SORPTION COMPARISON OF TRIVALENT CHROMIUM ON VARIOUS FICUS CARICA CHARCOAL FROM TANNERY WASTEWATER

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Abstract. In this study, equipped charcoal of *Ficus carica* without being impregnated impregnated with potassium hydroxide (KOH), zinc chloride ($ZnCl_2$) and phosphoric acid (H_3PO_4) was used for sorption comparison of trivalent chromium, Cr (III) from tannery wastewater. The equipped charcoals are characterized by Fourier transforms infrared spectroscopy (FT-IR) before and after sorption of Cr(III). The quantitative elemental analysis of the charcoal is performed using PGT Energy dispersive X-ray spectrometry (EDX). The Cr(III) sorption efficacy of charcoal was examined investigating charcoal dose, contact time, and relative pH. Batch sorption test revealed that *Ficus carica* charcoal without impregnation had the maximum sorption capacity of Cr(III). At the same conditions, Cr(III) sorption efficiency on the *Ficus carica* charcoal without impregnation, impregnated with potassium hydroxide, zinc chloride, and phosphoric acid was 98.9%, 98.8%, 8.9% and 2.5%, respectively. The study could be helpful to design the sorption of trivalent chromium from the tannery wastewater in-house prior to discharge.

Keywords: Sorption, Cr (III) extraction, Impregnation, Environment

1 Introduction

The leather industry has a significant position in Bangladesh economy considering its importance in production, employment and export. In the absence of effluent treatment plant (ETP), about 113 tanneries in Bangladesh generate approximately 20,000 m^3 tannery effluent per day (Paul et al. 2013). Usually, leather processing operations are conducted with a huge amount of chemicals. But a majority of these chemicals are not up-taken by the pelt. Mostly, chemicals remaining in wastewater are discharged as waste without being treated causing serious pollutions. Chrome tanning is mostly used to obtain an extraordinary dyeing, hydrothermal stability, and excellent mechanical resistance in leather. More than 90% of the global leather production of 18 billion sq. ft is conducted through the chrome-tanning process (Sundar et al. 2002). Only 60-70% of chromium (Cr) applied in the tanning process are consumed by leather where untreated wastewater holds 1500-3000 mg/L of Cr (Aravindhan et al. 2004). Every day approximately 1.25 tons of chromium is discharged into the Bangladeshi river (UNIDO, 2000). Usually, trivalent chromium, Cr (III) discharging through the wastewater is further oxidized to hexavalent chromium, Cr (VI) that is acutely and chronically toxic to humans even in low concentrations. Therefore, it is essential to remove Cr from chrome tanning effluent before it is released.

By using biological treatment, dissolved solids like Cr removal are not possible. Remediation of Cr from tannery waste effluent can be performed by ion exchange (Rengaraj et. al. 2003), chemical precipitation (Zhou et al. 1995), membrane separations (Kozlowski et. al. 2002), electrochemical precipitation (Kongsricharoern et al. 1996) but high capital and operational costs limit these methods to use commercially. Moreover, a separate pre-treatment or a set of treatments are required for most of the treatment processes. But in the case of the adsorption process, no pre-treatment is required with cheap, simple and easy application.

For having the availability of extensive surface area, microporous structure and high adsorption capacity; the production of charcoal from cheaper materials has gained significant attention for wastewater treatment (Anirudhan and Sreekumari, 2011). All carbonaceous materials are possible to be converted into charcoal, though the properties of the final product will be different, depending on the nature of the raw material, activating agent and activation processes (Bansal and Goyal, 2005). A large number of products, such as coffee husks (Oliveira et al. 2009), mahogany sawdust (Santra et al. 2008), cocoa shell (Ahmad et al. 2012), waste tea (Auta and Hameed, 2011), coffee grounds (Reffas et al. 2010), pomegranate shell (Ghaedi et al. 2012), mahogany sawdust (Malik, 2003), rice husk (Malik, 2003; Santra et al. 2008), coconut shell (Santra et al. 2008), etc. have been successfully converted into low-cost charcoal. The major use of activated carbon is for removing taste, colour, odours, and impurities from liquids/wastewaters and also in solution purification. Besides, in recent times it has been increasingly used for the prevention of environmental pollution (Onyeji and Aboje, 2011).

Ficus carica, a plant is the source of fruit known as fig. It is widely grown throughout the world without any special caring for being dispersed by birds and mammals. In some countries, *Ficus carica* has been used for medicinal benefits (Duke et al. 2002) and a supplement food for diabetics (Mawa et al. 2013) but in Bangladesh, it has no conventional utilization. *Ficus carica* charcoal can be effectively used for removal of Cr from tannery effluent. It has been found that after chemical or thermal modifications, carbonaceous material exhibited tremendous Cr removal capability. Thermal modification is easy and inexpensive but in chemical activation, chemical reagents like zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4), potassium hydroxide (KOH) are used (Buczek, 2016). The drawback of activation with $ZnCl_2$ is the occurrence of pollution with zinc salts which are difficult to remove (Owabor and Iyaomolere, 2013). Others the price of $ZnCl_2$ is higher and extra treatment like washing and pH maintenance are required after activation. From washing, chloride (Cl^-) is usually released that inhibits the growth of plants, bacteria, and fish in surface waters with occurring surface salinity. Activation with H_3PO_4 results in a pitch like sticky charcoal inhibiting the application with additional chemical costs. But natural *Ficus carica* charcoal preparation is possible without any chemical treatment and additional costs. Only thermal modification using pyrolysis is enough to make this type of charcoal. The main advantages of using this charcoal are cheap, accessible and available in abundant quantity.

The aim of this study was using *Ficus carica* to produce charcoal adsorbent to remove Cr (III) from the wastewater. The investigation could fulfil the purpose of Cr (III) removal from tannery wastewater using a low-cost adsorbent prepared from *Ficus carica* which is not generally used profitably in Bangladesh.

2 Materials and Methods

2.1 Sample Collection

Chrome containing wastewater was collected from the SAF Leather Limited, Khulna, Bangladesh. The chrome liquor was collected in a high-density polyethylene container. Before collecting the chrome liquor the container was washed with diluted nitric acid according to the standardized laboratory method. The industrial wastewater was primarily filtered to remove unexpected suspended solids and the filtered liquor was used for treatment. *Ficus carica* was collected from university campus of Khulna University of Engineering & Technology, Khulna, Bangladesh.

2.2 Charcoal Preparation

The collected *Ficus carica* were chopped into small pieces and sun-dried. Afterwards, it was burnt at 600 ^oC in a furnace and crushed with mortar to produce a charcoal powder. Lastly, the required size of the charcoal adsorbent was obtained by sieving on 80-mesh. Fig. 1(a) shows the prepared *Ficus carica* charcoal.

2.2.1 Preparation of KOH impregnated charcoal

Dried *Ficus carica* was mixed with ground KOH in a ratio (1:3). Treatment carried out at 600^{o}C in a furnace. Then, the solution was neutralized with 5% HCl at pH 6.5. After filtration, it was dried at 120 ^{o}C in the oven (Buczek, 2016). Lastly, the required charcoal adsorbent was obtained by crushing with mortar. Fig. 1(b) shows the KOH impregnated *Ficus carica* charcoal.

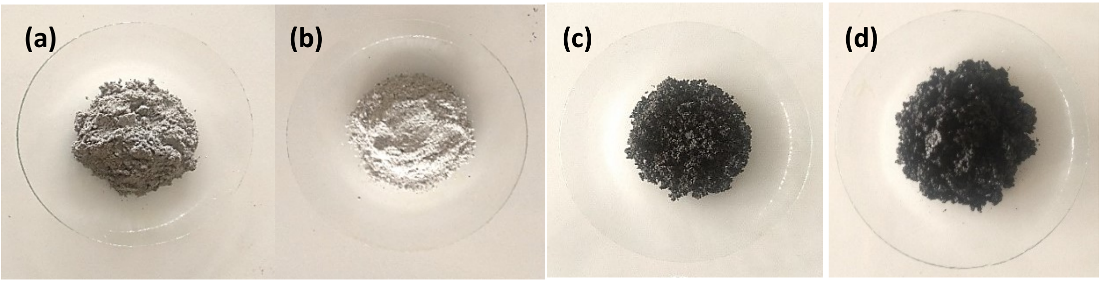

Fig.1. *Ficus carica* **(a)**, KOH impregnated **(b)**, $ZnCl_2$ impregnated **(c)** and H_3PO_4 impregnated **(d)** charcoal

2.2.2 Preparation of $ZnCl_2$ impregnated charcoal

To prepare $ZnCl_2$ impregnated charcoal, dried *Ficus carica* was impregnated in an aqueous solution of 0.05M $ZnCl_2$ for 72 h with occasional stirring. It was then dried and carbonized at 600°C. Then, the solution was neutralized with 5% HCl solution. Finally washed with distilled water to remove (Cl^-) and dried in an oven (El-Maghraby et al. 2014). Then the charcoal adsorbent was obtained by crushing with mortar. Fig. 1(c) shows the $ZnCl_2$ impregnated *Ficus carica* charcoal.

2.2.3 Preparation of H_3PO_4 impregnated charcoal

The dried *Ficus carica* was soaked in a boiling solution of 40 % H_3PO_4 for 1 h and then kept at room temperature for 24 h (El-Maghraby et al. 2014). After that, the *Ficus carica* was separated, air dried and carbonized in the furnace at 600°C. Then the material was washed with water to remove residual acid, dried and stored in an airtight plastic container for adsorption studies. Fig. 1(d) shows the H_3PO_4 impregnated *Ficus carica* charcoal.

2.3 Reagents

The reagents that were used in this experiment were potassium hydroxide (Merck, India), zinc chloride (Merck, India), hydrochloric acid (Merck Specialties Private Limited, Mumbai), phosphoric acid (Merck Specialties Private Limited, Mumbai), pure concentrated nitric acid (Merck Specialties Private Limited, Mumbai), sulfuric acid (Merck Specialties Private Limited, Mumbai), perchloric acid (Merck, India), ammonium iron (Merck, India), sulfate hexahydrate (Merck Specialties Private Limited, Mumbai) and *N*-phenyl anthranilic acid (Loba Chemie, India), filter paper (Whatman No. 1), anti-bumping agent glass beads (Loba Chemie, India). All of the reagents were collected from local scientific store, Khulna, Bangladesh.

2.4 Effect of Impregnated Charcoal

To know the effect of KOH, $ZnCl_2$ and H_3PO_4 impregnated adsorbent dosage on the uptake of Cr(III), 50 mL of filtered solution was taken in three different conical flasks incubated with 2 g of natural *Ficus carica* charcoal, KOH impregnated, $ZnCl_2$ impregnated and H_3PO_4 *Ficus carica* charcoal, respectively.

The flasks were agitated in a shaker at 120 rpm for 10 minutes at room temperature. After 10 minutes of settling, filtration was performed. Then, the Cr (III) content in the supernatant with different types of adsorbent was determined.

2.5 Studies of Non-impregnated Charcoal Dose

To know the effect of adsorbent dosage on the uptake of Cr (III), 50 mL of filtered Cr (III) solution at pH 4 was taken in five different conical flasks incubated with 0.5, 1, 1.5, 2 and 2.5 g of natural *Ficus carica* charcoal. The flasks were agitated in a shaker at 120 rpm for 10 min at room temperature. After 10 min of settling, filtration was performed. Then, the Cr (III) content in the supernatant with different dosage of adsorbent was determined.

2.6 Characterization of Wastewater and Treated Effluent

2.6.1 Chromium and pH determination

Quantitative analysis of Cr (III) in the waste liquor and treated liquor was ascertained by the titrimetric method according to the Society of Leather Technologist and Chemists (1996) official method of analysis SLC 208 (SLT6/4) (SLTC, 1996). At first, 25 mL sample was taken in a 500 mL conical flask and 20 mL nitric acid and 20 mL of perchloric acid and the sulfuric acid mixture was added into it. Then the heat was applied gently to boil the mixture until it became a pure orange-red colour and the boiling was continued for one minute after the point had been reached. Later, the flask was taken aside from the heating source before exhilaration. Afterwards, the flask was inserted into a cold bath for rapid cooling and then 100 mL distilled water was carefully poured into the flask with glass beads. The heat was applied for 10 minutes to make the mixture chlorine free and after that 10 mL of 30% (v/v) sulphuric acid was carefully added. Finally, when the mixture was cooled, titration was performed with freshly prepared 0.1N ammonium iron (II) sulfate solution with six drops of *N*-phenyl anthranilic acid as an indicator and the end colour was pointed out as a colour change from violet to green. The pH of the raw chrome tanning wastewater and treated effluent was measured using calibrated pH meter (UPH-314, UNILAB, USA).

2.7 Characterization of Charcoal

The charcoal (pure and Cr (III) loaded) samples were analyzed using Fourier transform infrared spectrometer (FTIR, Spectrum 100, PerkinElmer, USA) where data recorded at (4000–400 cm^{-1}) on potassium bromide (KBr) discs and Energy dispersive X-ray spectroscopy (EDX) analysis using PGT Energy dispersive X-ray spectroscopy (Sigma HV, Carl Zeiss Microscopy Ltd.).

3 Results and Discussion

3.1 Comparison of Impregnated and Non-impregnated Charcoal

The effect of natural *Ficus carica* charcoal and impregnated charcoal on the adsorption of Cr (III) was investigated. The removal efficiencies for *Ficus carica* charcoal, KOH impregnated, $ZnCl_2$ impregnated and H_3PO_4 impregnated *Ficus carica* charcoal were calculated 98.86%, 98.77%, 8.86%, and 2.5% respectively shown in Fig. 2. Removal efficiency for $ZnCl_2$ and H_3PO_4 impregnated *Ficus carica* charcoal being 8.86% and 2.46% respectively indicate that removal of Cr (III) from wastewater by using these charcoal was ineffective. In the case of activation with $ZnCl_2$, pollution with zinc salts occurs which are difficult to remove (Owabor and Iyaomolere, 2013). With costly

$ZnCl_2$ salt, washing requires too much water consumption. Moreover, pH maintenance requiring after activation with $ZnCl_2$ poses additional time-consuming step. Usually from washing, released Cl^- may inhibit the growth of plants, bacteria, and fish in surface waters with occurring surface salinity. Again, H_3PO_4 activated charcoals are not easy to apply because of its gummy nature. Also, the cost of H_3PO_4 used for activation is not negligible. Whereas, thermal modification using pyrolysis at 600°C was enough to prepare natural *Ficus carica* charcoal.

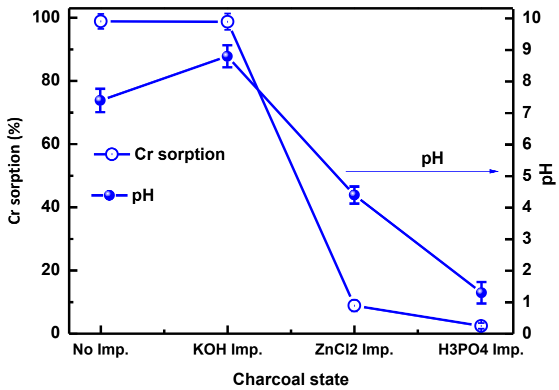

Fig. 2. Batch sorption of trivalent chromium: 2 g charcoal/75 mL tannery wastewater with contact time 10 min.

3.2 Effect of Adsorbent Dose on Chromium Uptake and pH

The effect of adsorbent dose on the adsorption of Cr (III) into natural *Ficus carica* charcoal was investigated. The maximum removal efficiency was calculated 98.26% with dose 2 g of the adsorbent with 50 mL of chromium solution.

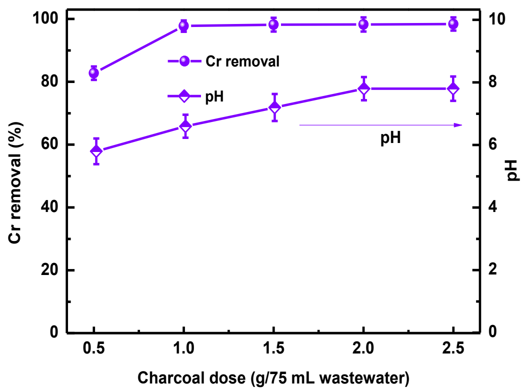

Fig. 3. Changes in chromium removal (%) and pH with *Ficus carica* charcoal dose

Fig. 3 shows the removal efficiency with respect to the adsorbent dose. As the adsorbent dose increases from 0.5 to 2 g the removal efficiency was found to increase. The removal efficiency with 2 g and 2.5 g dose was 98.26% and 98.39%, respectively. Removal efficiency slightly increases with 2.5 g dose which is negotiable. Thus considering the amount and removal efficiency 2 g was chosen as the best one. The effect of adsorbent dose on pH was also investigated (Fig. 3) where the pH was 5.8, 6.6, 7.2, 7.8, 7.8 for a dose of 0.5, 1.0, 1.5, 2.0, 2.5 g, respectively. In this case, pH was also found to increase with increasing adsorbent dose.

3.3 Characterization of Charcoal

3.3.1 FT-IR analysis

The sorption capacity of different charcoal depends upon porosity as well as the chemical reactivity of functional groups on the surface. The FT-IR spectrum of pure charcoal and Cr (III) loaded charcoal were compared and given in Fig. 4, Fig. 5 and Fig. 6.

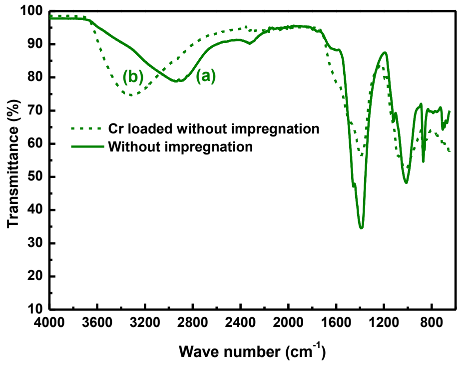

Fig. 4. FT-IR analysis of pure (a) and Cr (III) loaded (b) *Ficus carica* charcoal

In case of charcoal without impregnation, a broad region around 2918.2-2954 cm^{-1} wavelength is the indications of the presence C-H group, C-N at 2322.8-2138.1 cm^{-1}, alkane at 1405-1445 cm^{-1}, C=O, C-H, C=H groups at 1382- 1036 cm^{-1} (Kalaivani et al. 2014) as shown in Fig. 4(a). Again, a broad region around 3373-3422 cm^{-1} is the indications of the presence of O-H, N-H, C-H group, 1550-1560 cm^{-1} of secondary amine in case of Cr loaded charcoal without impregnation (Kalaivani et al. 2014) shown in Fig. 4(b).

In case of KOH impregnated charcoal, 3000 cm^{-1} wavelength is the indications of the presence C-H group, 2322.8-2138.1 cm^{-1} of C-N, 1654-1646 cm^{-1} of C=O, C=O, C-H, C=H groups at 1382- 1036 cm^{-1} (Kalaivani et al. 2014) shown in Fig. 5(c). Again, 1550-1560 cm^{-1} is the indications of the presence of secondary amine in case of Cr loaded KOH impregnated charcoal (Kalaivani et al. 2014) shown in Fig. 5(d).

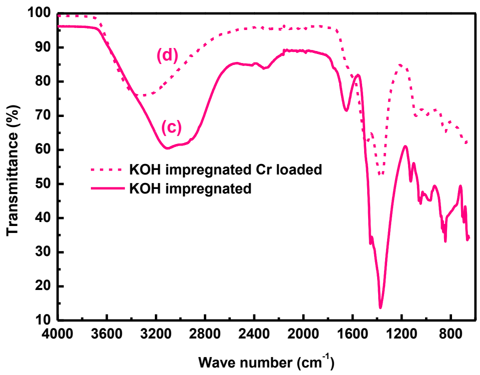

Fig. 5. FT-IR analysis of pure KOH impregnated **(c)** and Cr loaded KOH impregnated **(d)** *Ficus carica* charcoal

In the case of $ZnCl_2$ impregnated charcoal, 2918.2-2954 cm^{-1} wavelength is the indications of the presence C-H group (Kalaivani et al. 2014) shown in Fig. 6(e) and 1550-1560 cm^{-1} are the indications of the presence of secondary amine, 1050-1030 cm^{-1} of C-N (Kalaivani et al. 2014) for Cr loaded $ZnCl_2$ impregnated charcoal shown in Fig. 6(f). The functional groups in the $ZnCl_2$ impregnated *Ficus carica* charcoal were relatively less than two others which were the cause of less Cr removal by this charcoal. It ensures the involvement of different functional groups like carbonyl and carboxylic groups of pure charcoal in the sorption process. From FT-IR analysis it is found that after Cr sorption the functional groups in charcoal changed their positions as Cr was up-taken.

It is noticeable that without impregnated charcoal has a higher sorption capacity. Conversely, impregnation with chemical requires cost involvement, time-consuming, long process time, and not safe. Fig. 4, Fig. 5 and Fig. 6 depict a shift in the peak intensity which indicates the change of frequency in the functional groups of the charcoal due to chromium sorption. It indicates various responsible functional groups for the removal of Cr(III) through *Ficus carica* charcoal.

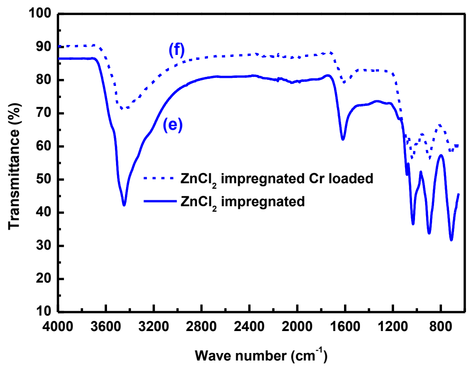

Fig. 6. FT-IR analysis of pure $ZnCl_2$ impregnated (e) and Cr loaded $ZnCl_2$ impregnated (f) *Ficus carica* charcoal

3.3.2 EDX analysis

Fig. 7(a) and Fig. 7(b) represent the EDX analysis of pure *Ficus carica* charcoal and Cr loaded *Ficus carica* charcoal, respectively. The presence of Cr is clear that non-impregnated *Ficus carica* charcoal has the sorption capacity. The impregnated charcoal analysis for before and after treatment is shown in Fig. 8 (a), (b), (c) and (d) representing KOH impregnated *Ficus carica* charcoal, Cr loaded KOH impregnated *Ficus carica* charcoal, $ZnCl_2$ impregnated *Ficus carica* charcoal, Cr loaded $ZnCl_2$ impregnated *Ficus carica* charcoal respectively. The comparison between before and after treatment showed the presence of Cr-after treatment confirming sorption of Cr(III).

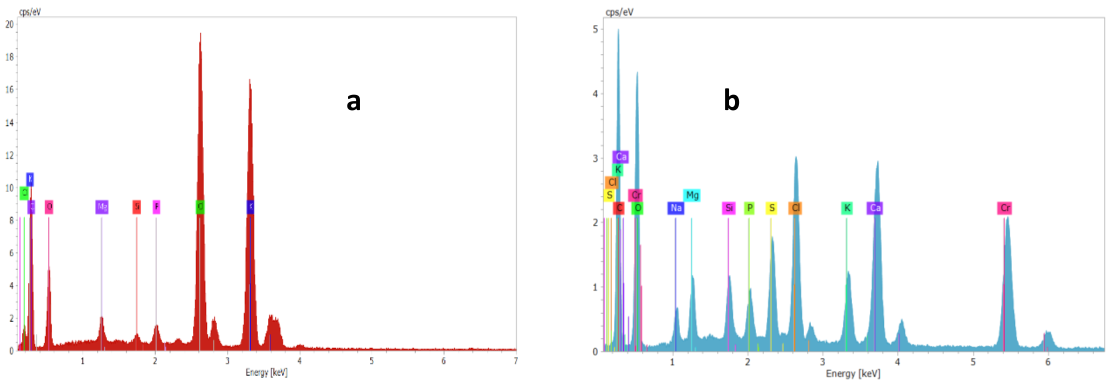

Fig. 7. EDX analysis of (a) *Ficus carica* Charcoal (b) Cr loaded *Ficus carica* Charcoal

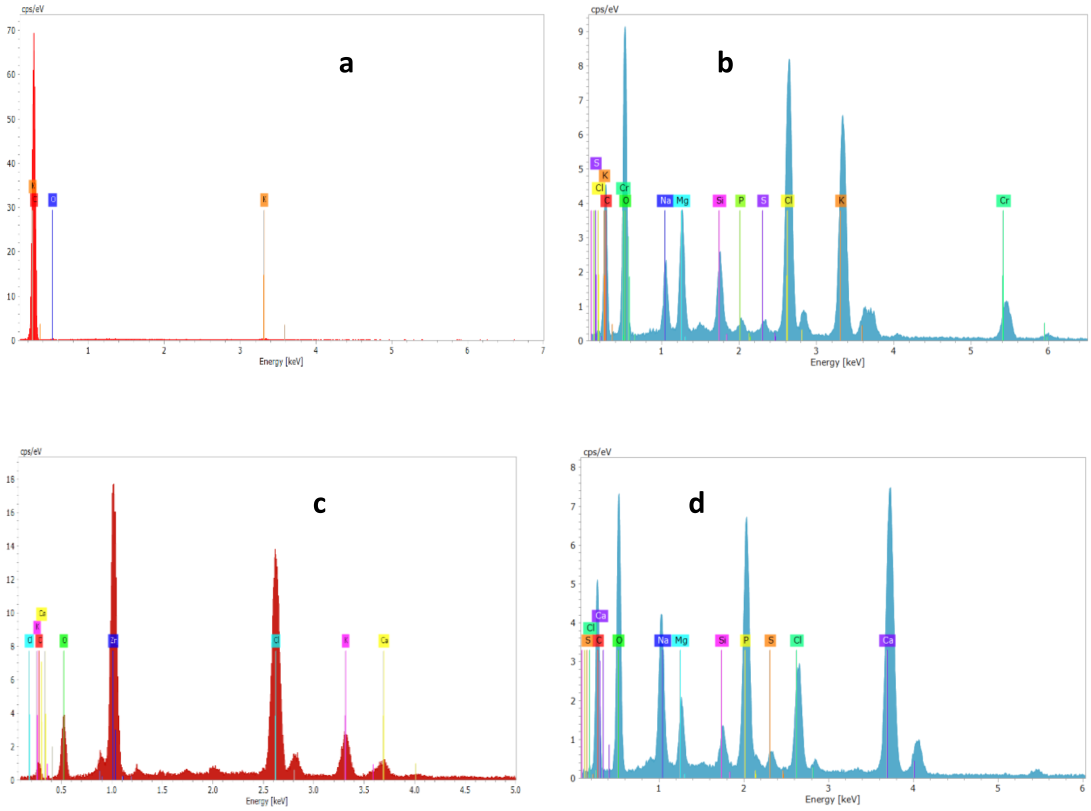

Fig. 8. EDX analysis of (a) KOH impregnated *Ficus carica* charcoal (b) Cr loaded KOH impregnated *Ficus carica* charcoal (c) $ZnCl_2$ impregnated *Ficus carica* charcoal (d) Cr loaded $ZnCl_2$ impregnated *Ficus carica* charcoal

From Fig. 7(b), 8 (b) and 8 (d) it is clearly evident that the non-impregnated *Ficus carica* charcoal showed the presence of higher Cr content than the impregnated samples. It indicates a higher sorption capacity of *Ficus carica* charcoal in natural condition without any impregnation. Between impregnated samples, Fig. 8 (b) showed some presence of Cr but in Fig. 8 (d) it was untraceable.

4 Conclusion

This study shows that without chemical impregnation *Ficus carica* charcoal has better trivalent chromium removal efficiency (98.9%). Although potassium hydroxide impregnated charcoal provided upright efficiency (98.8%), the higher chemical cost reduces its potentiality. The examination indicates that it was an effective method to reduce pollution load especially trivalent chromium from the spent chrome liquor. Preparation of natural *Ficus carica* charcoal is easy and inexpensive. It could be simply applied industrially for chromium removal from wastewater with some further investigation on cost analysis and input-output ratio.

References

1. *Ahmad F., Daud W.M.A.W., Ahmad M.A., Radzi R.: 'Cocoa (Theobroma cacao) shell-based activated carbon by CO_2 activation in removing of cationic dye from aqueous solution: kinetics and equilibrium studies', Chem. Eng. Res. Des., 90 (10), 1480-1490, 2012*
2. *Anirudhan T. S., Sreekumari S. S.: 'Adsorptive removal of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons'. J. Environ. Sci., 23(12), 1989–1998, 2011*

3. *Aravindhan R., Madhan B., Rao J.R., Nair B.U., Ramasami T.: 'Bioaccumulation of chromium from tannery wastewater: an approach for chrome recovery and reuse', Environ. Sci. Technol., 38(1), 300-306, 2004*
4. *Auta M., Hameed B.H.: 'Optimized waste tea activated carbon for adsorption of Methylene Blue and Acid Blue 29 dyes using response surface methodology', Chem. Eng. J., 175, 233-243, 2011*
5. *Bansal R. C., Goyal M.: Activated carbon adsorption, CRC Press, 5, 2005*
6. *Buczek B.: 'Preparation of active carbon by additional activation with potassium hydroxide and characterization of their properties', Advances in Materials Science and Engineering, 2016, 1-4, 2016*
7. *Duke J. A., Bugenschutz-Godwin M. J., Du Collier J., Duke P. K.: Hand Book of Medicinal Herbs. 2nd edition, Boca Raton, Fla, USA: CRC Press, 2002*
8. *El-Maghraby A., Taha N. A., Mahmoud A., El- Aziz A.: 'Preparation of activated carbon (chemically and physically) from banana pith for heavy metal removal from wastewater', Sci-Afric Journal of Scientific Issues, Research and Essays, 2 (9), 399-403, 2014*
9. *Ghaedi M., Tavallali H., Sharifi M., Kokhdan S.N., Asghari A.: 'Preparation of low cost activated carbon from Myrtus communis and pomegranate and their efficient application for removal of Congo red from aqueous solution', Spectrochim., Acta A 86, 107-114, 2012*
10. *Kalaivani S. S., Vidhyadevi T., Murugesan A., Thiruvengadaravi K. V., Anuradha D., Sivanesan S., Ravikumar L.: 'The use of new modified poly (acrylamide) chelating resin with pendent benzothiazole groups containing donor atoms in the removal of heavy metal ions from aqueous solutions', Water Res. Ind., 5, 21-35, 2014*
11. *Kongsricharoern N., Polprasert C.: 'Chromium removal by a bipolar electrochemical precipitation process', Water Sci. Technol., 34(9), 109-116, 1996.*
12. *Kozlowski C. A., Walkowiak W.: 'Removal of chromium (VI) from aqueous solutions by polymer inclusion membranes', Water Res., 36(19), 4870-4876, 2002*
13. *Malik P.K.: 'Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36', Dyes Pigments, 56 (3), 239-249, 2003*
14. *Mawa S., Husain K., Jantan I.: 'Ficus carica L. (Moraceae): Phytochemistry, Traditional Uses and Biological Activities', Evid. Based Complement Alternat. Med., 2013, 2013.*
15. *Oliveira L.C., Pereira E., Guimaraes I.R., Vallone A., Pereira M., Mesquita J.P., Sapag K.: 'Preparation of activated carbons from coffee husks utilizing $FeCl_3$ and $ZnCl_2$ as activating agents', J. Hazard. Mate., 165 (1-3), 87-94, 2009*
16. *Onyeji L. I., Aboje A. A.: 'Removal of Heavy Metals from Dye Effluent Using Activated Carbon Produced from Coconut Shell', Int. J. Eng. Sci. Technol., 3(12), 8238-8246, 2011*
17. *Owabor C. N., Iyaomolere A. I.: 'Evaluation of the influence of salt treatment on the structure of pyrolyzed periwinkle shell', J. Appl. Sci. Environ. Manage., 17 (2), 321-327, 2013*
18. *Paul H. L., Antunes A. P. M., Covington A. D., Evans P., Phillips P. S.: 'Bangladeshi Leather Industry: An Overview of Recent Sustainable Developments', J. Society Leather Technol. Chem., 97 (1), 25–32, 2013*
19. *Reffas A., Bernardet V., David B., Reinert L., Lehocine M.B., Dubois M., Batisse N., Duclaux L.: 'Carbons prepared from coffee grounds by H_3PO_4 activation: characterization and adsorption of methylene blue and Nylosan red N-2RBL', J. Hazard. Mater., 175 (1-3), 779-788, 2010*
20. *Rengaraj S., Joo C. K., Kim Y., Yi J.: 'Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H', J. Hazard Mater., 102, 257-275, 2003*
21. *Santra A.K., Pal T.K., Datta S.: 'Removal of metanil yellow from its aqueous solution by fly ash and activated carbon produced from different sources', Separ. Sci. Technol, 43 (6), 1434-1458, 2008*
22. *Society of Leather Technologist and Chemists, Official Methods of Analysis. Northampton, UK, 1996*
23. *Sundar V. J., Rao J. R., Muralidharan C.: 'Cleaner chrome tanning—emerging options', J. cleaner production, 10, 69–74, 2002*
24. *UNIDO, Environmental impact assessment (EIA) on the industrial activities at Hazaribagh area, Dhaka Project-US/RAS/97/137-EIA, Final Report, Government of Bangladesh and United Nations Industrial Development Organization, Vienna, Austria, 2000*
25. *Zhou X., Korenaga T., Takahashi T., Moriwake T., Shinoda S.: ' A process monitoring/controlling system for the treatment of wastewater containing chromium (VI)', Water Res., 27, 1049-1054, 1995*