Proceedings of XXXVI IULTCS Congress 2021 3rd – 5th November 2021, Addis Ababa, Ethiopia

Preparation and characterization of Graphene-based adsorbent for Cu(II) and Cd(II) removal from tannery wastewater

Sobur Ahmed[a,b], Fatema-Tuj-Zohra[a,b], Meem Muhatasim Mahdi[a], Md. Zahangir Alam[b], Md. Nurnabi[b*]

[a]Institute of Leather Engineering and Technology, University of Dhaka, Bangladesh

[b]Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Bangladesh

*Corresponding author; E-mail: nnabi@du.ac.bd

Abstract

In this study, graphene oxide (GO) was synthesized from commercial graphite flakes for the adsorptive removal of copper (Cu^{2+}) and cadmium (Cd^{2+}) from harmful tannery effluents. Various analytical methods viz. X-ray diffraction, Field emission scanning electron microscopy, Zeta potential charge, and Fourier transform infrared spectroscopy were employed to evaluate the surface morphology and chemical nature of prepared GO. The adsorption experiments were conducted through a batch process under a constant stirring condition (200 rpm). The operational parameters (OPs) were optimized to find the maximum metal adsorption capacity. The plausible sorption mechanism, sorption nature, and randomness were interpreted in terms of isothermal, chemical kinetics models, and thermodynamic study. GO is prone to adsorb metal as it is deprotonated and anionic nature at higher pH. The highest metal removal was observed at pH 6 for Cu(II) and 7 for Cd(II). The metal removal capacity for each metal was positively correlated with the other OPs of the adsorption process. The sorption of the metal ions followed both Langmuir and Freundlich isotherms showing a complex (both monolayer and multilayer) adhesion phenomenon and the maximum removal capacity (q_m) of cadmium (231.48 mgg^{-1}) was higher than that of copper (193.05 mgg^{-1}). Moreover, the pseudo-second-order reaction model adequately described the chemical kinetics of each metal demonstrating a chemisorption nature of the adsorbent. The adsorption process was spontaneous at ambient temperature and exothermic. Thus, the GO can be an efficient and affordable adsorbent for the removal of these toxic heavy metals from tannery wastewater.

Introduction

Leather sector in Bangladesh is the most labour intensive export earning sector which offers huge value addition and contribution to the socio-economic development. However, Tanneries have been recognized as a potential source of generating heavy metal load to the environment [1]. During leather production, a substantial amount of different heavy metals such as, Cr, Cu, Cd, Ni, Pb, As, Hg, Ba, Fe, etc. are discharged with wastewater [2]. The effluent of chrome tanning process contain 2,000-5,000 mg L^{-1} of Cr(III), while the composite effluents of a tannery contain 100-250 mg L^{-1} of Cr(III) [3]. The chromium (Cr) of tannery effluent is very much harmful to human health, animals, and plants [4]. The general methods for removal of heavy metals from the effluents are precipitation, neutralization, membrane filtration, ion exchange, floatation, adsorption, etc. Among them, adsorption is the most economic and effective separation technique [5]. The prepared graphene based adsorbent was used to remove heavy metals like Cd and Cu from tannery wastewater

Preparation of Graphene Oxide

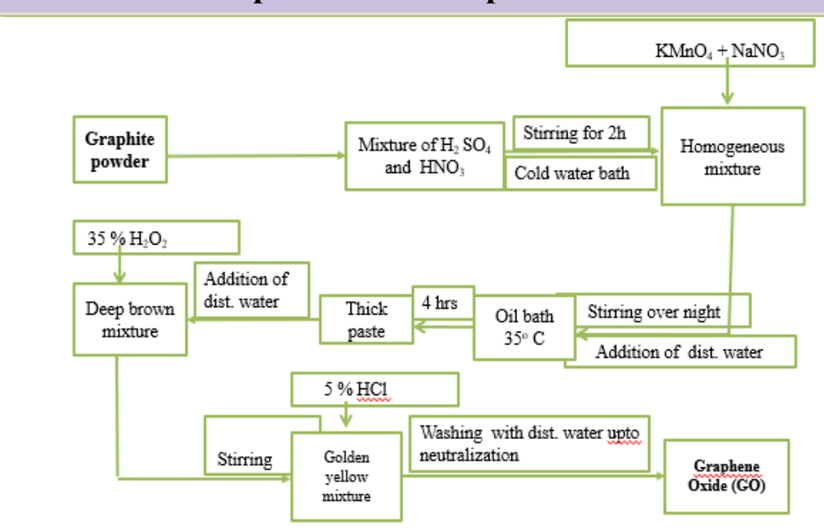

Fig. 1: Flow Chart of Graphene Oxide Preparation

Characterization of Graphene Oxide

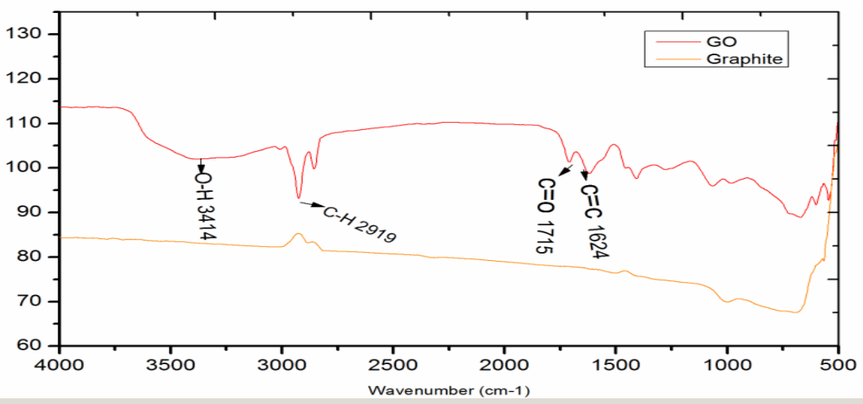

Fig. 2: FTIR spectrum of GO

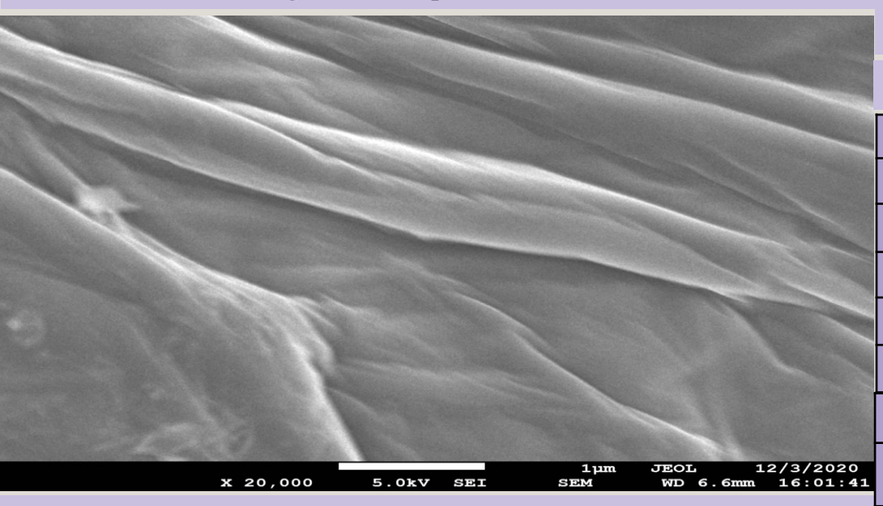

Fig. 3: FESEM image of graphene oxide

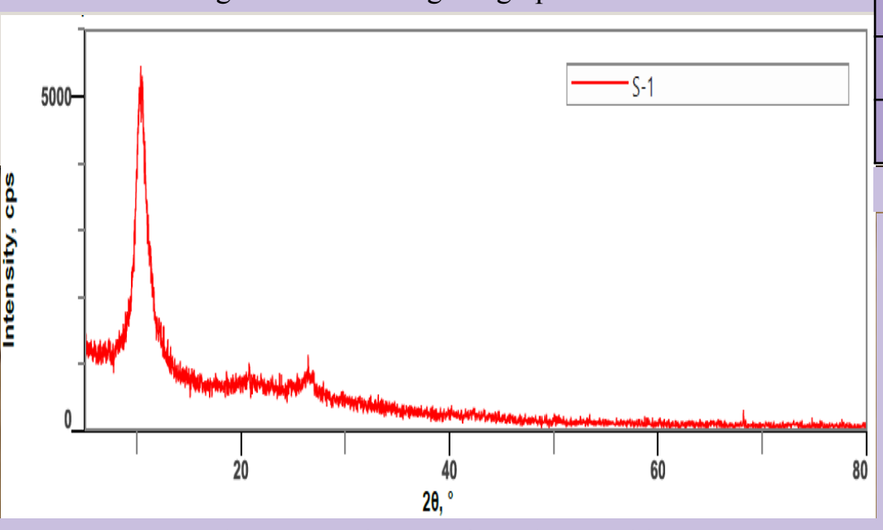

Fig. 4: XRD image of graphene oxide

Zeta potential value at different pH

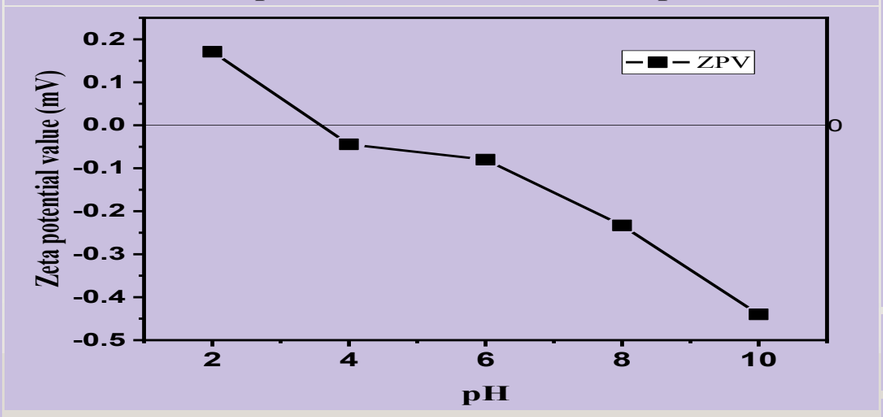

Fig. 5: Zeta potential value at different pH

Effect of Doses on Capacity & Removal %

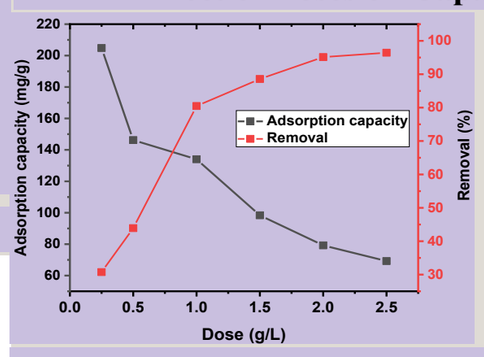

Fig. 6: Effect of doses on capacity and % of removal for Cu(II)

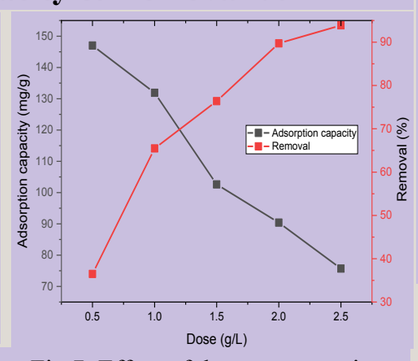

Fig.7: Effect of doses on capacity and % of removal for Cd(II)

Effect of Time and Concentration on Capacity

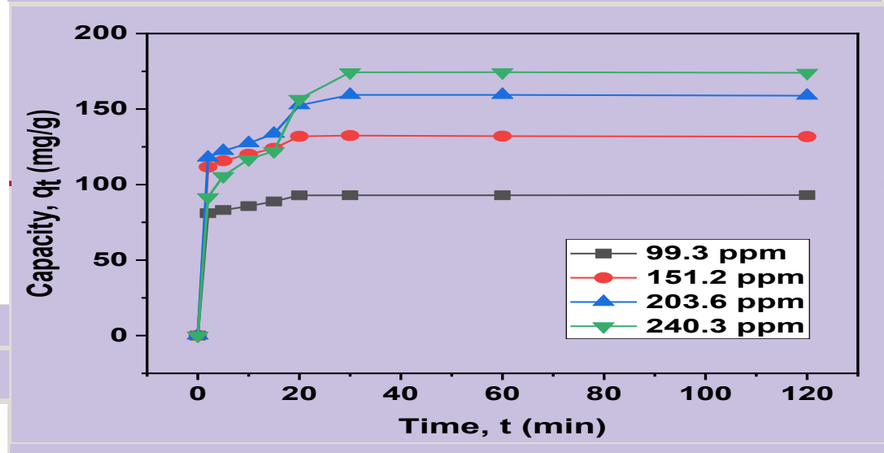

Fig.8: Effect of time and concentration on capacity for Cu(II)

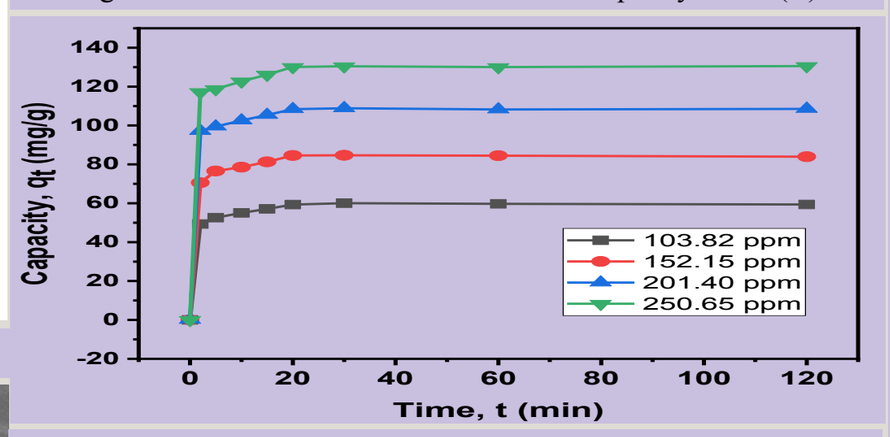

Fig.9: Effect of time and concentration on capacity for Cd(II)

Table. 1. Langmuir Isotherm

Parameters	Cu(II)	Cd(II)
Q_m	193.05 mg/g	231.48 mg/g
B	0.1239 L/mg	0.023 L/mg
R_L	0.032	0.148
R^2	0.997	0.999

Table. 2. Freundlich Isotherm

Parameters	Cu(II)	Cd(II)
K_f	57.23	12.019
n	3.70	1.675
R^2	0.991	0.996

Pseudo First-Order Kinetics

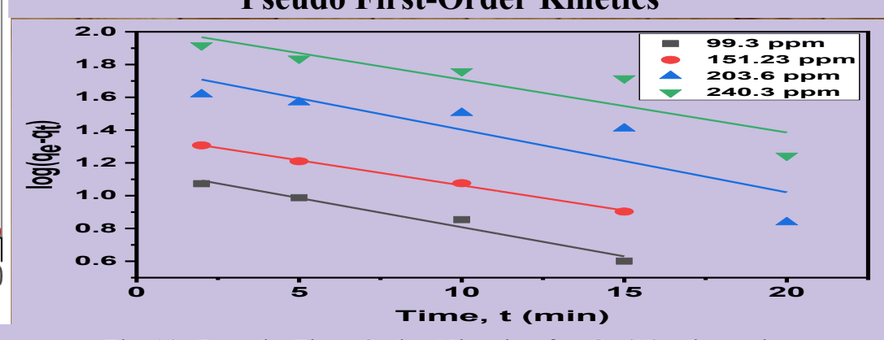

Fig.10: Pseudo First-Order Kinetics for Cu(II) adsorption

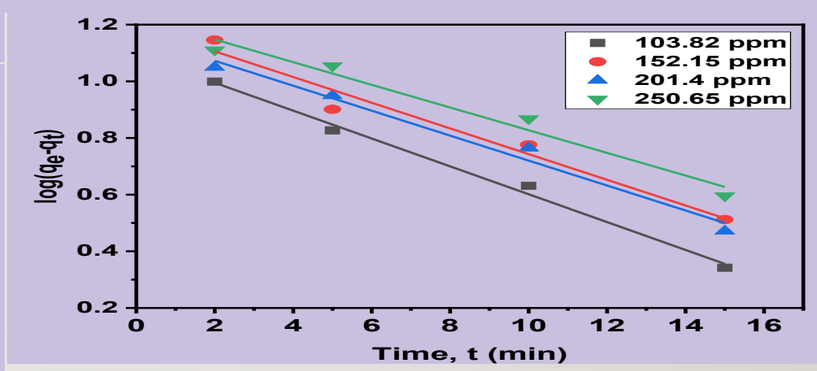

Fig.11: Pseudo First-Order Kinetics for Cd(II) adsorption

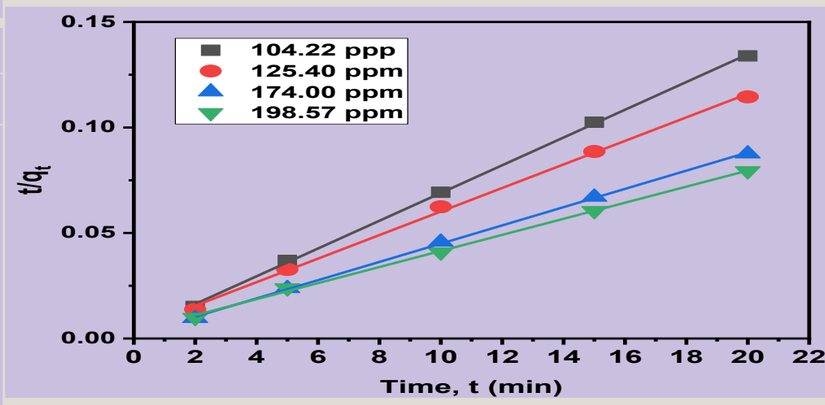

Fig.12: Pseudo Second-Order Kinetics for Cu(II) adsorption

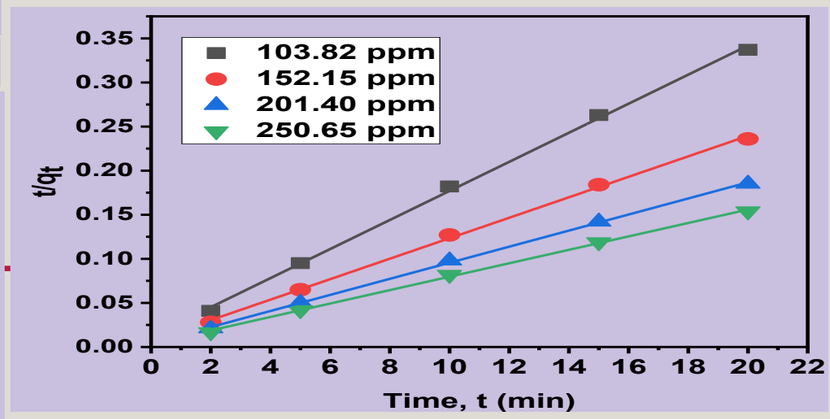

Fig.13: Pseudo Second-Order Kinetics for Cd(II) adsorption

Conclusion

The adsorption capacity of the prepared graphene oxide are 193.05 mg/g for Cu(II) at pH 6 and 231.48 mg/g for Cd(II) at pH 7, which is quite significant. The pseudo-second order kinetic model showed a better correlation for Cu and Cd adsorption compared to the pseudo-first-order model. The adsorption isotherm followed both the Langmuir and Freundlich models, preferably the Langmuir model. The value of Gibb's free energy and enthalpy is negative at different temperature, which reveals the adsorption processes are spontaneous and physico-chemical in nature. Therefore, the graphene oxide can be used as an efficient adsorbent for the removal of heavy metals from water media.

References

1. Mondal NK and Chakraborty S. Adsorption of Cr(VI) from aqueous solution on graphene oxide (GO) prepared from graphite: equilibrium, kinetic and thermodynamic studies. App. Water Sci. 2020; 10:61
2. Mwinyihija M. Essentials of ecotoxicology in the tanning industry. 1st Edition. Springer Science Business Media LLC, 2010.
3. Hashem MA, Hasan M, Momen MA, Payel S, Nur-A-Tomal MS. Water hyacinth biochar for trivalent chromium adsorption from tannery wastewater. Environ Sustain Indic 5: 100022, 2020.
4. Nur-E-Alam M, Abu Sayid Mia M, Ahmad F, Mafzur Rahman M. An overview of chromium removal techniques from tannery effluent. Appl Water Sci 10(5): 205, 2020.
5. Wijaya R, Andersan G, Santoso SP, Irawaty W. Green reduction of graphene oxide using kaffir lime peel extract (Citrus hystrix) and its application as adsorbent for methylene blue. Sci Rep 10: 67, 2020.

Acknowledgement

The authors would like to thank Dr. Tasrina Rabia Choudhury, PSO, Analytical Chemistry Laboratory, Chemistry Division, Atomic Energy Center, Dhaka, Ms. Dipa Islam and Ms. Evana Parvin Lipi, Senior Scientific Officer, Biomedical and Toxicological Research Institute, BCSIR for their lab support