Application of fullerenes-extracted soot modified with ethylenediamine as a novel adsorbent of hexavalent chromium in water

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Abstract

Fullerenes-extracted soot, the by-product of fullerene synthesis, is a carbon composite. The application of this material for water treatment has not yet been developed. Herein, fullerenes-extracted soot in the form of powder containing amino groups was prepared by reacting the soot with ethylenediamine, and was used as an adsorbent of hexavalent chromium [Cr(VI)] for removing Cr(VI) from aqueous solutions; this removal was studied by batch adsorption experiments. The effect of experimental parameters such as the pH, initial Cr(VI) concentration, and agitation time on the adsorption process was investigated. The adsorption of Cr(VI) was highly pH-dependent and the optimal pH for the adsorption process was 3.0. The data of Cr(VI) adsorption by fullerenes-extracted soot modified with ethylenediamine (FES-ED) fit the Langmuir isotherm equation well. The maximum Cr(VI)-uptake capacity of FES-ED was 93 mg g^{-1}. The desorption of Cr(VI) from the adsorbent was also studied. The adsorbed Cr(VI) was eluted with 20 mL of an aqueous solution with pH 12 and the percentage recovery of Cr(VI) was determined as 75%. The adsorption and desorption test using the same FES-ED powder was repeated in triplicate to examine the reusability of the adsorbent. The adsorption was 97% and the desorption was > 70% through the adsorption–desorption cycles. The adsorption of methyl orange onto the FES-ED was also examined. The dye was almost quantitatively removed from the aqueous solution by the adsorbent (the initial concentration

of methyl orange: 40 μg mL^{-1}; the adsorbent added: 10 mg/40 mL). Thus, we concluded that

the FES-ED can be used as a novel adsorbent for removing pollutants from water.

1. Introduction

Fullerene has attracted significant interest because of its unique spherical structure, electronic properties [1,2], and its various applications such as a cosmetic ingredient with radical-scavenging ability, optical and electronic materials (especially for organic photovoltaic cells), and sporting goods with improved mechanical properties [3,4]. Fullerene is produced on a large industrial scale by the combustion of hydrocarbons such as toluene [5,6] followed by extraction from the resulting raw soot using an aromatic solvent. The content of extractable fullerenes is ca. 18 wt%, and the residual product called "fullerenes-extracted soot" is an abundant and unavoidable by-product, although it still contains a fullerene-like carbon structure; e.g., bowl-shaped π-conjugating sp^2-planes, polymerized fullerenes, and physically/chemically entrapped fullerenes attached to the amorphous carbon skeleton in the fullerenyl cage. These curved sp^2-carbon surface moieties including 5-membered rings are similar to fullerenes, and display similar reactivity toward chemical functionalization.

A few studies have been conducted on the application of this material. Chen *et al.*[7] reported that fullerenes-extracted soot, generated from graphitized carbon by evaporation under arc discharging, could be used as an adsorbent to collect volatile organic compounds from ambient air. Recently, Kokubo *et al.*[8] demonstrated that by treating fullerenes-extracted soot by moderately heating in aqueous hydrogen peroxide afforded hydrophilic soot , which was attributed to the

introduction of carboxylic and hydroxyl functionality. This material displayed a high radical-scavenging ability compared to fullerene C_{60}, polyhydroxylated fullerene $C_{60}(OH)_{36}$, and even catechin. However, fullerenes-extracted soot has not yet been used for water treatment.

Carbon-based materials such as activated carbon, fullerene C_{60}, carbon nanotubes, and graphene have been widely applied in water purification technology [9-12]. In particular, activated carbon, which is a micro-porous adsorbent, is very useful for the removal of various pollutants from water [13-15]. Activated carbon possesses a large surface area with a number of micro-pores that are ideal for use as an absorbent. However, the chemically inert carbon skeleton in activated carbon is unsuitable for further chemical modification to enhance metal-chelation properties, e.g., by introducing heteroatom functionality to the material surfaces. In this study, we investigated the utility of chemically modified fullerenes-extracted soot as an adsorbent for hexavalent chromium [Cr(VI)].

Cr(VI) is highly toxic and carcinogenic, which has been used extensively in the metal-plating industry [16-17]. In addition, it has been reported that Cr(VI) is present in the effluents of cement/ concrete production, and is eluted from concrete products [18]. The effluent standard for Cr(VI) in Japan is established at 0.5 mg L^{-1}. Therefore it is important to develop novel methods for the efficient removal of Cr(VI) from wastewater. In general, ion-exchange resins and adsorbents have been used for the removal of Cr(VI) from aqueous solutions. Ion-exchange resins show high

efficiency for the removal of Cr(VI); however, their use is not cost-effective for clean-up technologies. Activated carbon has been widely used as an adsorbent for Cr(VI) [19-21]. However, there is a drawback to its use; the adsorbed Cr(VI) on activated carbon is partially reduced to Cr(III) and eluted from the adsorbent [22-23]. Recently, several novel adsorbents for the removal of Cr(VI) has been developed. For example, Badruddoza et al. [24] reported a method to remove Cr(VI) from water using ionically modified magnetic nano-particles. The maximum adsorption capacity was 35.2 mg g^{-1} and the adsorbent was magnetically separable.

We anticipate that fullerenes-extracted soot will not display a high adsorption activity with Cr(VI) in water because it is highly hydrophobic. However, several well-established techniques have been reported that can be used for the surface modification of carbon materials [25-26]. Therefore, we envisaged that the fullerenes-extracted soot could be converted into a novel adsorbent for Cr(VI) by introducing hydrophilic functional groups with an affinity for Cr(VI) to the surface of this material. In this study, fullerenes-extracted soot containing amino groups on the surface was prepared upon treatment with ethylenediamine. The utility of this material as an adsorbent of Cr(VI) was assessed. The efficient adsorption of Cr(VI) by fullerenes-extracted soot modified by ethylenediamine (FES-ED) was expected because the introduction of two closely tethered amino groups to the carbon material is suitable for metal-chelation. Furthermore, the toxicity and cost of ethylenediamine are low, and its reactions with various carbon materials have been established. In

addition, the reaction of primary and secondary amines with fullerene C_{60} under mild conditions has

been reported [25-26]. Using this precedent, we chose to use ethylenediamine as the material for the

modification of the fullerenes-extracted soot.

2. Experimental

2.1. Materials

Fullerenes-extracted soot produced by the combustion method as a residue of the extraction of C_{60},

C_{70}, and other higher fullerenes from the raw soot was obtained from the Frontier Carbon

Corporation (Nanom Black™; Kitakyusyu, Japan). Activated carbon powder, diethyl ether,

ethylenediamine, methanol, and potassium dichromate were purchased from Wako Pure Chemicals

(Osaka, Japan). Pure water was prepared using an automatic water distillation apparatus (MQ

academic A10, Millipore, Billerica, MA, USA). Cement powder was purchased from Home Science

(Osaka, Japan).

2.2. Preparation of fullerenes-extracted soot modified with ethylenediamine (FES-ED)

Ethylenediamine (1.0 mL) was added dropwise to a suspension of fullerenes-extracted soot (1.0

g) in diethyl ether (30 mL) at 5 °C (cooled using an ice-water bath) under an ambient atmosphere.

The reaction mixture was then sealed with a rubber septum and stirred at 25 °C for 24 hours. The

resulting black suspension was centrifuged at 7500 rpm for 5 min. After decantation to remove the

supernatant liquid, the residual black solid was washed with diethyl ether three times with sonication

and centrifuged again. After drying overnight at room temperature, the product, fullerenes-extracted

soot modified with ethylenediamine (FES-ED), was obtained as a black powder (1.27 g), which was

used for the adsorption test.

The activated carbon modified with ethylenediamine (AC-ED) was prepared via reaction of

activated carbon with ethylenediamine using the procedure described beforehand to prepare the

FES-ED powder. The zeta potentials of the FES-ED, fullerenes-extracted soot (FES), AC-ED, and

activated carbon (AC) at pH 3.0 were measured using Zetasizer Nano Series (Malvern Instruments

Limited, Worcestershire, UK). Infrared spectra were recorded using an FTIR-300E spectrometer

(JASCO Ltd., Tokyo, Japan). The powders were visualized using a scanning electron microscope

(SEM; JSM-6010LA; JEOL, Tokyo, Japan). The samples were sputtered with platinum using a

JFC-1600 instrument (JEOL, Tokyo, Japan).

2.3. Adsorption and desorption experiments of FES-ED

The adsorption capacity and isotherm curve for Cr(VI) were determined via batch adsorption

experiments. The batch experiments were carried out using various initial concentrations of Cr(VI)

(10, 20, 40, 100, 140, and 200 μg mL^{-1}, at pH 3), in the presence of the adsorbent (20 mg/20 mL) at

20 ℃ with an agitation time of 30 min. The FES-ED powder (20 mg) and distilled water (10 mL) were added to a flask, and the pH of the liquid was adjusted. The suspension and 10 mL of the pH-adjusted aqueous solution of Cr(VI) were mixed. The pH levels of the suspension and the aqueous solution containing Cr(VI) were conformed to avoid drastically changing the pH of the mixture upon adding the adsorbent. Next, the solutions was agitated at 100 rpm by shaker at 20 ℃ for 30 min. The tested suspension was filtered through a cellulose membrane with a pore size of 0.45 μm (Millipore Corporation, Bedford, USA), and the filtrate was used for measuring the chromium concentration. Similar adsorption experiments for FES, AC, and AC-ED were conducted and the adsorption behaviors of Cr(VI) with these sorbents were compared.

The desorption behavior of Cr(VI) adsorbed onto FES-ED was also investigated. First, the adsorbent (20 mg) was introduced to an aqueous solution of Cr(VI) (20 μg mL^{-1}, 20 mL) at pH 3.0 for 30 min. The suspension was filtered through a cellulose membrane, and the residue was washed with distilled water (50 mL). The recovered adsorbent was treated with an aqueous solution of NaOH aqueous solution (20 mL) at pH 12 and agitated at 100 rpm by shaker at 20 ℃ for 30 min. The tested suspension was filtered through a cellulose membrane, and the filtrate was used for measuring the chromium concentration.

To investigate the reusability of FES-ED, the adsorption and desorption of Cr(VI) using the same FES-ED powder was repeated. FES-ED (20 mg) was introduced to an aqueous solution of Cr(VI)

(20 μg mL^{-1}, 20 mL) at pH 3.0 for 30 min. The suspension was filtered, and the residue washed with

distilled water (50 mL) and added to an aqueous solution of NaOH (20 mL) at pH 12 for 30 min.

The tested suspension was filtrated and the recovered FES-ED powder was washed with distilled

water (20 mL), and reintroduced to the Cr(VI) solution. The adsorption-desorption procedure was

repeated three times.

For the evaluation of FES-ED as an adsorbent for Cr(VI), the removal of Cr(VI) in a cement

effluent using FES-ED, FES, AC, and AC-ED was studied. Cement powder (10 g) in distilled water

(100 mL) was agitated for 120 min. The mixture was filtered through a cellulose membrane, the pH

of the filtrate was adjusted to 3.0, and the resulting aqueous solution was used as the test solution for

Cr(VI) adsorption by FES-ED. In addition, 400 μg of Cr(VI) was added to a portion of the test

solution (20 mL). The resulting solution was also used for the adsorption test.

Chromium concentrations in the aqueous solutions were measured using an ICP emission

spectrometer SPS 3100 (SSI Nanotechnology, Tokyo, Japan) using the following experimental

operating parameters: RF power, 1.2 kW; plasma gas flow rate (Ar), 16 L min^{-1}; carrier gas flow rate,

1.0 L min^{-1}; auxiliary gas flow rate, 1.0 L min^{-1}. The working wavelength for chromium was

205.5523 nm, and the detection limit of Cr was 7 μg L^{-1}. The concentration of Cr(VI) in the test

solutions was measured by the diphenylcarbazide method.

3. Results and Discussion

3.1. Characterization of FES-ED

The fullerenes-extracted soot used in this study is the by-product of the commercial production of fullerenes C_{60} and C_{70} obtained by the combustion method using toluene. To date, only a few studies have been reported on the characterization of fullerenes-extracted soot. However, it has been reported that the fullerene-extracted soot produced by the combustion of hydrocarbons contains higher fullerenes such as C_{70}, C_{84}, and C_{86} [27]. The fullerenes-extracted soot used in this study probably contains fullerenes of a much higher molecular weight.

To the best of our knowledge, the preparation of surface-modified fullerenes-extracted soot using ethylenediamine has been reported only by our group [7]. The results of the elemental analysis of the FES-ED used in this study are shown in Table 1. FES-ED contains a higher nitrogen content (6.57%) than FES (0.05%), as well as a reduced carbon content (from 93.21% to 78.23%), clearly indicative of the introduction of a substantial amount of nitrogen groups. Fig. 1a shows the FTIR spectra of FES and FES-ED, in which the broad and strong N-H stretching vibration bands ranging from 3000 to 3700 cm^{-1} correspond to the amino groups introduced to FES. Furthermore, the peaks at 1654 and 1105 cm^{-1} in the FTIR spectrum of FES-ED correspond to the N-H bending and C-N stretching vibrations, respectively. These results strongly indicate the existence of amino groups on the surface of FES-ED. The strong signals at 2849 and 2920 cm^{-1} in the FTIR spectrum of FES were attributed

to the C-H stretching vibration due to the residual methyl groups of toluene and/or 1,3,4-trimethylbenzene, because fullerenes-extracted soot is prepared by the combustion of toluene and the use of the alkyl-substituted aromatic solvent is used for the extraction of fullerene. Similar observations were found in the elemental analysis (Table 1) and FTIR spectra (Fig. 1b) of AC-ED indicating the possible physical adsorption of ethylenediamine. However, the characteristic peaks for the chemical introduction of the amino groups in AC-ED are rather unclear when compared with those found with FES-ED.

The morphology of the FES-ED was observed using SEM; the images reveal that the FES-ED had macroporous structure (Fig. 2). Using SEM, we confirmed that the FES structures was similar to that of FES-ED. Chen *et al.* [8] reported that fullerenes-extracted soot generated by graphitized carbon evaporating under arc discharging is a multicomponent mixture with abundantly porous and large specific area unlike graphite and graphitized carbon produced from carbon blacks.

It is well known that the structure of activated carbon is microporous and that the pores play an important role in the adsorption process [28]. The differences between the surface structure of fullerenes-extracted soot and activated carbon should influence their adsorption properties and mechanisms.

The zeta potential of FES-ED shows a peak at 42.2 mV at pH 3.0, which indicates that the FES-ED powder was dispersed with a positive charge in water at pH 3.0. The FES-ED surface is

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positively charged because of the protonation of the amino groups. The zeta potentials of FES, AC, and AC-ED were 9.27, -2.65, and 24.2 mV, respectively.

3.2. Adsorption properties of FES-ED

To investigate the adsorption properties of FES-ED for Cr(VI), the FES-ED powder (20 mg) was added to an aqueous solution of the Cr(VI) (10 µg mL^{-1}, 20 mL) at pH 3.0 (Table 2, entry 1).

The level of Cr(VI) in the aqueous solution treated with FES-ED was lower than that of the effluent standard of Japan (0.5 µg mL^{-1}). The Cr levels of the solutions treated with AC, AC-ED, and FES were > 0.5 µg mL^{-1}, i.e., 2.2, 2.3, and 2.0 µg mL^{-1}, respectively. These results show that FES-ED was useful as an adsorbent for Cr(VI) compared with AC, AC-ED, and FES used in this study. In addition, the removal (%) of Cr(VI) in the absence of an adsorbent was <5%. This result indicates that the adsorption of Cr(VI) onto the glass vessels and membrane filter was low under the experimental conditions used in this study.

FES did not display a high adsorption ability without modification by ethylenediamine (Table 2, entries 7 and 10), i.e., the amino groups on the surface of the adsorbent contribute to the adsorption of Cr(VI) onto FES-ED. The result of the zeta potential indicates that the amino groups of FES-ED are protonated at pH 3.0, means that the protonated amino groups interact with Cr(VI).

The duration of the adsorption tests on FES-ED, FES, AC, and AC-ED were changed and the

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effect on the Cr(VI) removal (%) was measured to determine the equilibration time for the adsorption of Cr(VI). The equilibrations of Cr(VI) adsorption was achieved in 10 min for FES-ED, AC, and AC-ED, whereas the equilibration of Cr(VI) adsorption was 420 min for FES (Fig.3 for FES-ED). These results indicate that it is difficult for Cr(VI) to access the adsorption sites in FES compared with the other adsorbents because of the highly hydrophobic properties of FES.

After the adsorption test (initial Cr(VI) concentration: 40 μg mL^{-1}, pH 3.0, 30 min), the filtrate was used to determine the Cr(VI) and total Cr concentrations to understand the reduction of Cr(VI) to Cr(III) by the adsorbents during the adsorption test. As a result, the reduction of Cr(VI) to Cr(III) by AC was confirmed. The yield of Cr(III) was calculated as 5% of the initial concentration of Cr(VI) when using AC as the adsorbent. On the other hand, the Cr(III) yield using FES-ED was 1.3% and lower than that found with AC. The reduction reaction of Cr(VI) by activated carbon is well known [29]. Equation (1) shows that the reduction reaction of Cr(VI) to Cr(III) by activated carbon.

$$HCrO_4^- + 7H^+ + 3e^- \rightleftharpoons Cr^{3+} + 4H_2O \tag{1}$$

The adsorptive sites of FES-ED for Cr(VI) are most likely the protonated amino groups. The reductive ability of the protonated amino groups is low, and therefore, the percentage reduction of Cr(VI) by FES-ED is lower than that observed for AC.

It has been reported that Cr(III) is less easily adsorbed onto activated carbon than Cr(VI) [30].

Therefore, the percentage removal of Cr(VI) for AC is lower than that for FES-ED, probably because of the difference in the reductive activities of the adsorbents.

Subsequently, the pH value of the Cr(VI) aqueous solution was varied in the adsorption tests (Fig. 4). The maximum percentage removal of Cr(VI) was observed at pH 3.0. When the pH value of the solution was >3, the adsorption of Cr(IV) to the protonated amino groups would compete with that of the hydroxyl ions. The filtrate of the adsorption test of FES-ED at pH 2.0 was turbid and brownish-red. This result could be caused by the decomposition of FES-ED under the strongly acidic conditions, and therefore, the percentage removal of Cr(VI) at pH 2.0 was lower than that at pH 3. In addition, the optimal level of pH for Cr(VI) removal by AC and AC-ED was 3.0, which is similar to that of FES-ED. Reduction of Cr(VI) to Cr(III) can occur at lower pH values when using activated carbon, whereas it barely occurs at higher pH values. The low percentage removal of Cr(VI) at pH 2.0 for AC and AC-ED could be attributed to the reduction reaction of Cr(VI). In fact, a significant reduction of Cr(VI) to Cr(III) at pH 2 for coconut-shell based activated carbon has been reported [29]. Based on these results, the pH level of the tested solutions was set at pH 3.0 for the adsorption test in this study.

The adsorption of Cr(VI) on FES-ED, AC or AC-ED in solutions containing several metal ions was observed to investigate the influence of the presence of other metal ions such as Cu(II) and Ni(II) have on the removal of Cr(VI) by these adsorbents (Fig. 5). Under the same initial

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concentrations of Cr(VI), Cu(II) and Ni(II) (20 μg mL^{-1}), the percentage of Cr(VI) removal by

FES-ED was higher than for Cu(II) and Ni(II). The percentage removal of Cr(VI) by FES-ED did

not significantly decrease in the presence of Cu(II) and Ni(II) ions (Fig. 5 and Table 2, entry 2). The

competition from coexisting metal ions was negligible. This result was attributed to the differences

between the adsorption sites on FES-ED for Cr(VI) and the other metal ions. Therefore, FES-ED can

be used as an adsorbent that selectively removes Cr(VI) in an aqueous solution containing Cu(II) and

Ni(II) ions. However, small effects on the percentage removal of Cr(VI) in the presence of Cu(II)

and Ni(II) were observed when using AC and AC-ED (Fig.5 and Table 2, entry 8 and 9). These

results could be attributed to the complex adsorption mechnanisms of activated carbon caused by its

micro-porous structure. It is well known that activated carbon adsorbs metal ions via several

mechanisms such as Coulomb interactions and Van der Waals interactions [31].

The adsorption mechanism of FES-ED for Cr(VI) was determined in the batch adsorption

experiments (Table 3). The obtained adsorption data were fitted to the Langmuir and Freundlich

adsorption isotherms. Langmuir and Freundlich adsorption isotherms can be expressed in Eq. (2) and

(3), respectively.

$$C_e/q_e = C_e/q_m + 1/(q_m \cdot K_L) \tag{2}$$

$$\ln q_e = (1/n) \ln C_e + \ln K_F \tag{3}$$

where C_e is the equilibrium concentration of Cr(VI), q_e is the observed uptake capacity, q_m is the

maximum adsorption capacity, K_L is the Langmuir constant related to the energy of the adsorption, K_F and n are the Freundlich constants related to the adsorption capacity and the intensity of the adsorbent, respectively.

The Langmuir adsorption model is the model of monolayer adsorption onto the surface of an adsorbent. Likewise, the Freundlich adsorption model is not a monolayer adsorption, and it contains several kinds of adsorption patterns.

In the case of FES-ED, the Langmuir isotherm model ($r^2 = 0.998$) describes the isotherm better than the Freundlich isotherm model ($r^2 = 0.926$), which suggests that the adsorption of Cr(VI) on the FES-ED occurs via a monolayer adsorption onto the surface of the FES-ED (Fig.6). Furthermore, the result indicates that the protonated amino groups of FES-ED act mainly as the Cr(VI) adsorption sites and adsorb Cr(VI) on a one-on-one basis.

We focused on the Langmuir constants of the FES-ED to compare the adsorption ability of FES-ED with that of the published adsorbents for Cr(VI) removal (Table 4). The maximum uptake capacity of FES-ED for Cr(VI) was higher or similar to those of the other adsorbents listed in Table 4, with the exception of Chattim tree saw dust [37]. The Chattim tree saw dust has high q_m, the result would be attributed to the large number of adsorption sites (carbonyl, hydroxyl, and amide groups) on the cell surface of the adsorbent. The K_L value of FES-ED for Cr(VI) was higher than that of the other adsorbents listed in Table 4, with the exception for the adsorbents listed in reference 38. The

larger Langmuir constant K_L, the higher is the adsorption energy that resulted in a fast increase in adsorption at low concentrations of the adsorbate.

3.3. Desorption of Cr(VI) from FES-ED

The desorption behavior of Cr(VI) adsorbed onto FES-ED was observed. The percentage recovery of Cr(VI) following treatment with an aqueous solution of NaOH adjusted to pH 12 was 75%. The recovery in percent was calculated using the adsorbed Cr(VI). This suggests that some of the Cr(VI) adsorption sites of FES-ED are attacked by OH$^-$, and that the exchange from Cr(VI) to OH$^-$ occurs at pH 12. In addition, the percentage desorption of Cr(VI) from FES-ED observed by the batch tests using an aqueous solution at a pH 3-7 were <0.45%. The Cr(VI) adsorbed onto FES-ED was retained over this pH range.

A similar desorption test was studied using AC. The percentage Cr(VI) recovery for AC in the batch test using an aqueous solution at pH 12 was 59%, which is lower than that found for FES-ED. The result suggests that FES-ED is suitable for reuse as a Cr(VI) adsorbent in comparison with AC.

The adsorption and desorption tests using the same FES-ED sample was repeated three times to observe the reusability of FES-ED, and the results are shown in Fig. 7. The adsorption was 97% and the desorption ~75% throughout the adsorption–desorption cycles (1–3 times). Therefore, FES-ED can be used repeatedly as an adsorbent to remove Cr(VI) from water by eluting Cr(VI) with an

aqueous solution of NaOH adjusted to pH 12.

3.4 Application of FES-ED to the adsorbent of Cr(VI) in the eluate of a cement sample

It is well known that the eluates of cement contain Cr(VI) [39]; there are several examples that show

that the leaching of concrete waste leads to Cr(VI) pollution of soil and ground water [40]. It was

reported that the Cr(VI) concentrations that leached from mortar are higher than the limit set by the

US EPA [41]. To evaluate the FES-ED as an adsorbent of Cr(VI) in an environmental sample, the

removal of Cr(VI) from a cement eluate by FES-ED was investigated. The Cr(VI) concentration of

the cement eluate was 0.18 µg mL^{-1}. After the sample was treated with FES-ED, the Cr(VI)

concentration of the test aqueous solution decreased to 0.044 µg mL^{-1}. The Cr(VI) concentration

using AC and AC-ED as the adsorbents for Cr(VI) were 0.083 and 0.089 µg mL^{-1}, respectively. The

environment standard of Cr(VI) in Japan is 0.05 µg mL^{-1}. From these results, it is confirmed that

FES-ED is useful for the removing Cr(VI) from wastewater.

The cement eluate (20 mL) with an additional 400 µg of Cr(VI) was used for the adsorption test

in order to observe the influence of environmental matrices on the removal of Cr(VI) by FES-ED.

The Cr(VI) concentration of the solution was ~20 µg mL^{-1}. The removal (%) of Cr(VI) by FES-ED

was 79%. On the other hand, the removal (%) by AC and AC-ED were 68% and 64%. The removal

(%) of Cr(VI) from the test solution by FES-ED was lower than that from the Cr(VI) aqueous

solution without environmental matrices (97%, Table 2, entry 2). However, the removal (%) of

Cr(VI) by FES-ED was higher than those by AC and AC-ED. In addition, the cement eluate was

observed by ICP-AES and it was ascertained that the solution contained many kinds of elements

such as Ca, Li, B, Mg, Si, K, Fe and As.

3.5 Adsorption of methyl orange

To evaluate the adsorption ability of FES-ED for organic compounds, the adsorptive removal of

methyl orange, a widely used commercially available azo dye, was studied. The dye was almost

quantitatively removed from an aqueous solution by FES-ED, AC and AC-ED (the initial

concentration of the dye: 20-40 μg mL^{-1}; added adsorbent: 10 mg/40 mL; agitation duration: 120

min). The optimal pH for the adsorption of methyl orange by FES-ED was at pH 3.0. The Langmuir

isotherm model (r^2 = 0.995) describes the isotherm better than the Freundlich isotherm model (r^2=

0.985), which suggests that the adsorption of methyl orange on the FES-ED occurs via monolayer

adsorption onto the surface of the FES-ED. The maximum uptake capacities of FES-ED and AC for

methyl orange were 246 and 274 mg g^{-1}, respectively. In addition, the desorption behavior of methyl

orange from the adsorbent was studied. The adsorbed methyl orange was eluted using 40 mL of an

aqueous solution of NaOH (at pH 12). The percentage of recovery of methyl orange was 84%.

Interestingly, the percentages of methyl orange recoveries for AC and AC-ED were only 8% and

17%, respectively. These results suggest that FES-ED can be useful for a novel adsorbent of methyl orange.

4. Conclusion

The application of FES-ED as an adsorbent for Cr(VI) is presented in this study. Fullerenes-extracted soot is obtained as the by-product of fullerene synthesis by the combustion of toluene. Therefore, this method makes use of an abundant chemical by-product. In addition, the preparation of FES-ED is relatively simple, rapid and cost-effective.

In the desorption tests, the percentage recovery of Cr(VI) was ~75% using an aqueous solution of NaOH adjusted to pH 12 as the eluent. In addition, the FES-ED desorbed Cr(VI) by aqueous solution (pH 12) could be used again as an adsorbent of Cr(VI). FES-ED showed good reusability.

In addition, the adsorption of methyl orange onto the FES-ED was investigated. The dye was almost quantitatively removed from an aqueous solution by the adsorbent. In addition, we confirmed that congo red was also quantitatively removed from aqueous solutions by FES-ED under the same conditions used for the removal of methyl orange. Therefore, FES-ED could be widely used as an adsorbent of various environmental pollutants. From these results, we conclude that FES-ED is useful for water-purification technology. FES-ED reveals several different properties for the adsorption and desorption of pollutants compared to those of activated carbon, and can play a

potential role in environmental purification at various polluted sites in combination with activated

carbon.

Acknowledgements

References

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, C_{60}: Buckminsterfullerene.

Nature 318 (1985) 162-163.

[2] Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. Felipe, J. Fure, L. Wang, J. M. Alford, R. E. Smalley,

Fullerenes with metals inside, J. Phys. Chem. 95 (1991) 7564-7568.

[3] L. Mu, R. L. Sprando, Application of nanotechnology in cosmetics, Pharmaceutical Res. 27

(2010) 1746-1749.

[4] Y.-P. Sun, J. E. Riggs, Organic and inorganic optical limiting materials. From fullerenes to

nanoparticles, Int. Rev. Phys. Chem. 18 (1998) 43-90.

[5] R. Taylor, G. L. Langley, H. W. Kroto, D. R. M. Walton, Formation of C_{60} by pyrolysis of

naphthalene, Nature 366 (1993) 728-731.

[6] X. Armand, N. Herlin, I. Voicu, M. Cauchetier, Fullerene synthesis by laser pyrolysis of

hydrocarbons, J. Phys. Chem. Solids 158 (1997) 1853-1859.

[7] C. Chen, J. Chen, X. Wang, S. Liu, G. Sheng, J. Fu, Fullerene-extracted soot: a new adsorbent for collecting volatile organic compounds in ambient air, J. Chromatogr. A 886 (2000) 313-317.

[8] K. Kokubo, S. Yamakura, Y. Nakamura, H. Ueno, T. Oshima, Radical-scavenging ability of hydrophilic carbon nanoparticles: From fullerene to its soot, Fuller. Nanotub. Car. N. in press.

[9] J. M. Dias, M. C. M. Alvim-Ferraz, M. F. Almeida, J. Rivera-Utrilla, M. Sánchez-Polo, Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review, J. Environ. Manag. 85 (2007) 833–846.

[10] X. Cheng, A. T. Kan, M. B. Tomson, Naphthalene adsorption and desorption from aqueous C_{60} fullerene, J. Chem. Eng. Data 49 (2004) 675-683.

[11] J.-L. Gong, B. Wang, G.-M. Zeng, C.-P. Yang, C.-G. Niu, Q.-Y. Niu, W.-J. Zhou, Y. Liang, Removal of cationic dyes from aqueous solution using magnetic multi-wall carbon nanotube nanocomposite as adsorbent, J. Hazard. Mater. 164 (2009) 1517–1522.

[12] G. Zhao, L. Jiang, Y. He, J. Li, H. Dong, X. Wang, W. Hu, Sulfonated graphene for persistent aromatic pollutant management, Adv. Mater. 23 (2011) 3959-3963.

[13] A. E. Nemr, O. Abdelwahab, A. El-Sikaily, A. Khaled, Removal of direct blue-86 from aqueous solution by new activated carbon developed from orange peel, J. Hazard. Mater. 161(2009) 102–110.

[14] S. Chen, J. Zhang, , C. Zhang, Q. Yue, Y. Li, C. Li, Equilibrium and kinetic studies of methyl orange and methyl violet adsorption on activated carbon derived from Phragmites australis, Desalination 252 (2010) 149-156.

[15] S. Azizian, M. Haerifar, H. Bashiri, Adsorption of methyl violet onto granular activated carbon: Equilibrium, kinetics and modeling, Chem. Engineer. J. 146 (2009) 36–41.

[16] J. A. Alcedo, K. E. Wetterhahn, Chromium toxicity and carcinogenesis, Int. Rev. Exp. Pathol. 31 (1990) 85-108.

[17] F. Akbal, S. Camcı, Copper, chromium and nickel removal from metal plating wastewater by electrocoagulation, Desalination 269 (2011) 214-222.

[18] S. S. Potgieter, N. Panichev, J. H. Potgieter, S. Panichev, Determination of hexavalent chromium in South African cements and cement-related materials with electrothermal atomic absorption spectrometry, Cement Concrete Res. 33 (2003) 1589–1593.

[19] V. K. Gupta, I. Ali, T. A. Saleh, M. N. Siddiqui, S. Agarwal, Chromium removal from water by activated carbon developed from waste rubber tires, Environ. Sci. Pollut. Res. 20 (2013) 1261-1268.

[20] M. Owlad, M. K. Aroua, W. M. A. W. Daud, Hexavalent chromium adsorption on impregnated palm shell activated carbon with polyethyleneimine, Biores. Technol. 101 (2010) 5098–5103.

[21] J. Acharya, J. N. Sahu, B. K. Sahoo, C. R. Mohanty, B. C. Meikap, Removal of chromium(VI)

from wastewater by activated carbon developed from Tamarind wood activated with zinc chloride, Chem. Engineer. J. 150 (2009) 25–39.

[22] F. D. Natale, A. Lancia, A. Molino, D. Musmarra, Removal of chromium ions form aqueous solutions by adsorption on activated carbon and char, J. Hazard. Mater. 145 (2007) 381–390.

[23] J. L. Gardea-Torresdey, K. J. Tiemann, V. Armendariz, L. Bess-Oberto, R. R. Chianelli, J. Rios, J. G. Parsons, G. Gamez, Characterisation of Cr(VI) binding and reduction to Cr(III) by the agricultural byproducts of *Avena monida* (Oat) biomass, J. Hazard. Mater. B80 (2000) 175–188.

[24] A. Z. M. Badruddoza, Z. B. Z. Shawon, M. T. Rahman, K. W. Hao, K. Hidajat, M. S. Uddin, Inonically modified magnetic nanomaterials for arsenic and chromium removal from water, Chem. Engineer. J. 225 (2013) 607-615.

[25] H.-L. Ma, Y. Zhang, Q.-H. Hu, D. Yan, Z.-Z. Yu, M. Zhai, Chemical reduction and removal of Cr(VI) from acidic aqueous solution by ethylenediamine-reduced graphene oxide, J. Mater. Chem. 22 (2012) 5914-5916.

[26] Z. Li, X. Chang, X. Zou, X. Zhu, R. Nie, Z. Hu, R. Li, Chemically-modified activated carbon with ethylenediamine for selective solid-phase extraction and preconcentration of metal ions, Anal. Chim. Acta 632 (2009) 272–277.

[27] X. Armand, N. Herlin, I. Coicu, M. Cauchetier, Fullerene synthesis by laser pyrolysis of hydrocarbons, J. Phys. Chem. Solids 58 (1997) 1853-1859.

[28] C. Pelekani, V. L. Snoeyink, Competitive adsorption in natural water: Role of activated carbon pore size, Water Res. 33 (1999) 1209-1219.

[29] C. Selomulya, V. Meeyoo, R. Amal, Mechanisms of Cr(VI) removal from water by various types of activated carbons, J. Chem. Technol. Biotechnol. 74 (1999) 111-122.

[30] C. P. Huang, M. H. Wu, The removal of chromium(VI) from dilute aqueous solution by activated carbon, Water Res., 11 (1977) 673-679.

[31] H. Marsh, F. Rodrígues-Reinoso, Activated Carbon, Elsevier, Amsterdam, 2006.

[32] V. K. Gupta, A. Rastogi, A. Nayak, Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material, J. Colloid Interface Sci. 342 (2010) 135–141.

[33] D. C. Sharma, C. F. Fors, Removal of hexavalent chromium using Sphagnum moss peat, Wat. Res. 27 (1993) 1201-1208.

[34] T. Karthikeyan, S. Rajgopal, L. R. Miranda, Chromium(VI) adsorption from aqueous solution by *Hevea Brasilinesis* sawdust activated carbon, J. Hazard. Mater. B124 (2005) 192-199.

[35] C. Namasivayam, M. V. Sureshkumar, Removal of chromium(VI) from water and wastewater using surfactant modified coconut coir pith as a biosorbent, Biores. Technol. 99 (2008) 2218-2225.

[36] Z. Hu, L. Lei, Y. Li, Y. Ni, Chromium adsorption on high-performance activated carbons from

aqueous solution, Separation Purification Technol. 31 (2003) 13-18.

[37] R. Saha, I. Saha, R. Nandi, A. Ghosh, A. Basu, S. K. Ghosh, B. Saha, Application of chattim tree (devil tree, *Alstonia scholaris*) saw dust as a biosorbent for removal of hexavalent chromium from contaminated water, Can. J. Chem. Engineer. 91 (2013) 814-821.

[38] C. Jung, J. Heo, J. Han, N. Her, S.-J. Lee, J. Oh, J. Ryu, Y. Yoon, Hexavalent chromium removal by various adsorbents: Powdered activated carbon, chitosan, and single/multi-walled carbon nanotubes, Separate. Purif. Technol. 106 (2013) 63-71.

[39] M. Frías, M. I. Sánchez de Rojas, N. García, M.P. Luxán, Contributuon of toxic elements: Hexavalent chromium in materials used in the manufacture of cement, Cement Concrete Res. 24, (1994) 533-541.

[40] M. A.Idachaba, K. Nyavor, N. O. Egiebor, The leaching of chromium from cement-based waste form via a predominantly biological mechanism, Adv. Environ. Res. 8 (2004) 483–491.

[41] S. Sinyoung, P. Songsiriritthigul, S. Asavapisit, P. Kajitvichyanukul, Chromium behavior during cement-production process: A clinkerization, hydration, and leaching study, J. Hazard. Mater. 191 (2011) 296-305.

<u>Figure captions</u>

Fig. 1: FTIR spectra: (a) FES and FES-ED, (b) AC and AC-ED.

Fig. 2: Scanning electron micrographs: (a) FES and (b) FES-ED ($\times$50000).

Fig. 3: Effect of contact time on the adsorption of Cr(VI) onto FES-ED.

Fig. 4: Effect of solution pH on Cr(VI) removal by FES-ED, AC, and AC-ED (initial Cr(VI) concentration, 10 μg mL^{-1}; duration, 30 min; pH 3; adsorbent amount, 20 mg/20 mL).

Fig. 5: Removal rate (%) of Cr(VI), Cu(II), and Ni(II) by FES-ED, AC-ED, and AC powder (initial concentration, 20 μg mL^{-1} for each metal ion; duration, 30 min; pH 3; adsorbent amount, 20 mg/20 mL).

Fig. 6: a) Langmuir plot of Cr(VI) adsorption on FES-ED b) Freundlich plot of Cr(VI) adsorption on FES-ED. c_e, the equilibrium concentration of Cr(VI); q_e, the observed uptake capacity.

Fig. 7: Adsorption and desorption of Cr(VI) on FES-ED (initial Cr(VI) concentration, 20 μg mL^{-1}; adsorbent loading, 20 mg/10 mL; aqueous solution for desorption, water adjusted to pH 12).

Highlights

►Fullerenes-extracted soot, the by-product of fullerene production, was used to purify water.

►Fullerenes-extracted soot modified with ethylenediamine (FES-ED) shows high adsorption activity for Cr(VI) in water and good reusability. ► FES-ED also removed methyl orange from

water with high efficiency. ►This is the first example of the application of functionalized

fullerenes-extracted soot to water-purification technology.

Table 1 The result of elemental analysis (%) and zeta potential (mV) of the carbon materials used in this study

Samples	Abbreviation	C	H	N	Zeta potential[a] (mV)
Fullerenes-extracted soot modified with ethylenediamir	FES-ED	78.23	2.75	6.57	41.8
Fullerenes-extracted soot	FES	93.21	1.31	0.05	9.27
Activated carbon modified with ethylenediamine	AC-ED	76.66	3.55	5.72	24.2
Activated carbon	AC	84.20	2.36	0.62	-2.65

[a] Zeta potential was measured at pH 3.

Table 2 Removal (%) of Cr(Vi) from water using fullerenes-extracted soot modified with ethylenediamine (FS-ED), fullerene-extracted soot (FS), activated carbon (AC), and activated carbon modified with ethylenediamine (AC-ED) under

Entry	Adsorbent	Cr(VI) initial solution (μg mL^{-1})	pH value of Cr(VI) solution	Agitation (min)	Equilibrium Cr concentration (μg mL^{-1})	Removal of Cr(VI) (%)
1	FS-ED	10	3	30	0.24	98
2	FS-ED	20	3	30	0.47	98
3	FS-ED	40	3	30	1.6	96
4	FS-ED	100	3	30	25	75
5	FS-ED	140	3	30	55	60
6	FS-ED	200	3	30	110	46
7	FS	20	3	300	8.7	57
8	AC	20	3	30	4.4	78
9	AC-ED	20	3	30	4.0	80
10	FS	20	3	30	10	50
11	AC	20	3	300	5.9	71
12	AC-ED	20	3	300	6.0	70
13	AC	40	3	30	12	71
14	FS-ED	10	2	30	1.4	86
15	FS-ED	10	4	30	0.38	96
16	FS-ED	10	6	30	2.7	73
17	FS-ED	10	8	30	7.8	22
18	FS-ED	10	10	30	9.0	9.6

Table 3 Langmuir and Freundlich parameters of carbon materials used in this study

Adsorbent	Langmuir constants			Freundlich constants		
	Q_m(mg/g)	K_L(g L^{-1})	R^2	K_F	1/n	R^2
FES-ED	93	0.30	0.998	22	0.34	0.926
FES	30	0.080	0.970	7.5	0.26	0.958
AC-ED	59	0.060	0.990	6.8	0.44	0.937
AC	63	0.060	0.985	7.2	0.44	0.936

Table 4 . Langmuir constants for adsorption of Cr(VI) on various adsorbent

Adsorbent	Langmuir constants		
	q_m (mg g^{-1})	K_L (L mg^{-1})	References
Ionically modified magnetic nanoparticles	35.21	0.10	24
Fertilizer industry waste material (carbon slurry)	15.24	0.0024	32
Sphagnum moss peat	26.5	0.0233	33
Hevea Brasilinesis sawdust activated carbon	44.05	0.2215	34
Surfactant modified coconut coir pith	76.3	0.124	35
Activated carbon, GA-3	101.47	0.143	36
Chattim tree saw dust	303	0.116	37
Powdered activated carbon	46.9	1.022	38
Single-walled carbon nanotubes	20.3	1.831	38
Multi-walled carbon nanotubes	2.48	0.838	38
Fullerenes-extracted soot modified with ethylenediamine	93.5	0.302	This work

Fig. 1

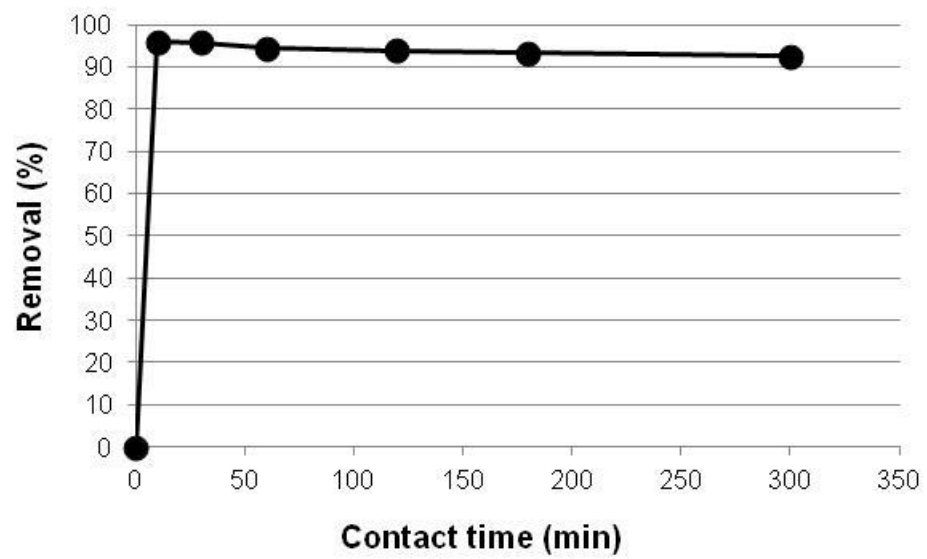SEI 15kV WD10mm SS40   x1,000   10 μm
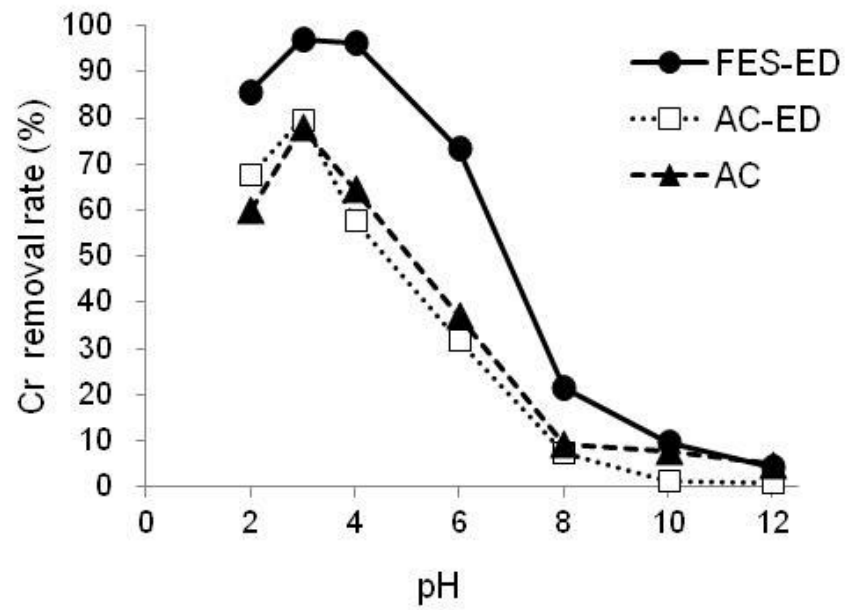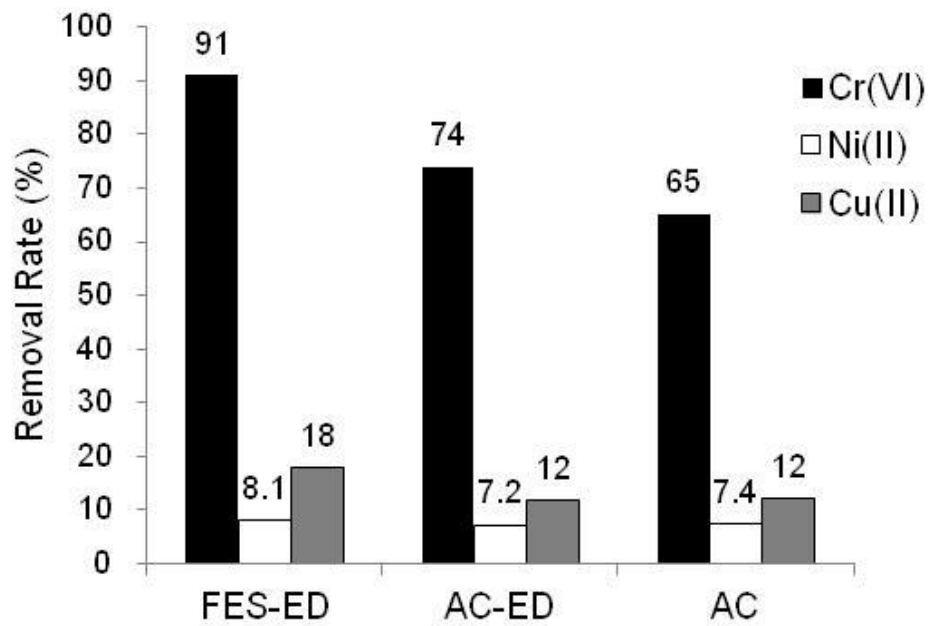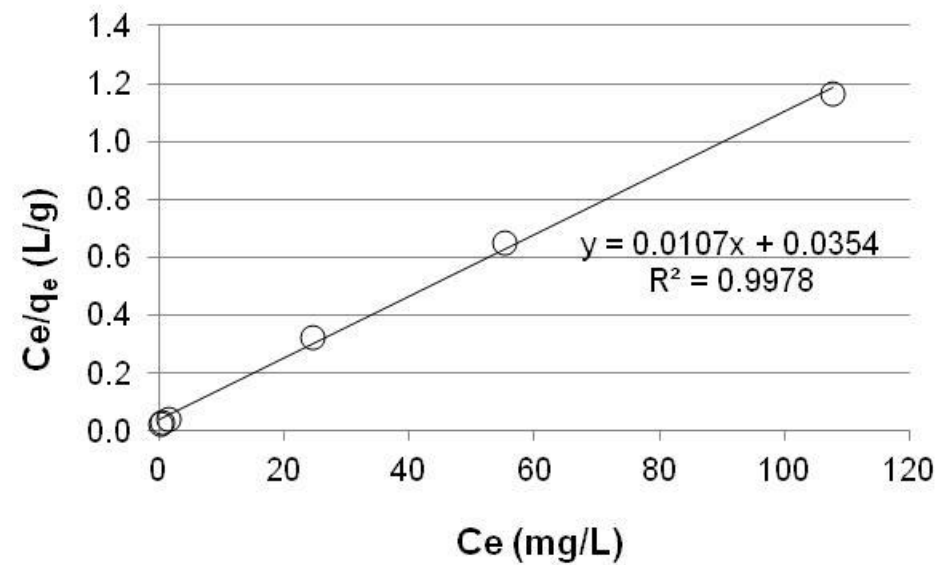Sample   794   Jul 17, 2013

Fig. 2

Fig. 3

Fig. 4

Fig. 5

a)

b)

Fig. 6

Fig. 7