

## Synthesis of Hybrid Ultrasonicated Eggshell Biochar nanomaterial for decontamination of cationic and anionic dyes from aqueous solutions

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### KEYWORDS

Adsorption capacity; hybrid nanomaterial; porous biochar; Ultrasonicated eggshells.

### SHORT SUMMARY

*This study highlighted the synthesis of a green hybrid eggshell biochar adsorbent (HUSEBA). The hybrid nanomaterial was produced from ultrasonicated eggshell and porous biochar, obtained from thermal catalytic degradation of green pea wastes. The feasibility of the adsorbent against decontamination of model pollutants, i.e., cationic methylene blue (MB) and anionic methyl orange (MO), was tested. The characteristics of the hybrid material were assessed using SEM, TEM, BET, FTIR, XRD and point of zero charge techniques. The sorption of MB and MO was conducted in a batch system with respect to composite dosage, solution pH, initial dye concentrations, systems temperature, and time. The synthesized hybrid nanomaterial demonstrated outstanding performance against sorption of MB and MO, achieving 85.49 and 53.45%, respectively, at an equilibration time of 2 hrs. The validation of the sorption process with numerical isotherm models demonstrated Langmuir recorded a better fit than Freundlich at  $R^2$  of 0.9888 and 0.9939 mg/g with MB and MO, respectively. Moreover, the monolayer sorption capacities were 31.95 and 24.57 mg/g. The kinetics study demonstrated that the pseudo-second-order model appropriately fitted the kinetic data. Therefore, the synthesized hybrid nanomaterial demonstrated good capability in decontaminating organic pollutants from wastewater systems.*

### EXTENDED ABSTRACT

Dyes are chemically bound coloured compounds in anionic, cationic, and non-ionic forms. Reactive dyes are anionic, whereas cationic and non-ionic are considered basic and dispersive dyes [1]. The presence of these dyes makes the environment aesthetical displeasing, obscure light penetration and impact against photosynthetic activities. Moreover, the prolong exposure of humans to these wastes can cause mutagenesis, carcinogenesis, renal dysfunction and teratogenesis.

Based on the alarming challenges, conventional techniques such as photocatalytic degradation,

coagulation, precipitation, ultrafiltration, membrane filtration, ion exchange, and adsorption have been explored [2]. Adsorption using activated carbon is the most attractive though it has associated drawbacks of high production and regeneration costs.

Eggshell refers to cheap and abundant biogenic household waste material produced from the ever-increasing global breeding of chickens for eggs and meat, estimated at 2.5 billion [3]. These eggshells are non-edible and easily discardable as waste in landfills, thus posing a pollution threat with microbial growth and pollution production [4][5]. Hence, Egg shells can capitalize multi-biomaterial

complex structural interwoven fibrous components of collagen, glycoprotein, sulfur enriched proteins and keratin [6]. Biochar is a carbonaceous material obtained from the thermal degradation of biomass under an anoxic environment. These materials are cheaply produced with high surface area, pores, and intrinsic functional groups.

This research evaluates the effectiveness of synthesized HUSEBA material in decontamination of coloured pollutants. In respect to the above, methylene blue (MB) and methyl orange (MO) were used as model pollutants. The hybrid nanomaterial shall be synthesized from green pea peels and eggshell to produce material, characterized and its performance tested at varying pH, time, concentration, temperature, and dosage. Numerical validation of sorption process was also performed using Langmuir, Freundlich, First order and second order.

### Materials and Methods

Biochar was obtained from thermal degradation of green pea peels over sodium carbonate catalyst. Nano eggshell was synthesized by bath ultrasonication method to obtain nanosized materials. Eggshell at nanometric level and biochar were mixed by hydrothermal method to obtain composite (HUSEBA).

### Characterization

The hybrid nanomaterial was characterized using XRD, BET, FTIR, SEM, and TEM

### Experimental Design

Batch adsorption study of MB and MO was performed to study adsorption at contact time (0-120 mins), pH (2- 12), temperature (20- 60 °C), concentration (50- 250 mg/l) and dosage (50- 250 mg/100 ml) using synthesized HUSEBA material. Adsorption capacity ( $Q_t$ ) and removal percentage (% removal) obtained by;

$$Q_t = v * \frac{C_i - C_e}{Wm}$$

$$\% \text{ removal} = 100 * \frac{C_i - C_e}{C_i}$$

$C_i$  is initial concentration,  $C_e$  is equilibrium concentration,  $Wm$  is mass of adsorbent

### Result and Discussion

#### XRD, BET and FTIR

The HUSEBA exhibited peaks at 23.28°, 29.47°, 36.08°, 39.41°, 43.24°, 47.59°, 48.58°, 57.51°, 60.62° and 65.60° that were excellently indexed to (012), (104), (110), (113), (202), (016), (018),

(122), (224) and (036) miler's planes were prominent to calcite in reference to (JCPDS No 47-1743) Fig1(a). FTIR demonstrated vital peaks at 714 $\text{cm}^{-1}$  and 870 $\text{cm}^{-1}$  ascribing to in-plane and out-plane deformation indicating the existence of  $\text{CaCO}_3$  [7]. Moreover, the peak at 1419  $\text{cm}^{-1}$  corresponds to carbonate mineral stretching within the HUSEBA matrix As shown in Fig 1 (b)

BET surface area was 232.77  $\text{m}^2\text{g}^{-1}$ , mean pore diameter was 2.8634 nm and total pore volume was 0.1666  $\text{cm}^3\text{g}^{-1}$

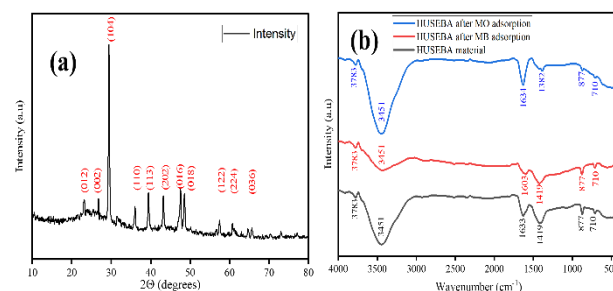


Fig 1. (a) XRD and (b) FTIR of HUSEBA

### Validation of adsorption isotherms and kinetics studies of HUSEBA material against sorption MB and MO dyes.

The numerical validated data of sorption of two materials are presented in Table 1 below.

Table 1: Parameters of isotherm and kinetics models of MB and MO sorption

Category	Models	Parameters	Dye pollutant	
			MB	MO
Sorption model	Langmuir	$q_{max}$ (mg/g)	31.95	24.57
		$R_L$	0.0775	0.2605
		$K_L$ (L/mg)	0.1191	0.0284
		$R^2$	0.9888	0.9939
Freundlich	$K_f$	$1/n$	7.52	2.53
		$R^2$	0.3147	0.4235
		$R^2$	0.9685	0.9834
Kinetics model	PFM	$K_1$ ( $\text{min}^{-1}$ )	-0.0020	-0.0012
		$q_e$ , exp (mg/g)	20.79	13.30
		$q_e$ , cal (mg/g)	8.467	6.725
		$R^2$	0.9292	0.9166
	PSM	$K_2$ (mg/g/min)	0.0677	0.0578
		$q_e$ , exp (mg/g)	20.79	13.30
		$q_e$ , cal (mg/g)	21.41	13.51
		$R^2$	0.9997	0.9994

### Conclusion

The prepared HUSEBA demonstrates good adsorption capabilities against MB and MO dyes.

### References

- [1] O. Eskikaya, M. Gun, R. Bouchareb, Z. Bilici, N. Dizge, R. Ramaraj, D. Balakrishnan, Chemosphere Photocatalytic activity of calcined chicken eggshells for Safranin and Reactive Red 180 decolorization, 304 (2022).



- [2] P.H. Jai, J.S. Wook, Y.J. Kyu, K.I.M.B. Gil, L.E.E.S. Mok, Removal of heavy metals using waste eggshell, 19 (2007) 1436–1441.
- [3] H. Wang, B. Gao, J. Fang, Y. Sik, Y. Xue, K. Yang, Engineered biochar derived from eggshell-treated biomass for removal of aqueous lead, *Ecol. Eng.* 121 (2018) 124–129. <https://doi.org/10.1016/j.ecoleng.2017.06.029>.
- [4] J. Lee, J. Kim, S. Yoo, E. Hea, C. Lee, S. Park, Chemosphere Restoring phosphorus from water to soil: Using calcined eggshells for P adsorption and subsequent application of the adsorbent as a P fertilizer, 287 (2022).
- [5] V. Vandeginste, Food waste eggshell valorization through development of new composites : A review, 29 (2021).
- [6] X. Chen, Y. Chen, B. Fu, K. Li, D. Huang, C. Zheng, M. Liu, D. Yang, International Journal of Biological Macromolecules Eggshell membrane-mimicking multifunctional nanofiber for in-situ skin wound healing, 210 (2022) 139–151.
- [7] M.S. Tizo, L. Andre, V. Blanco, A. Cris, Q. Cagas, B. Rangel, B. Dela Cruz, J.C. Encoy, J. V. Gunting, R.O. Arazo, V. Irvin, F. Mabayo, Efficiency of calcium carbonate from eggshells as an adsorbent for Cadmium removal in aqueous solution Sustainable Environment Research Ef fi ciencia of calcium carbonate from eggshells as an adsorbent for cadmium removal in aqueous solution, *Sustain. Environ. Res.* 28 (2018) 326–332. <https://doi.org/10.1016/j.serj.2018.09.002>.