

# Adsorption properties of Biomass Ash/ Graphene Oxide Composite for the Removal of Copper from Industrial Waste Water

Shivangi Omer, Ajay Singh

School of Applied and Life Sciences, Uttaranchal University, Dehradun Uttarakhand, India

[shivangiomer@gmail.com](mailto:shivangiomer@gmail.com)

## Abstract

Biomass ash is a complex inorganic-organic mixture with polycomponent, heterogenous or byproduct from biomass feedstock shows adsorption capacity for heavy metals and could be economical and environment friendly adsorbent. Graphene oxide (GO) are efficient adsorbent for removal of dyes, metal ions and toxic compounds. When biomass ash is used as composite formation along with Graphene Oxide then its adsorption capacity is enhanced. In the present work, Biomass ash on Graphene oxide base composite adsorbent (GO-g-BA) is synthesized for the effective removal of Cu (II) ions present in industrial waste water. They were characterized by FTIR, UV, FESEM and adsorption was studied by employing AAS with variables like pH. The results showed that BA-g-GO composite is an efficient adsorbent with 55.7 % for Cu(II) at pH 4.5. GO-g-BA composite was significant adsorbent for the removal of Cu(II) ions present in waste water.

**Keywords:** Biomass ash; Graphene oxide; Composite.

## 1. Introduction

Scientifically, biomass is termed as the total mass of all species, plant, animal or any naturally occurring materials present in our surroundings whereas technically, it constitutes organic and inorganic matters from various plants and animal sources (Usmani et al., 2017). The global growth of biomass is evaluated between 112 and 220 billion tonnes per year and produces about 95–97% of the world's bioenergy (Demirbas et al., 2005; Fouilland et al., 2010; Zhang et al., 2010; Vassilev et al., 2012).

Iron (Fe) induced biochar prepared by the method that results in the direct hydrolyses of iron salt onto biochar as a low-cost arsenic (As) sorbent (Xu et al., 2018). Composite of manganese-oxide/biochar is synthesised for the removal of lead from water and ontreating with Mn, the removal percentage of Pb(II) in biochar raised to 98.9 % at pH 5.00. Thermodynamically Pb(II) sorption process is spontaneous and endothermic (Wang et al., 2014). Graphene is a thick sheet of sp<sup>2</sup> hybridised carbon atoms and is the starting material for other carbon structures like nanotubes and graphite etc. (Justin et al., 2013). Graphene oxide (GO), prepared from natural graphite, has unique structure, chemically stable, excellent mechanical property, good biocompatibility which makes it a highly promising material for many applications in nanocomposites (Ordikhani et al., 2014).

## 2. Materials and Methods

In this study, we synthesized a new adsorbent namely, BA-g-GO composite by modification of biomass ash with graphene oxide backbone. The batch experiments had been carried out to measure the removal efficiency of synthesized composite for the removal of copper ions present in industrial waste water. For this, biomass Ash was collected from local iron foundry, confectionary and Hindustan National Glass & Industries Ltd., Rishikesh. Graphite powder was procured from Rankem.

### 2.1. Modification of Biomass Ash

In order to maintain a uniform size of Biomass ash (BA), it was mechanically riddled and sieved through 80 mesh and 100 mesh. Biomass was frequently rinsed with distilled water and dried at 120°C. 5.0 g of BA was mixed with 6.0 g solid NaOH in order to carryout bleaching process. The mixture was kept at 600°C in muffle furnace for 2 hrs under N<sub>2</sub> atmosphere. Then, 60 ml of deionized water was added and mixture was heated at 100°C for 72 h.

## 2.2. Preparation of Graphene Oxide

Graphene oxide (GO) was prepared as reported previously (Hummers and Offeman 1958), 1.9 g of graphite powder was mixed with 0.5 g of  $\text{NaNO}_3$  and 50 ml of  $\text{H}_2\text{SO}_4$ , and stirred for 30 min at  $4^\circ\text{C}$ . After stirring, 10 g of the  $\text{K}_2\text{Cr}_2\text{O}_7$  was added and continuously stirred for 120 mins at  $35 \pm 3^\circ\text{C}$ . Then after, 100 ml of water was added with 50 ml of 30 %  $\text{H}_2\text{O}_2$  and stirred for 15 min at  $100^\circ\text{C}$ . The color of the mixture turned yellow. The mixture was sequentially washed and filtered with 100 ml of 5% HCl. Separated and dried at  $40 \pm 5^\circ\text{C}$  in an oven.

## 2.3. Preparation of BA-g-GO composite

To prepare a composite, 0.45 g of obtained GO homogeneously dispersed in 20 ml of water was added to BA mixture with continuous stirring for 6 hrs and stored overnight at room temperature. A dense black coloured suspension was obtained. Five ml of deionized water was added and stirred for 15 min by which a uniform suspension of GO/BA was obtained and crosslinked by addition of 5 ml of 25% (v/v) Glutaraldehyde as a crosslinking agent (Ali M.E.A., 2018), at  $45^\circ\text{C}$  for 5 h. A dense, thick and crosslinked product was obtained which was filtered and washed with deionized water and then dried at  $50 \pm 5^\circ\text{C}$  in an oven.

## 3. Instrumentation

Calibration curve was drawn with blank solution of  $\text{Cu}(\text{CH}_3\text{COO})_2$  by UV-Visible Spectrophotometer (Systronics). Fourier transform infrared (FT-IR) spectra were recorded using FT-IR spectrometer (Perkin-Elmer 100). The surface morphology was studied by Scanning Electron Microscope (Zeiss Ultra Plus 4322). After the equilibration, the residual concentration of Cu (II) was determined by Perkin Almer Atomic Absorption Spectrophotometer (AAS-200).

## 4. Results and Discussion

### 4.1 UV adsorption studies

Fig. 1 shows UV-Visible spectra of BA-g-GO composite, at different concentration of metal solutions in water at 280 nm for  $\text{Cu}(\text{CH}_3\text{COO})_2$ .

### 4.2 SEM analysis

Fig. 2 represents SEM images of Biomass ash (a) and BA-g-GO composite (b). Images were recorded in accelerating voltage of 15-20 kV in various magnifications. The surface of reduced graphene oxide turned into rough, crumpled morphology.

### 4.2 FT-IR analysis

Fig. 3 of FT-IR spectra represents the interaction among Biomass ash and GO shows major characteristic peaks at  $3330\text{ cm}^{-1}$ , which is due to the O-H groups in GO. A new peak appears at  $850$  and  $1044\text{ cm}^{-1}$  for the Si-O-Si symmetric and asymmetric vibration. The peak appears at  $3000$  and  $3600\text{ cm}^{-1}$  corresponding mainly to improved number of silanol groups. The characteristic peaks at  $1488.2\text{ cm}^{-1}$  indicates N-H group of synthesized composite.

### 4.3 Effect of pH

The adsorption of  $\text{Cu}^{2+}$  on the BA-g-GO composite was analysed. The pH ranges from 2 to 7 was used to study and effective removal occurred at pH 4.5 for Cu(II) at an initial adsorbent dose of  $90\text{ mg}/100\text{ ml}$  at room temperature and pH higher than 6, minimal changes occurred. (Fig. 4).

## 5. Conclusion

In the present study, BA-g-GO composite was synthesized in which biomass ash were formed a composite on a base of graphene oxide, in order to enhance its adsorption efficiency. It was characterized by FTIR, UV, FESEM and AAS with the variable such as pH were optimized. The obtained results showed that BA-g-GO composite was an efficient adsorbent with removal efficiency of 55.7 % for Cu (II) at pH 4.5 for Cu (II). Overall, BA-g-GO composite was found to be significant adsorbent for the removal of Cu (II) ions present in waste water.

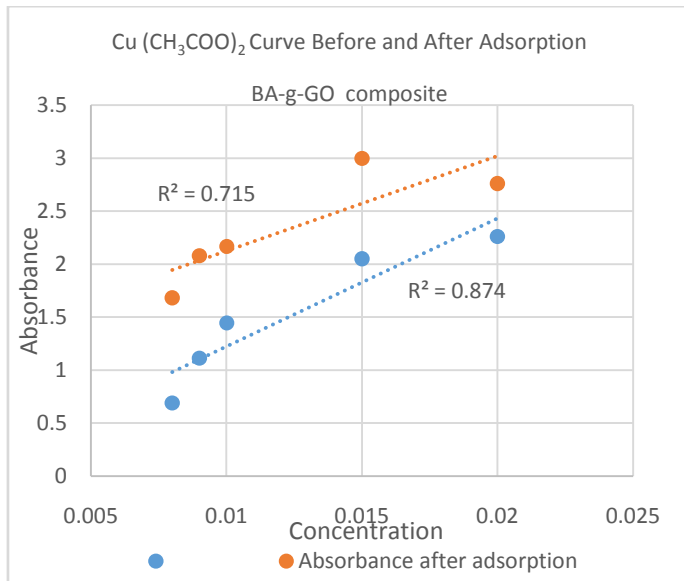


Fig. 1

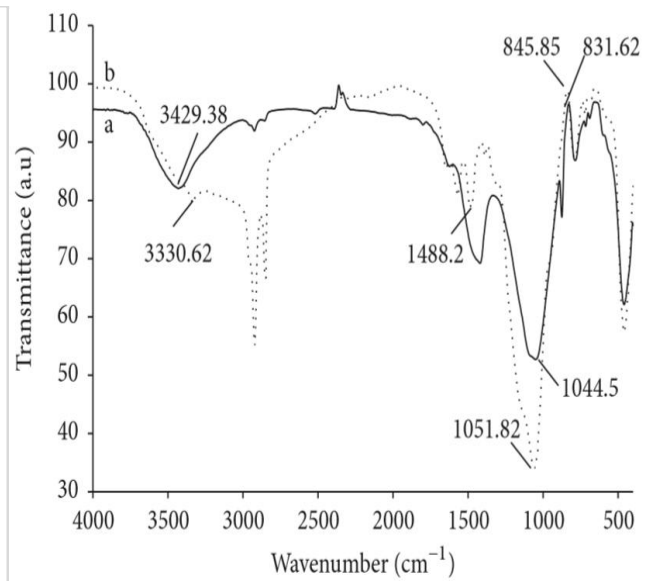


Fig. 2

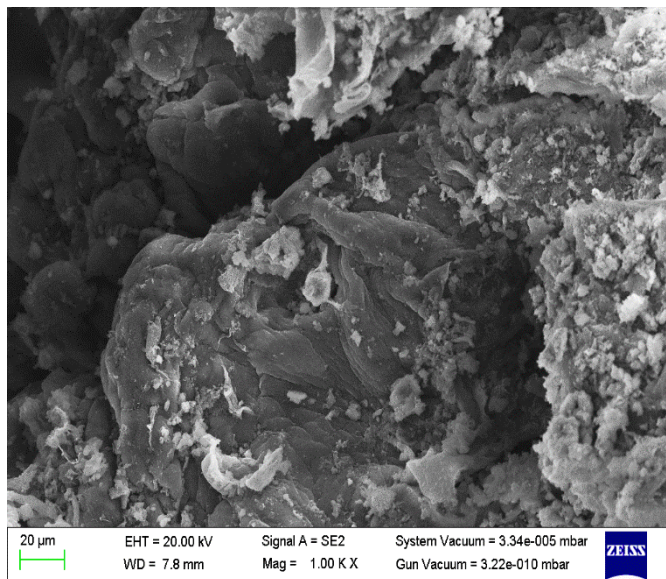


Fig. 3

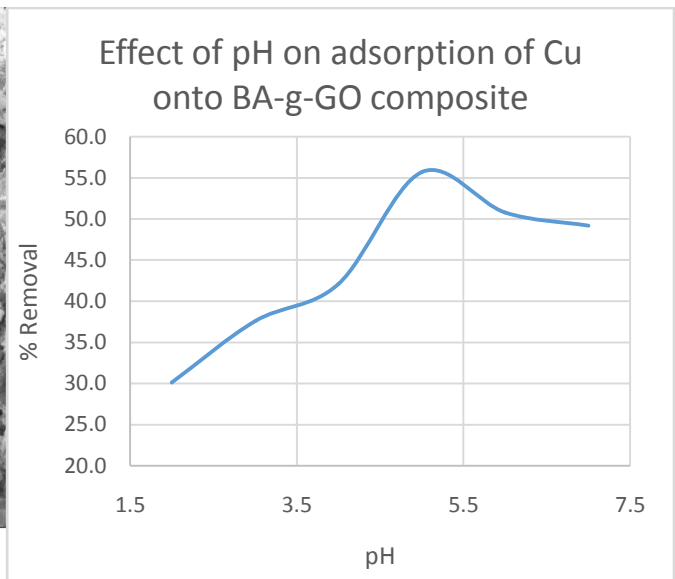


Fig. 4

## References

1. Ali, M.E.A. (2016). Synthesis and adsorption properties of chitosan- CDTA-GO nanocomposite for removal of hexavalent chromium from aqueous solutions. *Arabian J. of Chem.* <http://dx.doi.org/10.1016/j.arabj.2016.09.010>
2. Demirbas, A., (2005). Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues, *Prog Energ Combust.* 31:171–92.
3. Fouilland, T, Grace, JR, Ellis, N., et al (2010). Recent advances in fluidized bed technology in biomass processes. *Biofuels.* 1:409–33.
4. Hummers, W.S. and Offeman, R. E. (1958). Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* 80: 1339-1339.
5. Justin, R., and Chen, B., (2013). Characterisation and drug release performance of biodegradable chitosan–graphene oxide nanocomposites. *Carbohydrate Polymers.* 103: 70– 80.

6. Ordikhani. F., Ramezani. F. M., Dehghani. M., Tamjid. E. and Simchi. A. (2014). Physicochemical and biological properties of electrodeposited graphene oxide/chitosan films with drug-eluting capacity. Carbon. doi: <http://dx.doi.org/10.1016/j.carbon.2014.11.052>
7. Usmani. M. A., Khan. I., Haque. A., Bhat. A.H., Mondal. D. and Gazal. U. (2017). Biomass-based composites from different sources: Properties, characterization, and transforming biomass with ionic liquids. Lignocellulosic Fibre and Biomass-Based Composite Materials. <http://dx.doi.org/10.1016/B978-0-08-100959-8.00004-4>.
8. Vassilev. S.V., Baxter. D., Andersen. L.K. and Vassileva. C.G. (2012). An overview of the composition and application of biomass ash. Part 1. Phase–mineral and chemical composition and classification. Fuel. 105: 40–76.
9. Xu. L., Cui. H., Zheng. X., Liang. J., Xing. X., Yao. L., Chen. Z. and Zhou. J. (2018). Adsorption of Cu<sup>2+</sup> to biomass ash and its modified product. Water Science and Technology. DOI: 10.2166/wst.2018.095.
10. Zhang. L., Xu. C., Champagne. P. (2010). Overview of recent advances in thermochemical conversion of biomass. Energy Convers Manage. 51:969–82.
11. Xin. L., Hong-ying. H., Ke. G. and Ying-xue. S. (2010). Effects of different nitrogen and phosphorus concentrations on the growth, nutrient uptake, and lipid accumulation of a freshwater microalga *Scenedesmus* sp. Bioresour Technol. 101:5494–5500.