The enhanced adsorption capacity of Cr(III) using tannic acid doped iron/ graphene oxide@activated carbon as a magnetic composite adsorbent

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Abstract: In this study, preparation and characterization of a magnetic composite material consisting of iron oxide, graphene oxide, activated carbon and tannic acid (Fe_3O_4-GO-AC-TA) as an adsorbent was carried out. The magnetic adsorbent was synthesized by co-precipitation method associated with an ultrasound irradiation using tannic acid (TA) as its increase in multi-functionalization. Characterization of the magnetic composite was performed by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). Their adsorption efficiency for Cr(III) ion in aqueous solution expressed as the adsorption capacity (q_e) using UA-MSPE method followed by AAS was studied. From the results, it is evident that the synergic effect of TA can drastically enhance the q_e and/or removal of Cr(III) ion via their electrostatic interactions among the intrinsic functional components of the magnetic composite material in the adsorption-desorption system.

Keywords: Iron oxide, Graphene oxide, Activated carbon, Tannic acid, Adsorption capacity

1. Introduction

Discharging of the polluted water from industry into the aquatic environment causes a harmful effect in all the living system since it often contains heavy metals such as chromium ions (Cr^{3+}/Cr^{6+}) [1]. While, the existence of chromium ions in the water even with extremely high content appears to be invisible and it might be believed that the polluted water can be used for human being. Thus, chromium ion can be absorbed by organs in human body and causes a harmful effect [2]. That is to say, the water involving chromium results in strong damage to human being, such as dysfunction of the kidneys, and blood diseases.

Recently, numerous industrial graphene of the carbon based materials for Biology and Chemistry applications have been much interested in routine consumption [3-7]. Graphene oxide (GO) is one of most popular graphene based materials, and it is widely used as an adsorbent for toxic metal. GO is a two-dimensional material [8,9]. It has been

oxidized, with O functional group on the surface of the sp^2 basal plane and a strong interest due to their extraordinary properties [10], such as chemical stability, large surface area, and hydrophility [11,12]. The large specific surface area and the abundance of functional groups on surface of graphene oxide exhibits a capability for the adsorption of toxic metal and the surface of graphene oxide can be modified with various ligands and easy to use for contaminants removal from aqueous solution.

In this work, graphene oxide will be modified its surface with the tannic-magnetic property and used as an adsorbent for removal of toxic metal from aqueous solution. GO is regarded the best supporting materials is the most of carbonaceous composite. The activated carbon is regarded as efficient adsorbent for the organic pollutants due to pores distribution and the surface area [13-15]. In particular, iron oxide can be separated easily because of magnetic property and besides, tannic acid can bond with positive ion because tannic acid contains a lot of hydroxyl functional group which ionize to hydronium ion [16-19].

Advantages of graphene oxide, iron oxide, activated carbon and tannic acid were exploited to be conjugated for cost reduction of the adsorbent products and the production of a composite also possesses high adsorption performance. Characterization of the obtained composite adsorbent was performed by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). The adsorption efficiency for Cr(III) ion both in the presence and absence of iron oxide determined by using atomic absorption spectrometry (AAS) was investigated and compared.

2. Materials and Methods

2.1 Chemicals and reagents

All the chemicals used throughout this study are analytical grades including activated carbon (Sigma-Aldrich, USA), tannic acid (Sigma-Aldrich, USA), sodium chloride (Sigma-Aldrich, USA), Tris(hydroxymethyl) aminomethane (Sigma-Aldrich, USA), hydrochloric acid (Sigma-Aldrich, USA), graphene oxide (Sigma-Aldrich, USA), chromium (III) standard solution (Acros organics, Belgium). Deionized (DI) water with a resistivity of 18.2 MÙ cm produced using a Millipore water purification system (Molsheim, France) was used throughout the experiments.

2.2 Instruments and apparatus

The attenuated total reflectance - Fourier transform infrared (ATR-FTIR) spectrum was measured by TENSOR 27 system (Bruker Optics, Germany) in the range of 500-4000 cm^{-1}. Surface image was recorded using a HITACHI S-3000N scanning electron microscope (SEM, Hitachi Co. Ltd., Japan). An ultrasonic bath (Model GT Sonic, China) at size tank of 36x65x40 cm, a frequency of 40 kHz, the maximum ultrasound power of 720 W and heater 20-80 C with heating power of 800 W was applied for the ultrasound assisted magnetic solid-phase extraction (UA-MSPE). pH value was measured using UB-10 Ultra Basic pH meter. Cr(III) ion in water samples were determined by atomic

absorption spectrometer (ASS, Perkin Elmer Instrument AAnalyst 100, Connecticut, USA). The operational system is controlled by AA Winlab software. Centrifuge used is from Centurion Scientific 1010 (UK). An orbital shaker is from Yamato Scientific (Japan).

2.3 Preparation of tannic acid doped graphene oxide@activated carbon composite

The graphene oxide@activated carbon (GO-AC) was a subject to prepare as core substrate adsorbent. At first, 0.15 g of activated carbon (AC) was added into 50 mL of deionized water then stirred with a magnetic stirrer for 3 h. The same amount of the prepared powder GO was sonicated in 50 mL of deionized water for 2 h. This sonicated GO sample was then added into the AC solution and the resulting mixture was then stirred at 80 C for 12 h. The mixture solution was poured into a petri dish and dried in an oven at 70 C overnight.

For a multi-functionalization purpose, tannic acid doped graphene oxide@activated carbon (GO-AC-TA) was to synthesized as followed: 0.2 g of GO-AC was dispersed in 200 mL of 0.1 mol L^{-1} Trisbase buffer pH 8.5. By addition of 0.25 g of TA to the mixture, it was stirred at room temperature for 24 h. The resulting solution was centrifuged at 3500 rpm and washed three times with deionized water and dried at 40 C overnight.

2.4 Preparation of tannic acid doped iron/graphene oxide@activated carbon composite (Fe_3O_4-GO-AC-TA)

To increase the magnetic property of the GO-AC-TA composite, the procedure for the preparation of Fe_3O_4-GO-AC-TA was conducted in the similar way as mentioned above (section 2.3) except using the prepared Fe_3O_4-GO by co-precipitation method, as a starting material instead of GO.

2.5 Characterization of the magnetic composite adsorbent

The characterization of the magnetic composite adsorbent obtained was performed only by both scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

2.6 Determination of Cr by AAS

The determination of the metal ions was carried out by using atomic absorption spectrometer (AAS), which has the instrumental conditions for AAS setting program for the wavelength of Cr is 357.9 nm. The sample solution containing the metal ion was analyzed by preparation of the calibration curve for five concentration levels of 1, 3, 5, 7 and 10 ppm. The linear range was performed in the range of 1-10 ppm for Cr(III) ion with its regression coefficient (r^2).

2.7 Optimization of ultrasonic assisted magnetic solid-phase extraction (UA-MSPE)

The simultaneous optimization conditions were conducted in details including solution pH 2-12, 0.01-0.05 g amount of the adsorbent used and 10-60 min sonication time,

respectively. The experimental data were expressed by its Cr absorbance unit full scale at 357.9 nm of the AAS, and each experiment was performed at least in triplicate.

The determination of Cr(III) ion using the magnetic composite adsorbent of Fe_3O_4-GO-AC-TA under the optimum conditions of the UA-MSPE was done. First, the adsorbent 0.01 g in 10 mL with phosphate buffer solution pH 7.0 was added into the test tube. Then, the mixture was sonicated by an ultrasonic bath at 0.5 kW for 30 min. Subsequently, the supernatant was removed by an external magnetic field using a simple magnet prior to determination of the Cr(III) ion by AAS.

When the determination of Cr(III) concentration in the extracted solution was done by AAS, the results were expressed in terms of the equilibrium adsorption capacity (q_e, mg g^{-1}) by the equation: $q_e = (C_o - C_e) *V/ m$, where, q_e is the equilibrium adsorption capacity (μg g^{-1}). C_o (μg g^{-1}) is an initial concentration and C_e (μg g^{-1}) is a residual concentration after equilibrium of the metal ion, and m (g) is mass of the magnetic adsorbent, and V is volume of the metal ion solution used.

3. Results and Discussion

3.1 Characterization by SEM and FTIR

SEM image of the activated carbon, used as one of the main starting materials, is shown in Fig 1. It is shown that basically it has many pores along the piece. Since it has no active functional group on the surface, it would commonly serve a good adsorption property of organic and inorganic compounds, prior to production of the magnetic composite material. From Fig. 2a and 2b, FTIR spectra show that both tannic acid doped graphene oxide@activated carbon (GO– AC – TA) and tannic acid doped iron/graphene oxide@activated carbon (Fe_3O_4 – GO – AC – TA) have more C-O stretching and more O-H stretching. Thus, it is likely confirmed that the simple synthesis of the magnetic composite materials would be successfully obtained. After coating Fe_3O_4 nanoparticles on GO, the peaks from 1000 to 1200 cm^{-1} were observed (Table 1), indicating the C–O vibration mode of epoxy groups, the peaks around 3340 cm^{-1} (the O–H vibration of hydroxyl group) and the peak at 1690 cm^{-1} (the C=O vibration of carboxylic group) [20,21].

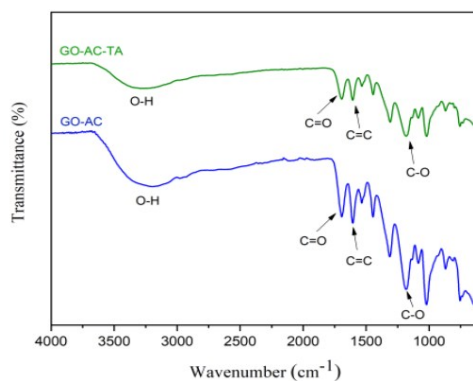Fig. 1   SEM image of the activated carbon used as the composite substrate (magnitude x800 with 100 μm scale)
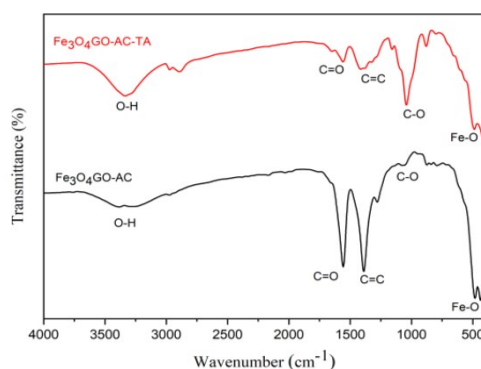
Fig. 2a   FTIR spectra of GO-AC-TA and GO-AC composites

Fig. 2b   FTIR spectra of Fe_3O_4–GO–AC and Fe_3O_4 – GO – AC – TA magnetic composites

Table 1. FTIR assignment of four kinds of the obtained composite materials

Functional group	Wavenumber, cm^{-1}			
	GO-AC-TA	GO-AC	Fe_3O_4 – GO – AC – TA	Fe_3O_4–GO–AC
O-H	3304	3290	3340	3340
C=O	1690	1695	1556	1556
C=C	1605	1609	1391	1391
C-O	1174	1182	1044	1037
Fe-O	-	-	503	494

3.2 The optimum conditions for UA-MSPE

3.2.1 Effect of pH

The effect of pH is a major factor affecting on pre-concentration procedure because of different functional groups of the adsorbent and the target analyte. Hydronium ion (H_3O^+) in the solution are directly involved at the active sites of the adsorbent. From Fig.3, it was found that the absorbance raises according to the pH increasing from 3 to 7 indicating higher concentration of Cr after the adsorption experiments. However, the absorbance remains rather constant with pH between 7 and 12. Therefore, the optimum condition of pH around 7-9 can be chosen for further experiment.
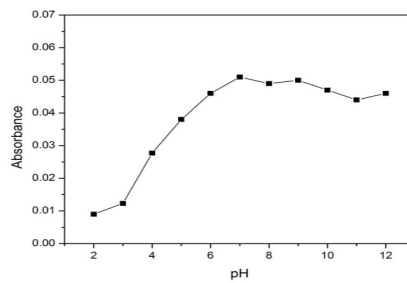
Fig. 3 Effect of the solution pH

3.2.2 *Effect of the adsorbent dosage*

An amount of the adsorbent used is also an influent parameter for the adsorption procedure because using minimum dosage of the adsorbent provides Cr(III) ion ability to be adsorbed. The absorbance obtained versus various amounts of the adsorbent seemed to have no significant difference in ranging of 0.01-0.05 g. Thus, the amount of adsorbent 0.01 g was chosen in such case study.
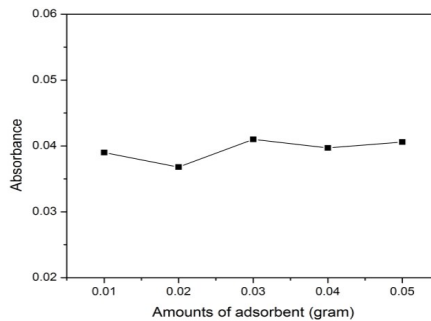

Fig. 4 Effect of the amount of adsorbent used

3.2.3 *Effect of the adsorption time*

From Fig. 5, the absorbance taken from this adsorption time more than 30 min also seemed to have no significant difference to each other until 60 min. Thus, the optimum adsorption time approximately 30 min was relatively justified for reasonable equilibrium adsorption situation.
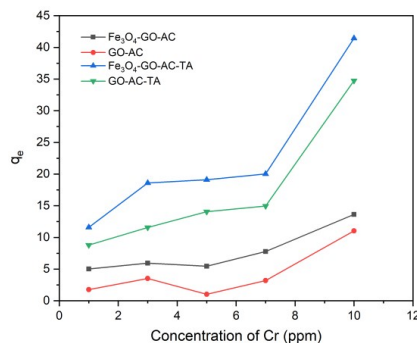

Fig. 6 The effect of Cr(III) concentrations on the q_e of Cr(III) using four composite adsorbents

3.3.2 *Effect of iron oxide and tannic acid*

Using AAS, standard curve for Cr determination was ranged between 1 ppm and 10 ppm as y = 0.0111x – 0.0059 (r^2 = 0.9937) (*data not shown*). This calibration curve of Cr was used to calculate q_e for Fe_3O_4-GO-AC and GO-AC composites. For both GO-AC-TA and Fe_3O_4-GO-AC-TA composites, the standard curve for Cr was as followed: y = 0.0104x – 0.0065 (r^2 =0.9906) (*data not shown*). Therefore, the average q_e of four adsorbents was compared to each other as shown in Fig. 7. Fe_3O_4-GO-AC-TA has the most average q_e. It is due to an iron oxide taken as co-functionalized with graphene oxide prior to be doped with tannic acid. However, the role of tannic acid can play much more adsorption effect when compared with other adsorbents without tannic acid doping (Table 2). Both GO-AC-TA (q_e of 16.82) and GO-AC (q_e of 4.10) or Fe_3O_4-GO-AC (q_e of 7.57) indicates clearly the effect of tannic acid doping in the composite materials. In such case, Fe_3O_4-GO-AC-TA gave q_e of 22.16 compared with GO-AC-TA, attributing around 1.3 folds higher or 32% enhancement of the adsorption capacity of Cr(III) ion in aqueous solution.
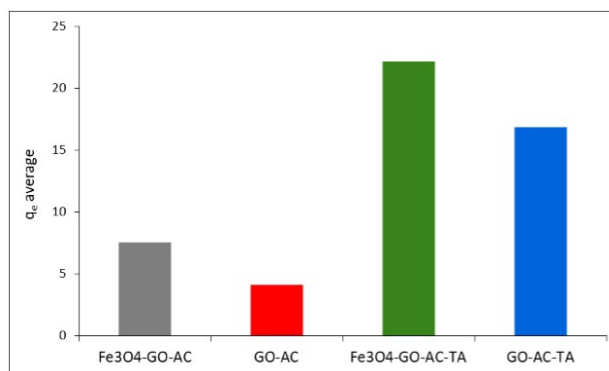

Fig. 7　The average q_e of Cr(III) showing the enhanced adsorption capacity by the magnetic composite adsorbent

Table 2 The average q_e of the four composite materials used in the adsorption of Cr(III) ion

Composite adsorbent	q_e of Cr(III), mg g^{-1}	Effect of TA doping (fold)
GO-AC	4.10	-
GO-AC-TA	16.82	4.1
Fe_3O_4-GO-AC	7.57	-
Fe_3O_4-GO-AC-TA	22.16	2.9

Conclusion

In this study, an ultrasound-assisted (UA) technique with MSPE method was used for simultaneous pre-concentration and determination of trace amounts of Cr(III) ion prior to AAS analysis by using Fe_3O_4-GO-AC-TA as a novel adsorbent that synthesized by co-precipitation method in association with an ultrasound irradiation using tannic acid for their multi-functionalization of the Fe_3O_4 – GO – AC substrate. The magnetic composite material has various of pronounced advantages, such as easily eluting the target element and high surface area. The ultra-sonication was a beneficial tool for an increasing the

dispersion of the adsorbent into the solution confirming the strong association of the ultrasound in mass transfer between absorbent and adsorbent. Thus, the combination of sonication with MSPE method can improve both efficiency for pre-concentration and determination of the metal ions i.e. Cr(III) ion. According to *Pearson's Hard Soft Acid-Base* theory, the hydroxyl group is the hard base characteristic which is a good affinity with hard acid. Thus, the magnetic composite, Fe_3O_4 – GO – AC – TA, can excellently adsorb Cr(III) ion which is hard acid. Based on these results, this method is a good alternative choice with high performance method for the adsorption of Cr(III) ion in the polluted water.

Acknowledgements

Notes

The authors declare no conflict of interest.

References

[1] Rakhunde, R., Deshpande, L. and Juneja, H.D. (2012). Chemical Speciation of Chromium in Water: A Review. *Critical Reviews in Environmental Science and Technology*, 42(7), 776-810.

[2] Baruthio, F. (1992). Toxic effects of chromium and its compounds. *Biol Trace Elem Res*. 32, 145-53.

[3] Unasri, A. and Chanthai, S. (2020). Carbon dots and graphene quantum dots doped and/or co-doped with labile elements as facile fluorescence turn-on/off sensors for heavy metals analysis: A Review. *J. Multifunctional Materials and Photoscience,* 11(1), 65-108.

[4] Zheng Bo, Xiaorui Shuai, Shun Mao, Huachao Yang, Jiajing Qian, Junhong Chen, Jian hua Yan and Kefa Cen. (2014). Green preparation of reduced graphene oxide for sensing and energy storage applications. *Scientific Reports*, 4: 4684, 1-8.

[5] Zambaga Otgonbayar, Kamrun Nahar Fatema, Sunhye Yang, Ick-Jun Kim, Minchul Kim, Sang Eun Shim and Won-Chun Oh. (2021). Temperature dependence for high electrical performance of Mn-doped high surface area activated carbon (HSAC) as additives for hybrid capacitor. *Scientific Reports*, 11: 534.

[6] Yujun Kim, Geunseok Jang and Taek Seung Lee. (2015). New fluorescent metal-ion detection using a paper-based sensor strip containing tethered rhodamine carbon nanodots. *ACS Applied Materials and Interfaces*, 7, 15649-15657.

[7] Yan Wang, ZiXing Shi and Jie Yin. (2011) Facile synthesis of soluble graphene via a green reduction of graphene oxide in tea solution and its biocomposites. *ACS Applied Materials and Interfaces*, 3, 1127-1133.

[8]. Stankovich, S., Dikin, D.A., Piner R.D., Kohlhaas, K.A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S.T. & Ruoff, R.S. (2007). Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. Carbon, 45, 1558-1565.

[9]. Su, C-Y., Xu, Y., Zhang, W., Zhao, J., Tang, X., Tsai, C-H., and Li, L-j. (2009). Electrical & spectroscopic characterizations of ultralarge reduced graphene oxide monolayers. Chemistry of Materials, 21, 5674-5680.

[10] He, H., Klinowski, J., Forster, M. & Lerf, A. (1998). A new structural model for graphite oxide. Chemical Physics Letters, 287, 53-56.

[11] Bradder, P., Ling, S.K., Wang, S. & Liu, S. (2011). Dye adsorption on layered graphite oxide. Journal of Chemical & Engineering Data, 56, 138-141.

[12] Lai, L.F., Chen, L.W., Zhan, D., Sun, L., Liu, J.P., Lim, S.H., Poh, C.K., Shen, Z.X. & Lin, J.Y. (2011). One-step synthesis of NH2- graphene from in situ graphene-oxide reduction and its improved electrochemical properties, Carbon, 49, 3250-3257.

[13] Li, Y., Du, Q., Liu, T., Peng, X., Wang, J., Sun, J., Wang, Y., Wu, S., Wang, Z., Xia, Y, & Xia, L. (2013). Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide and carbon nanotubes. Chemical Engineering Research and Design, 91, 361-368.

[14]. Abd-Elhamid, A.I., Kamoun, E.A., El-Shanshory, A.A., & Soliman, H.M.A. (2019). Evaluation of graphene oxide-activated carbon as effective composite adsorbent toward the removal of cationic dyes: Composite preparation, characterization and adsorption parameters. Journal of Molecular Liquids, 279, 530-539.

[15]. Bhattacharyya, A., Ghoraib, S., Ranac, D., Roya, I., Sarkara, G., Sahaa, N.R., Orasugha, J., Ded, S., Sadhukhana, S., & Chattopadhyay, D. (2021). Design of an efficient and selective adsorbent of cationic dye through activated carbon - graphene oxide nanocomposite: Study on mechanism and synergy. Materials Chemistry and Physics, 260, 124090.

[16]. Eftekhari, M., Gheibi, M., Akrami, M., & Iranzad, F. (2018). Solid-phase extraction of ultra-trace levels of lead using tannic acid-coated graphene oxide as an efficient adsorbent followed by electrothermal atomic absorption spectrometry; response surface methodology – central composite design. New Journal of Chemistry, 42, 1159-1168.

[17]. Kim, H.J., Choi, Y.-S., Lim, M.-Y., Jung, K.H., Kim, D.-G., Kim, J.-J., Kang, H., & Lee, J.-C. (2016). Reverse osmosis nanocomposite membranes containing graphene oxides coated by tannic acid with chlorine-tolerant and antimicrobial properties. Journal of Membrane Science, 514, 25-34.

[18]. Al Kinani, A., Gheibi, M., & Eftekhari, M. (2019). Graphene oxide–tannic acid nanocomposite as an efficient adsorbent for the removal of malachite green from water samples. Modeling Earth Systems and Environment, 5, 1627–1633.

[19]. Cheng, C., Jia, M., Cui, L., Li, Y., Xu, L., & Jin, X. (2020). Adsorption of Cr(VI) ion on tannic acid/ graphene oxide composite aerogel: kinetics, equilibrium, and thermodynamics studies. Biomass Conversion and Biorefinery, DOI: 10.1007/s13399-020-00899-4

[20] W. Yang, W. Hu, J. Zhang, W. Wang, R. Cai, M. Pan, C. Huang, X. Chen, B. Yan, H. Zeng, Tannic acid/ Fe^{3+} functionalized magnetic graphene oxide nanocomposite with high loading of silver nanoparticles as ultra-efficient catalyst and disinfectant for wastewater treatment, *Chemical Engineering Journal* 405 (2021) 126629.

[21] K. Yu, P. Shao, P. Meng, T. Chen, J. Lei, X. Yu, R. He, F. Yang, W. Zhu, T. Duan, Superhydrophilic and highly elastic monolithic sponge for efficient solar-driven radioactive wastewater treatment under one sun, *Journal of Hazardous Materials* 392 (2020) 122350.