Cu, and the prepared Cu/Cu₂O was characterized with scanning electron microscopy/energy-dispersive spectroscopy, x-ray photoelectron spectroscopy, and thermogravimetric analysis. While CF and Cu₂O themselves exhibited limited iodide adsorption performance, CF-AA-Cu exhibited fast adsorption kinetics with a half-life of 60 min as well as a high adsorption capacity of 10.32 mg/g, as obtained using the Langmuir adsorption isotherm model. Moreover, it exhibited high selectivity for iodide when high concentrations of other anions were present. The adsorption mechanism was proved by means of material characterization before and after adsorption. The coexistence of Cu⁰, Cu⁺, and Cu²⁺ in CF-AA-Cu make it effective in broader pH conditions via the redox reaction between Cu⁰ and Cu²⁺. Overall, iodide adsorbents in the form of filters with high adsorption capacity, selectivity, and ability over a wide pH range are potentially useful for removing iodide from water.

1. Introduction

With the increasing energy demand, the use of nuclear energy, which can replace fossil fuels and reduce greenhouse gas emissions, is growing (Forsberg, 2009). In 2018, nuclear energy accounted for 10% of the electricity generation worldwide, 450 nuclear power plants were in operation, and 55 plants were under construction (International Atomic Energy Agency, 2018). However, nuclear energy carries the risks of nuclear accidents, such as the Chernobyl nuclear accident in 1986 and the Fukushima nuclear accident in 2011. Radioactive iodine ($^{129}\mathrm{I},\,^{131}\mathrm{I})$ produced by uranium fission was the most radioactive material exposed to nature at the time of the Chernobyl and Fukushima nuclear accidents (Tagami and Uchida, 2011). After the Fukushima accident on March 11, 2011, Japan's Disaster Response Headquarters inspected tap water on March 16, 2011 and found >100 Bq/L of ¹³¹I (World Health Organization Western Pacific Region, 2011). Therefore, it is necessary to respond to radioactive iodine exposure to the environment in the event of a nuclear accident.

 129 I has a very long half-life of 1.57×10^7 years, whereas 131 I has a short half-life of only 8.02 days (Aljerf et al., 2019). However, because it

is used not only for nuclear power generation but also for medical research related to radiotherapy and treatment of thyroid disease, a significant amount of radioactive ¹³¹I is released into the water system and directly affects human metabolism (Eisenbud et al., 1962; Zheng et al., 2019). Radioactive iodine causes thyroid cancer because the thyroid gland does not distinguish between radioactive iodine (¹³¹I, ¹²⁹I) and stable ¹²⁷I (Eisenbud et al., 1962). Iodine exists in various forms such as iodide ion (I⁻), iodate ion (IO₃⁻), iodine molecule (I₂), HO¹³¹I, and organic ¹³¹I, depending on the characteristics of water (Kosaka et al., 2012). At the time of the Fukushima accident, radioactive iodine was released mainly in the form of iodide ions (CsI) (Tietze et al., 2013). Therefore, it is important to develop a method for removing radioactive iodide iond (I⁻) dissolved in the water system.

Adsorption is an economical and effective method for removing radioactive iodide, and additional treatment after the adsorption of radioactive iodide is not required. Studies have reported that chemical adsorption and physical adsorption can be employed to remove radioactive iodide from water systems. Chemical adsorption is mainly achieved through the chemical reaction of iodide with metal ions such as Bi^{3+} (Xiong et al., 2017), Hg^{2+} (Balsley et al., 1996), Ag^+ (Chapman

* Corresponding author. *E-mail address:* yhhwang@seoultech.ac.kr (Y. Hwang).

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Fig. 1. Synthesis scheme of CF-AA-Cu.

et al., 2010; Liu et al., 2015), Pb²⁺ (Huve et al., 2018), however, all of these ions are either expensive or toxic. Physical adsorption has been conducted using zeolites, which are inorganic porous adsorbents with hydrophobic surfaces (Liu et al., 2015), metal-organic frameworks (MOF) (Huve et al., 2018), and activated carbon (Eisenbud et al., 1962). However, the removal efficiencies of these materials are lower than that of chemical adsorption.

Cu, a metal that reacts with iodide ions, is cheaper than Ag and less toxic than Hg and Pb (Lefèvre et al., 2000). According to hard and soft acids and bases (HSAB) theory, Cu⁺ and I⁻ have an affinity toward each other because I⁻ is a soft Lewis base and Cu⁺ is a soft Lewis acid (Khan et al., 2011). However, in the case of Cu₂O alone, the surface is oxidized to form CuO, and it loses its affinity to I⁻ (Lefèvre et al., 2000). Therefore, researchers have attempted to remove iodide ions in the form of nanocomposites by combining Cu2O with zero-valence metals, such as Ag and Cu, to maintain the iodide removal ability of Cu₂O. It has been reported that Cu/Cu₂O showed comparable iodide adsorption capacity (22.9 mg/g) to Ag/Cu₂O (25.4 mg/g) but the price of the Cu precursor is much less than that of Ag (Mao et al., 2016; Mao et al., 2017). However, these nanocomposites are small particulate matters measuring 80-100 nm in size, which makes it difficult to collect them after adsorption of the radioactive iodide, and as a result, they easily agglomerate (Zhang et al., 2017).

Therefore, in this study, an iodide adsorbent with immobilized Cu/ Cu₂O is developed using a cellulose filter (CF) to facilitate radioactive iodide removal. A CF is used as the support material because it is commercially available in various convenient sizes and has high water permeability due to its porous structure (Roy et al., 2009; Kim et al., 2019; Sun et al., 2010). Cellulose-based materials are used to immobilize copper nanoparticles, mostly for catalytic reactions. The CF surface was modified with acrylic acid to enhance the immobilization of Cu²⁺ ions—the precursors of Cu/Cu₂O—to produce an iodide adsorbent with high Cu/Cu₂O content. Replacing the hydroxyl group in cellulose's chemical structure with a carboxyl group increases the cellulose's binding force with metal ions (Kim et al., 2019; Lin et al., 2017; Ge and Wang, 2017; Mohan et al., 2011).

Carboxyl groups and Cu/Cu₂O are formed on the CF filter by using a simple modification method and the hydrothermal synthesis method, respectively. Iodide adsorption kinetics and isothermal adsorption experiments are performed using the developed adsorbent. Besides, the effect of initial pH and competitive anions (Cl⁻, NO₃⁻, CO₃²⁻, SO₄²⁻) are investigated to discuss the adsorption mechanism.

2. Materials and methods

2.1. Materials

A CF (Taebong, Korea), which was selected as the support material for immobilizing Cu/Cu₂O, was used in the form of a thin cloth measuring 20 cm \times 20 cm \times 0.03 cm. Acrylic acid (AA, 99%; Samchun Chemical, Korea), potassium persulfate (KPS, 98%; Samchun Chemical, Korea), ethyl alcohol (C₂H₅OH, 99.5%; Samchun Chemical, Korea), and sodium chloride (NaCl, 99%, Daejung Chemical, Korea) were used for surface modification of the CF. Copper(II) nitrate trihydrate (Cu (NO₃)₂·3H₂O, >99%; Junsei Chemical, Japan) and poly(ethylenimine) solution (PEI, average MW ~2000 by LS, 50 wt% in H₂O; Sigma Aldrich, USA) were used for Cu/Cu₂O synthesis. The iodide solution used in the adsorption experiment was prepared by dissolving potassium iodide (KI, 99.5%; Samchun Chemical, Korea) in deionized water. The stable isotope ¹²⁷I was used in this study instead of radioactive iodide (Mao et al., 2017; Lin et al., 2017). Hydrochloric acid (HCl, 35-37%; Samchun Chemical, Korea) and sodium hydroxide (NaOH, ≥98%; Samchun Chemical, Korea) were used for pH adjustment. Copper (I) oxide (Cu₂O, 95%; Junsei Chemical, Japan) was used in a control test. Potassium chloride (KCl, 99.0%; Samchun Chemical, Korea), potassium carbonate anhydrous (K₂CO₃, 99.5%; Daejung Chemical, Korea), potassium sulfate (K₂SO₄, 99.0%; Junsei Chemical, Japan), and potassium nitrate (KNO₃, 99%; Samchun Chemical, Korea) were used to investigate the effect of competitive anions.

2.2. Preparation of CF with immobilized Cu/Cu₂O

2.2.1. Overall scheme

A schematic diagram of the synthesis process of a Cu/Cu₂O-based filter-type adsorbent for iodide removal is shown in Fig. 1. First, a CF was modified with AA (CF-AA) to graft a carboxyl group on the CF. Then, Cu^{2+} was combined with the amine groups of PEI to form a complex compound (Maketon et al., 2008; Sui et al., 2015). Cu^{2+} was bound not only to the PEI but also to the carboxyl group of CF-AA (Dai et al., 2010). The carboxyl group and hydroxyl group on the surface of CF-AA and the amine group in the PEI-immobilized copper complex were combined through glutaraldehyde crosslinking (Zhang et al., 2016; Ma et al., 2014). Therefore, Cu^{2+} was immobilized on the CF-AA filter by using the functional groups of CF-AA and PEI. Thereafter, in the hydrothermal synthesis process, PEI functioned as a strong reducing agent,

reducing Cu^{2+} to Cu^+ or metallic copper (Cu^0) (Zhang et al., 2017; Richardson et al., 2006). Finally, the Cu/Cu₂O-immobilized CF (CF-AA-Cu) was obtained.

2.2.2. CF surface modification by acrylic acid (CF-AA)

The CF surface was modified with AA to convert the hydroxyl groups in the CF to carboxyl groups, which would act as binding sites for subsequent Cu/Cu₂O immobilization. The overall reaction scheme was similar to that presented in our previous study on AA modification of CFs (Kim et al., 2019). CF modification by AA is a type of radical polymerization where the chemical initiator can form free radicals on the CF backbone. The free radicals thus formed can add to monomers to form covalent bonds between the monomer and the CF and the propagation of branches continues until termination. Fig. S1 provides a schematic diagram of the CF surface modification by AA.

A polymer solution was prepared by dissolving 2 mL of AA and 60 mg of KPS in 20 mL of deionized water. A 20×20 cm² CF was evenly spread on a 23×23 cm² glass plate. The prepared polymer solution was poured onto CF to ensure that it could be evenly absorbed. The CF saturated with the polymer solution was covered with the glass plate, placed in a vacuum oven, and reacted for 6 h at 70 °C in a nitrogen atmosphere. After the completion of this reaction, the CF was washed with a solution containing water and ethanol mixed in a volume ratio of 1:1 and subsequently immersed in the same solution for 24 h to obtain CF-AA.

To verify the enhanced Cu^{2+} adsorption performance of CF-AA compared to that of CF, we conducted Cu^{2+} adsorption experiments. To this end, 300 mg of CF and CF-AA were added to 50 mL of a 20 mg/L copper solution. The solution pH was adjusted to 7, and the adsorption experiment was carried out with continuous stirring for 24 h. The supernatant was collected, and its copper concentration was measured using an atomic absorption spectrometer (AAS, Elemental SOLAAR M6 AAS, Thermo Fisher Scientific, USA).

2.2.3. Cu/Cu₂O synthesis (CF-AA-Cu)

Cu/Cu₂O was synthesized on CF-AA according to the method reported in a previous study (Zhang et al., 2017). 1.52 g of Cu (NO₃)₂·3H₂O were dissolved in a mixture containing 97.88 mL of deionized water and 2.12 mL of PEI solution. Nine 3 cm \times 3 cm CF-AAs were added to the solution and stirred for 24 h to facilitate Cu²⁺ adsorption on CF-AA. Thereafter, the mixture was transferred to a PPL-lined autoclave (150 mL capacity) and heated at 220 °C for 3 h. After natural cooling, the filters were washed four times with deionized water and dried in vacuum at 60 °C, after which CF-AA-Cu was obtained.

2.3. Characterization

A Fourier-transform infrared spectrophotometer (FTIR spectrophotometer, Nicolet 6700, Thermo Scientific, USA) was used to confirm the surface functional groups. A high-resolution field emission scanning electron microscope with an energy-dispersive X-ray spectrometer (SEM-EDS, SU8010, Hitachi high technologies corporation, Japan) was used to analyze the surface morphology and chemical composition of CF-AA-Cu. A thermogravimetric analyzer (TGA, Discovery TGA, TA Instruments, USA) was used to investigate the copper content of CF-AA-Cu. TGA of the material was performed in a nitrogen atmosphere in a temperature range of 40–900 °C and a heating rate of 10 °C/min. X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo VG, U.K.) was performed to study changes in the chemical states of the constituent elements by using monochromated Al K α as the X-ray source.

2.4. Iodide adsorption experiments

2.4.1. Adsorption kinetics and isotherms

The sorption kinetics of iodide was evaluated by conducting a batch test with an initial iodide concentration of 10 mg/L. First, 50 mL of

10 mg/L iodide solution was placed in conical polyethylene (PE) tubes. Then, 100 mg of adsorbent (CF, commercially purchased Cu₂O, and CF-AA-Cu) was added to the tube, and the solution was sampled at 10, 30, 60, 120, 240, 480, 1440 min while the conical tubes were continuously stirred using a vertical stirrer operated at 20 rpm. The residual iodide concentration in the solution after adsorption was measured and analyzed at 225 nm using an ultraviolet-visible spectrometer (Libra S22, Biochrom, U.K.).

The adsorption kinetics was evaluated by applying the following pseudo-first-order (Eq. (1)) and pseudo-second-order kinetic equations (Eq. (2)) (Ko et al., 2017):

$$q_t = q_e (1 - e^{-k_1 t}) \tag{1}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t}$$
(2)

where q_t is the quantity adsorbed at time t (mg/g), q_e is the equilibrium concentration (mg/g), k_1 is a first-order rate constant (1/min), and k_2 is a second-order rate constant (g/mg·min).

The sorption isotherms were obtained using different iodide concentrations. The initial iodide concentration range was 1-25 mg/L. The tests were conducted by following the procedure described in the sorption kinetics experiment, but the sampling intervals were changed to 0 h and 24 h. The sorption isotherm data were fitted using the Langmuir (Eq. (3)) and the Freundlich (Eq. (4)) isotherms (Foo and Hameed, 2010).

$$q_e = q_m \frac{a_L C_e}{1 + a_L C_e} \tag{3}$$

$$q_e = K_F C^{1/n} \tag{4}$$

where q_e is the quantity of adsorbate adsorbed per unit weight of solid adsorbent, q_m the maximum sorption capacity of the adsorbent (mg/g), C_e the equilibrium concentration of the adsorbate in solution (mg/L), and a_L the Langmuir affinity constant. K_F and 1/n are constants representing the adsorption capacity and adsorption intensity, respectively.

2.4.2. Effect of pH

The effect of pH (3 -1 1) on iodide sorption onto CF, Cu₂O, CF-AA-Cu was scrutinized by following the experimental procedure described in Section 2.4.1. The initial iodide concentration and adsorbent dosage were set to 10 mg/L and 1.6 g/L, respectively. The pH was adjusted to the 3, 5, 7, 9, and 11 by adding 0.1 M HCl and 0.1 M NaOH. A sample was taken at 24 h, and its iodide concentration was determined as described in Section 2.4.1. The iodide concentration of the solution sampled at pH 3 was analyzed using the iodine blue spectrophotometry method (Ministry of Health of China, 2007).

Adsorbent stability was discussed in terms of the concentration of copper ions in the supernatant, which was measured using an AAS (Elemental SOLAAR M6 AAS, Thermo Fisher Scientific, USA).

2.4.3. Effect of competitive anions and water matrix

The effect of competitive anions was evaluated using the experimental procedure described in Section 2.4.2. The initial iodide concentration and CF-AA-Cu dosage were set to 4 mg/L and 1.6 g/L, respectively. The competitive anions Cl⁻, CO₃²⁻, SO₄²⁻, and NO₃⁻ were added in initial concentrations of 100 mg/L. The solution pH was adjusted to 6.5–7 by using 0.1 M HCl and 0.1 M NaOH solutions. A sample was obtained at 24 h, and its iodide concentration was determined using iodine blue spectrophotometry (Ministry of Health of China, 2007).

The water matrix effect on iodide adsorption was investigated using two types of synthetic water—soft and hard—and real stream water taken from the Danghyunchun River in Seoul. The synthetic soft and hard water were prepared as suggested by the literature (Smith et al.,



(a)

(b)



Fig. 2. SEM images of (a) CF, (b) CF-AA, (c) CF-AA-Cu (500x), (d) CF-AA-Cu (5,000x).

2002). Table S1 presents the characteristics of the synthetic and real stream water. The adsorption experiment was carried out with deionized water, soft water, hard water, and real stream water with an initial I concentration of 10 mg/L and 1.6 g/L of an adsorbent. The solution pH was adjusted to 6 using 0.1 M HCl and 0.1 M NaOH solutions. Samples were obtained at 24 h and their iodide concentration was measured with an ICP-mass spectrometer (ICP-MS, iCAP-Q, ThermoFisher Scientific, Germany).

3. Results and discussion

3.1. CF-AA-Cu characterization

3.1.1. Functional groups of CF-AA and CF-AA-Cu

FTIR analysis was performed to investigate changes in the surface functional groups of CF because of the AA modification and Cu/Cu₂O synthesis (Fig. S2). In the case of pure CF, hydroxyl, methyl, and carbonyl peaks were observed at 3640–3200, 3000–2850, and 1320–1000 cm⁻¹, respectively, and these peaks are consistent with the chemical composition of cellulose (Ciolacu et al., 2011). In case of the modified CF-AA, a new peak was observed at 1760–1690 cm⁻¹ (C⁻O, carboxyl group) (Kim et al., 2019). Therefore, it was confirmed that the surface modification led to the formation of a carboxyl group. In the case of CF-AA-Cu, the intensities of the OH peak near 3330 cm⁻¹, CH peak near 2894 cm⁻¹, and the CO peak near 1051 cm⁻¹ decreased. Moreover, the peak indicating primary amine NH₂ bending vibration (1560 cm⁻¹) was newly shown in the case of CF-AA-Cu (Yang et al., 2009). This amine

group originated from the PEI, which was used during the CF-AA-Cu preparation. These results show that the complex compounds of PEI and Cu^{2+} were well-attached on the CF-AA-Cu surface.

The effect of AA modification on Cu adsorption was investigated in a Cu adsorption test conducted using CF and CF-AA. The amounts of Cu adsorbed on CF and CF-AA were 0.35 mg/g and 3.45 mg/g, respectively. This confirmed that the Cu adsorption capacity of the surface-modified CF-AA was approximately 10 times higher than that of the pristine CF, and this difference can be ascribed to the stronger interaction between the carboxylic acid group and Cu compared to that between the hydroxyl group and Cu.

3.1.2. Morphological analysis

Fig. S3 presents the color changes during CF-AA-Cu preparation. The pristine CF was white and there was no noticeable color change during AA modification. The color changed to green after Cu^{2+} adsorption and red-brown after the hydrothermal reaction for Cu/Cu₂O formation. This red-brown color was weakened after iodide adsorption due to CuI formation, which will be discussed further.

Morphological change during CF-AA-Cu preparation was monitored using a SEM—EDS. Fig. 2 and S4 show SEM images of pristine CF, CF-AA, and CF-AA-Cu. Pristine CF has a smooth surface with tangled fiber strands and space between fiber strands. CF-AA is not significantly different from CF on the SEM images. By contrast, the SEM images of CF-AA-Cu, shown in Fig. 2(c) and 2(d), exhibit a different morphology from that of CF and CF-AA. We confirmed that two types of particles were attached to the filter surface—sea urchin-like particles and angular

Table 1

Weigh ratios of elements on the surfaces of CF, CF-AA, and CF-AA-Cu.

6			
Weight ratio (%)	CF	CF-AA	CF-AA-Cu
С	36.15	38.51	11.88
0	63.85	61.49	13.20
Cu	-	-	74.92

spherical particles. The sea urchin-like particles have been reported to be CuO crystals (Yao et al., 2016), while the shape of the angular spherical particles was similar to the Cu/Cu₂O particle shape reported in (Mao et al., 2017; Zhang et al., 2017). Therefore, we can confirm that Cu/Cu₂O hybrids and CuO were synthesized on the surface of CF-AA.

EDS analysis was performed to determine CF, CF-AA, and CF-AA-Cu's elemental composition, and the results are shown in Fig. S4 and summarized in Table 1. CF and CF-AA were composed of carbon and oxygen, consistent with the chemical structures of cellulose and acrylic acid. Interestingly, a high copper content was detected in CF-AA-Cu. As obtained by EDS analysis, the weight ratio of elemental copper was 74.92%, indicating that copper particles were well attached to the surface of the filter. Moreover, Fig. S1(c) shows that the spherical particles on the surface are composed mainly of copper and oxygen.

3.1.3. TGA analysis

TGA analysis was conducted to determine the thermal stability of the produced material and the copper content of CF-AA-Cu (Fig. S5). The weights of both CF and CF-AA-Cu decreased as the temperature increased from 300 to 600 $^{\circ}$ C, consistent with the chemical nature of

cellulose. Because the CF was composed of $(C_6H_{10}O_5)_n$, it decomposed into carbon dioxide and water as the temperature increased. At 900 °C, the CF decomposed almost completely, and its residual weight ratio was 0.26%. In the case of CF-AA-Cu, the residual weight ratio at 900 °C was 8.03%, which was attributed to its content of copper-based compounds, such as CuO, Cu₂O, and metallic Cu, which ultimately remained as CuO (Ashok et al., 2018). Therefore, the amount of copper-based particles in CF-AA-Cu was found to be 7.76% by weight.

3.2. Sorption kinetics and isotherm of CF-AA-Cu

Iodide adsorption kinetics experiments were carried out using CF, Cu_2O , and CF-AA-Cu to determine the respective adsorption equilibrium times. In the case of CF and Cu_2O , almost no iodide adsorption was observed. Therefore, the results for CF-AA-Cu are shown in Fig. 3(a). Adsorption kinetics results were analyzed using the pseudo-first-order kinetics (Eq. (1)) and pseudo-second-order kinetics (Eq. (2)) equations, and the results are summarized in Table S2.

Iodide was adsorbed quickly during the initial 120 min, and the adsorption equilibrium was reached after 240 min. The pseudo-firstorder kinetics and pseudo-second-order kinetics models exhibited good fits with the data, as indicated by the respective correlation coefficients. Within 60 min of contact time, half of the initial iodide was adsorbed onto CF-AA-Cu at a loading of 2.0 g/L. Moreover, adsorption equilibrium was reached after 4 h, and the equilibrium remained stable up to 24 h. Therefore, we set the isothermal adsorption experiment duration to 24 h in this study.

The kinetic constants were comparable with the values obtained in



Fig. 3. (a) Iodide adsorption kinetics of CF-AA-Cu (Initial I⁻ concentration of 10 mg/L and adsorbent dose of 2 g/L), (b) Adsorption isotherms of CF, Cu₂O, CF-AA-Cu for I⁻ removal (T: 25 °C, adsorbent dose: 2 g/L, I⁻ conc.: 1–25 mg/L, and adsorption time: 24 h), (c) R_L vs. C₀ for CF-AA-Cu, (d) Effect of pH on amount of I⁻ adsorbed in pH range 3–11 (adsorbent dose: 1.6 g/L, I⁻ conc.: 10 mg/L, and adsorption time: 24 h).

Table 2

Comparison of the iodide adsorption capacity of CF-AA-Cu with those of different copper-based adsorbents.

Adsorbent	C ₀ (mg/ L)	Adsorbent dose (g/L)	Adsorption capacity (mg/ g)	Ref.
Cu ₂ O (powder)	16.6	50	0.3	(Lefèvre et al., 2000)
Cu ₂ S (powder)	12.7	20	2.54	(Lefèvre et al., 2003)
Mg-Al (NO ₃) LDH (powder)	342.3	20	10.1	(Kentjono et al., 2010)
Modified zeolite (powder)	10–500	10	3.6	(Warchoł et al., 2006)
Ag/Cu ₂ O (powder)	0–38.1	1	25.4	(Mao et al., 2016)
Cu/Cu ₂ O (powder)	0–38.1	1	22.9	(Mao et al., 2017)
Cu/Cu ₂ O-LDH (powder)	0–240	1	137.8	(Zhang et al., 2017)
Nano Cu/Cu ₂ O-C (granule)	1–30	1	41.2	(Chen et al., 2020)
Micor/ nanostructured Bi Que (powder)	0.5–700	0.2	284.9	(Zhang et al., 2017)
Bi ₂ O ₃ /LDHs (powder)	20-200	1	101.9	(Liu et al., 2016)
CF-AA-Cu (filter)	1–25	2	10.32	This work

similar studies conducted using Cu-based adsorbents. Similar iodide adsorption kinetics were reported in the case of hollow Cu-based adsorbents (Mao et al., 2018). The hollow Cu-based adsorbents exhibited a half-life of 70 min with a loading of 1 g/L and an initial iodide concentration of 0.4 mM. Other studies conducted using powder-type Cubased composites yielded a slightly faster half-life. This was ascribed to easier Cu-iodide anion contact owing to the small size of the powdertype Cu-based composites. The half-life of Cu/Cu₂O-layered double hydroxides was reported to be 38 min with a loading of 1 g/L and an initial iodide concentration of 210 mg/L (Chen et al., 2020) while that of Ag@Cu₂O nanoparticles was reported to be 14 min with a loading of 1 g/L and an initial iodide concentration of 0.16 mM (Mao et al., 2016). Although the adsorption kinetics obtained in this study is not superior to those obtained in other studies, the adsorption kinetics obtained in this study was shown to be effective considering that filter-type adsorbent was used herein instead of nanoparticles in powder form.

The adsorption isotherm experiment was conducted by comparing the amount of iodide adsorbed onto the CF, Cu₂O powder, and CF-AA-Cu while varying the initial iodide concentration from 1 to 25 mg/L. The isothermal adsorption experiment results were applied to the Langmuir adsorption isotherm and the Freundlich adsorption isotherm, as shown in Fig. 3(b) and summarized in Table S3. First, CF did not adsorb the iodide at all. The commercially available Cu₂O powder exhibited a limited adsorption capacity of 0.49 mg/g when the initial I concentration was 25 mg/L. This means that Cu₂O alone loses affinity for iodide due to the oxidation of the surface to Cu²⁺ and cannot be used as an adsorbent (Lefevre et al., 2000).

By contrast, in the case of CF-AA-Cu, the amount of iodide adsorbed increased as the initial iodide concentration increased. When the results of this experiment were applied to the Langmuir adsorption isotherm (Fig. 3(b)), the maximum adsorption q_m value was 10.32 mg/g. The value of the dimensionless coefficient R_L (Eq. 3 (c)) was obtained using the value of K_L. Favorable adsorption occurs when $0 < R_L < 1$ (Gupta et al., 2010). The R_L was between 0 and 1 for all tested I⁻ concentrations (1–25 mg/L), indicating that the adsorption of I⁻ on CF-AA-Cu was favorable.

$$\mathbf{R}_{\mathrm{L}} = \frac{1}{1 + K_L C_0} \tag{6}$$

When applied to the Freundlich adsorption isotherm (Fig. 3(b)), the

value of K_F was 0.7476 g/mg·min and that of the adsorption intensity n was 1.438. When n is in the range of 1–10, it indicates the existence of an effective adsorbent–adsorbate interaction (Santhana Krishna Kumar et al., 2012). Because the value of n is 1.438, the electrostatic interaction between CF-AA-Cu and iodide is effective.

Table 2 summarizes the I adsorption capacities of various types of Cu-based adsorbents reported in the literature. The adsorption capacity of CF-AA-Cu (10.32 mg/g) was higher than the individual adsorption capacities of Cu₂O (Lefèvre et al., 2000), Cu₂S (Lefèvre et al., 2003), Mg-Al(NO₃)LDH (Kentjono et al., 2010), and modified zeolite (Warchoł et al., 2006). Moreover, the iodide adsorption capacity of Cu/Cu₂O reported in the existing literature is significantly higher than that of Cu₂O or Cu₂S alone. These results indicated that the redox interaction between Cu and Cu₂O played a critical role in iodide adsorption. However, CF-AA-Cu's adsorption capacity was inferior to that of the zero-valent metal/Cu₂O (Mao et al., 2016, 2017; Zhang et al., 2017; Chen et al., 2020) and bismuth oxide-based composite materials (Zhang et al., 2017; Liu et al., 2016) because CF-AA-Cu was the only filter-shaped adsorbent; the rest were powdered adsorbents. An adsorbent in the form of a filter has a low q_m value because of the reduced contact surface area with the adsorbate and inhibition of mass transfer compared to a powdered adsorbent.

Moreover, the overall Cu/Cu₂O content in CF-AA-Cu was 7.76%, as shown in Section 3.1.3. Therefore, the adsorption capacity of CF-AA-Cu can be recalculated based on its Cu content. The calculated iodide adsorption capacity for Cu alone was 133.0 mg/g, close to the highest value reported in the literature. Because CF-AA-Cu was used in the form of a filter in this study, it can be easily applied to water-treatment processes and conveniently recovered after adsorption. These advantages indicate that CF-AA-Cu is a potentially attractive adsorbent for efficient removal of Γ from water.

3.3. Effect of pH

3.3.1. Effect of pH on Γ removal

To investigate the effect of pH on the removal of I⁻, adsorption experiments were performed while varying the initial pH range from 3 to 11. As shown in Fig. 3(d), no iodide adsorption was observed in the case of CF, regardless of the pH. In the case of Cu₂O, the adsorption capacity was 5.62 mg/g at pH 3, but at pH 5 or higher, iodide adsorption was not observed. Because Cu₂O dissolved in the form of Cu⁺ into the aqueous solution at low pH, Cu⁺ and I⁻ formed CuI, and I⁻ was removed as a precipitate on the surface of Cu₂O. By contrast, at high pH, the surface of Cu₂O was oxidized to Cu(OH)₂ or CuO, and it lost affinity with I⁻; consequently, its I⁻ removal ability was negligibly low (Lefèvre et al., 2000).

In the case of CF-AA-Cu, the amount of I⁻ adsorbed was 6.30 mg/g at pH 3, and the adsorption capacity was 1.26 mg/g at pH 9, where the amount adsorbed decreased as the pH increased. Unlike Cu₂O, iodide adsorption occurred over a broader pH range. Even though Cu₂O is oxidized to CuO as the pH increases, CF-AA-Cu can react with I⁻ (Eq. (8)) to form a CuI precipitate with the help of metallic Cu (Eq. (7)) (Mao et al., 2017).

$$Cu+CuO\leftrightarrow Cu_2O \tag{7}$$

$$Cu_2O + 2I^- + H_2O \rightarrow 2CuI + 2OH^-$$
(8)

In addition, Fig. S6 shows the changes in pH before and after adsorption. The initial pH values of 3, 5, and 7 changed to 4.85, 8.12, and 8.47, respectively, after adsorption. These increases in pH were ascribed to the exchange of OH⁻ and I⁻ on the adsorbent surface according to (Eq. (8)), where I⁻ was adsorbed and OH⁻ was released into the solution. By contrast, almost no change in pH was observed when the initial pH was alkaline, for instance, pH 9 and 11. Moreover, the adsorption capacity decreased because the negatively charged OH⁻ acted as a competitive ion in the adsorption process of I⁻ on Cu/Cu₂O (Zhang et al., 2017).



Fig. 4. Effect of high concentration of interfering ions (Cl⁻, CO₃²⁻, SO₄²⁻, NO₃⁻) on I⁻ adsorption on CF-AA-Cu: (a) without pH adjustment, (b) initial pH adjusted to 6.5–7 (T: 25 °C, adsorbent dose: 1.4 g/L, I⁻ conc.: 4 mg/L, and adsorption time: 24 h).

3.3.2. Effect of pH on stability of Cu/Cu₂O

The amount of Cu^{2+} leached during iodide adsorption was monitored to investigate the stability of Cu/Cu_2O under various pH conditions. Fig. S7 shows that the amounts of Cu^{2+} eluted after 24 h at the initial pH values of 3, 5, 7, 9, and 11 were 39.1, 0.98, 0.90, 0.76, and 0.81 mg/L, respectively. When the initial solution pH was 3, the Cu^{2+} concentration in the supernatant was considerably higher than that under the other pH conditions. As discussed in Section 3.3.1, this difference can be ascribed to the fact that the copper particles in CF-AA-Cu dissolved as Cu^+ under acidic conditions. For pH values of 5 and higher, because the detected Cu^{2+} levels were lower than the WHO standard threshold of 2 mg/L, there was no problem of secondary contamination.

3.4. Effect of competitive anions and water matrix

3.4.1. Effect of competitive anions

Adsorption experiments were performed in the presence of high concentrations of Cl⁻, CO₃²⁻, SO₄²⁻, and NO₃⁻ anions to investigate the effect of competitive anions. The initial I⁻ concentration was 4 mg/L, and the other anions' concentration was set to 100 mg/L, which was 25 times higher than the I⁻ concentration. Fig. 4(a) shows that when the experiment was performed without pH adjustment, adsorption capacity of 1.69 mg/g was observed in the blank solution without interfering anions. In the presence of Cl⁻, CO₃²⁻, SO₄²⁻, and NO₃⁻ anions, the adsorption capacity values were 1.66 mg/g, 0.51 mg/g, 1.18 mg/g, and 0.96 mg/g, respectively. One-way ANOVA and Dunnett's test were used for the



Fig. 5. Effect of water matrix on iodide adsorption by CF-AA-Cu (initial iodide concentration 10 mg/L, adsorbent dose: 1.6 g/L).

statistical analysis of experimental data, especially for the effect of interfering ions. Without pH adjustment (Fig. 4(a)), the addition of 100 mg/L of CO_3^{2-} was determined to be statistically significant compared to the blank test (p < 0.05). Since CO_3^{2-} increased the solution pH, the removal of Γ anions was hindered under the resultant alkaline condition, as described in Section 3.3. This result showed that increasing the pH with CO_3^{2-} played a major role in decreasing the I- adsorption performance.

Thereafter, the initial solution pH was adjusted to 6.5–7, and the adsorption experiment was carried out again, as shown in Fig. 4(b). The blank with only iodide ions showed an adsorption capacity of 1.58 mg/g. In the presence of Cl⁻, CO₃²⁻, SO₄²⁻, and NO₃⁻ anions, the adsorption capacity values were 1.94 mg/g, 1.94 mg/g, 1.41 mg/g, and 1.21 mg/g, respectively. The NO₃⁻ was considered statistically significant when the initial pH was adjusted to 6.5–7. In this case, the effect of CO_3^{2-} was not statistically significant.

When the initial pH was adjusted to neutral range in the presence of CO_3^{2-} , the adsorption performance of the adsorbent was restored again. The interference effect of the CO_3^{2-} ion (Fig. 4(a)) can be attributed to an increase in pH, and this interference effect can be ignored in practice because the pH of real river water is 7.3–7.9. Fig. 4(b) shows that among the four anions, the interference effect of NO_3^{-} was the strongest. However, CF-AA-Cu exhibited high selectivity for I⁻ adsorption because it maintained an adsorption performance of 77% at an NO_3^{-} concentration that was 25 times higher than the I⁻ concentration.

3.4.2. Effect of water matrix

In addition, the effect on the water matrix was investigated to evaluate the practical feasibility of the CF-AA-Cu adsorbent. We used four water matrix types for this study: deionized, soft, hard, and real stream water. The soft and hard water were synthetic water matrixes used to represent ordinary surface water and groundwater. Both the artificial water and real stream water contained various anions, including CO_3^{2-} and NO_3^{-} , which can compete with I⁻, as described in Section 3.4.1.

Fig. 5 presents the measured iodide adsorption capacity and changed pH. The amount of adsorbed iodide was 2.4 mg/g in the DI water condition and this value increased to 5.5 mg/g, 4.6 mg/g, and 4.1 mg/g for the soft, hard, and real stream water, respectively. It is fascinating that the adsorption capacity was not reduced by the presence of competing anions in the water matrix.

Iodide was adsorbed 2.3, 2, and 1.7 times higher in soft, hard, and real stream water compared to DI water. These results are considered with the pH change observed during adsorption. The final pH of deionized water was 8.5, while those of the soft, hard, and real stream water were 7.3, 7.7, 7.3, respectively. As described earlier, pH was increased by OH^- ions excreted into the solution during iodide adsorption via ion exchange and a higher pH is not favorable for further iodide adsorption. Soft, hard, and real stream water contain alkalinity (16, 99, and 29 mg/L as CaCO₃, respectively), and so the pH change was



Fig. 6. XPS spectra of CF-AA-Cu: (a) survey scans obtained before and after I^- adsorption, (b) Cu LMM Auger spectra of adsorbent before and after uptake of I^- anions, (c) Cu 2p spectrum before I^- adsorption (d) Cu 2p spectrum after I^- adsorption, (3) O 1s spectrum before I^- adsorption (d) O 1s spectrum after I^- adsorption and (e) I 3d spectrum after I^- adsorption.

Table 3

Changes in atomic % O species in CF-AA-Cu before and after I^- adsorption as determined by performing XPS analysis.

Atomic %	Before adsorption	After adsorption
Cu ₂ O	28.7%	21.2%
С-О	60.7	64.5
C=O	10.6%	14.3%

minimized.

The amount of iodide adsorbed was the highest in the soft-water condition because the pH change was minimized at appropriate alkalinity and soft-water had less anion content than either hard-water or real stream water. In real stream water conditions, the amount of iodide adsorbed was smaller than that of the soft- or hard-water conditions due to the concentration of NO_3^- , which had the most considerable interference effect as seen in Section 3.4.1. Nevertheless, it showed 1.7 times greater iodide adsorption capacity in real stream water than in DI water; therefore, CF-AA-Cu has high selectivity toward iodide and strong potential for practical application in real water systems.

3.5. Oxidation state analysis by XPS and adsorption mechanism

EDS analysis (Section 3.1.2) confirmed that the particles found in CF-AA-Cu were copper-based particles, but the oxidation state of copper could not be distinguished. XPS analysis was performed to identify the chemical structure of the copper-based compounds in CF-AA-Cu. According to the XPS survey spectra in Fig. 6(a), CF-AA-Cu consists of C, O, N, and Cu. This is consistent with the EDS mapping results of CF-AA-Cu (Fig. S4(c)). Fig. 6(c) shows the Cu 2p peak of CF-AA-Cu. The binding energy peaks of 933.64 eV and 932.38 eV indicated the presence of CuO (Cu²⁺) and Cu₂O (Cu⁺) or metallic Cu, respectively (National Institute of Standards and Technology, 2000). However, the binding energies of metallic Cu (Cu⁰) and Cu₂O (Cu⁺) are almost equal (differing by only 0.1-0.2 eV). Therefore, it was difficult to distinguish metallic Cu and Cu+ presence based on the XPS Cu2p peak alone (Fig. 6(c)) (Wu et al., 2006). Therefore, we obtained Cu LMM Auger spectra to determine whether the binding energy peak of 932.38 eV indicated metallic Cu or Cu₂O (Fig. 6(b)). The black line in Fig. 6(b) represents the Auger Cu LMM spectra of CF-AA-Cu before iodide adsorption. The two main peaks at 570.0 eV indicate the presence of Cu⁺, while the peak at 567.7 eV indicates the presence of Cu⁰ (Zhang et al., 2015). Fig. 6(e) is the O 1s spectrum of CF-AA-Cu, and it showed mainly C-O and C=O at 532.8 and 534.1 eV, respectively, from the cellulose filter (Gao et al., 2012). The binding energy peaks at 531.1 eV indicated the presence of Cu₂O and Cu-OH (Niu et al., 2016; Geng et al., 2020). Overall, XPS analysis confirmed that the copper particles attached to CF-AA-Cu exist as CuO (Cu^{2+}) , Cu_2O (Cu^+) , and metallic Cu (Cu^0) .

XPS and SEM/EDS analysis of CF-AA-Cu were performed post I⁻ adsorption to discuss the removal mechanism in greater detail. Fig. 6(a) shows that the I 3d peak appears in the range of 615–635 eV in the XPS survey scan of the material after iodide adsorption. A magnified view of the 615–635 eV range is shown in Fig. 6(e), and the two main peaks appear in the I 3d spectra at the binding energies of 630.95 eV and 619.54 eV, indicating the presence of CuI (Mao et al., 2017).

The changes in Cu^{2+} , Cu^+ , and Cu^0 after I⁻ adsorption were examined using the Cu LMM Auger spectra (Fig. 6b). The peak at 567.7 eV, which indicates the presence of Cu^0 , diminished after adsorption compared with that before adsorption (Zhang et al., 2015). The peaks assigned to metallic Cu weakened, implying that metallic Cu (Cu⁰) played an essential role in removing I anions from water. According to Eqs. (7) and (8), metallic Cu reacted with CuO to generate Cu₂O, and then, the Cu₂O reacted with I⁻ to form CuI. The formation of CuI was also identified by analyzing the O 1s spectrum after I⁻ adsorption. As

Table 4

Changes in atomic % Cu species in CF-AA-Cu before and after I^- adsorption as determined by performing XPS analysis.

Atomic %	Before adsorption	After adsorption
Cu ²⁺	35.9%	43.2%
Cu ⁰ or Cu ⁺	64.1%	56.8%

presented in Fig. 6(f) and Table 3, the peak areas' proportion was slightly changed. The peak area for Cu_2O decreased after the iodide adsorption, which indicates the production of CuI after the reaction between Cu^+ (from Cu_2O) and iodide.

The Cu species ratios were calculated by deconvoluting the Cu 2p peaks (Fig. 6(c), (d)), and the resulting values are summarized in Table 4. The Cu species in CF-AA-Cu before the iodide adsorption experiment were 35.9% Cu^{2+} and 64.1% Cu^0 or Cu^+ . After the iodide adsorption experiment, the ratio changed to 43.2% Cu^{2+} and 56.8% of Cu^0 or Cu^+ . As shown in Fig. 6(b) and Table 4, the Cu^0 or Cu^+ portion decreased because Cu^0 involved in I⁻ adsorption (Eq, (7)). The increase of Cu^{2+} ratio means that Cu_2O which had not reacted with I⁻ was oxidized to CuO, as can be seen in the peaks of 943.07 and 934.2 eV.

In addition, the results of an SEM/EDS analysis of the CF-AA-Cu adsorbent after I⁻ adsorption are shown in Fig. 7 and S4(d). Fig. 7(a) shows the presence of sharpened particles in addition to spherical copper particles after iodide adsorption. The I⁻ adsorption experiments altered the morphology and phase structure of the spherical copper particles. This refers to the adsorption of I⁻ anions due to a chemical reaction that occurred in the CuI precipitate. Similar morphological and structural changes were reported for Ag nanoparticles and Bi2O2.33 particles (Liu et al., 2016; Tauanov and Inglezakis, 2019). Fig. 7(b) shows an elemental mapping image of the adsorbent after adsorption. This image confirms that elemental iodine was detected along the filter fibers. In our EDS analysis of CF-AA-Cu-I, the results summarized in Table 5, the weight ratios of C, N, O, Cu, and I were 25.63%, 4.71%, 32.02%, 36.48%, and 1.17%, respectively. Therefore, the XPS and SEM/ EDS results confirmed that the developed adsorbent material CF-AA-Cu adsorbs and removes I⁻ anions from water.

4. Conclusions

A new filter-type adsorbent called CF-AA-Cu for the removal of iodide was synthesized via a simple one-step hydrothermal synthesis method. The surface of a CF was modified with acrylic acid to increase copper loading in the filter. The results of FTIR analysis indicated the formation of the carboxyl group on the surface of the CF, and the amount of Cu^{2+} adsorption on the resulting surface increased by 10 times after the modification. SEM/EDS and XPS analyses confirmed that the copper particles were well immobilized on the CF surface. TGA analysis confirmed that the copper content in CF-AA-Cu was approximately 8%.

The synthesized CF-AA-Cu effectively removed iodide from water. While CF and Cu₂O alone exhibited limited I⁻ adsorption performances, CF-AA-Cu exhibited fast adsorption kinetics with a half-life of 60 min and high adsorption capacity of 10.32 mg/g, as determined using the Langmuir adsorption isotherm model. Iodide adsorption occurred over a broad pH range of 3–9, and there was no secondary contamination due to copper elution at pH 5 or higher. Moreover, CF-AA-Cu showed high selectivity for iodide in the presence of other anions in high concentrations, and the water matrix did not hinder the adsorption capacity.

The adsorption mechanism was demonstrated through the characterization of the material before and after adsorption. The coexistence of Cu^0 , Cu^+ , and Cu^{2+} in CF-AA-Cu make it effective over a broader range of pH conditions because of the redox reaction between Cu^0 and Cu^{2+} . Cu^0 played a major role in iodide removal, and the decrease of Cu^0 and increase of CuO by oxidation was confirmed by XPS analysis. Overall, iodide adsorbents in the form of filters with high adsorption capacity, selectivity, and ability over a broad pH range have the potential for application in processes for removing iodide from water.







Fig. 7. (a) SEM image of CF-AA-Cu-I (X10,000), and (b) EDS mapping images of CF-AA-Cu-I.

CRediT authorship contribution statement

Jaeyoung Seon: Investigation, Writing - original draft. Yuhoon Hwang: Conceptualization, Writing - review & editing.

Table 5

Weight ratios of elements on the surfaces of CF, CF-AA, CF-AA-Cu, CF-AA-Cu-I (500x magnification).

Weight ratio (%)	CF	CF-AA	CF-AA-Cu	CF-AA-Cu-I
С	36.15	38.51	11.88	25.63
N	_	-	-	4.71
0	63.85	61.49	13.20	32.02
Cu	_	-	74.92	36.48
Ι	_	_	-	1.17

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2020.124415.

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