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VALORISATION OF WASTE EGGSHELL FOR DEGRADATION OF SELECTED CATIONIC DYES FROM THE AQUEOUS ENVIRONMENT

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ABSTRACT

Egg production has been remarkably increased worldwide in the last thirty years, thereby it generates huge waste eggshell. Chicken waste eggshell is approximately 11% of the total egg weight and it contains calcium carbonate ($CaCO_3$) and calcium oxide (CaO). In this work, waste eggshell was modified by urea (UES) and used as a catalyst to degrade cationic dyes. Brilliant green and Malachite green were efficiently degraded via optimization of initial concentration of dyes, pH of media, time of contact and amount of catalyst. The reaction followed first order kinetics. The LC-MS study was performed to understand the catalytic degradation pathway of malachite green. Hence, the present study might be helpful for removal of selected organic dyes via valorisation of waste eggshell.

KEY WORDS: Eggshell, Dyes, First order kinetics, Catalyst, Degradation.

INTRODUCTION

Modern society faces a serious challenge due to the generation of enormous waste by rapid urbanization, industrialization and population explosion. It is a crucial problem to the economy as well as the environment. Despite of several environmental laws and regulations, waste management remains a global issue (Waheed, *et al*., 2020). Most of the industries are facing tremendous problems of waste handling and disposal now-a-days.

Poultry processing industry generates large amount of wastes *viz*. feather, eggshell etc. The egg consumption per capita in USA is increased from ~ 7951.8 million dozen in 2019 to over 8000 million dozen in 2020 as per the report of World Agriculture Supply and Demand Estimates. China, USA and India are leading egg-producer countries with total production of ~ 80 million metric tons in 2017 (Waheed, *et al.,* 2020 and Shrestha *et al.,* 2019). Worldwide egg production has been increased by 150% with significant growth of Asia continent by four-folds in last thirty years (FAO, 2020). Thus, higher utilisation of egg leads to disposal of eggshell to the landfill. China produced 24.8 billion kilogram of eggshells in 2019 as reported (FAO, 2019).

Environmental Protection Agency ranked eggshell waste as the 15th among major food industry pollutants (Waheed, *et al.,* 2020 and Shrestha *et al.,* 2019). But eggshell and eggshell membrane have been widely utilized as good adsorbents for the removal of heavy metals, anions, dyes and pigments, emerging contaminants etc. (Mittal *et al.,* 2016). In the review article, Jangho Kim summarized wide applications of eggshell membrane in the field of engineering. Eggshell membranes are used in functional platform for electronic devices, sensors, environmental and biomedical engineering appliances etc. It has high porosity and exhibits antibacterial or anti-inflammatory characteristics (Elwakeel and Yousif, 2010, Kim *et al.,* 2016). Egg shell is rich in nutrients (calcium, magnesium and phosphorous), minerals and amino acids (Rapo *et al*., 2020).

Many heterogeneous catalysts (TiO_2, ZnO, CuO, SnO_2, WO_3 etc.) are used for mineralization of dyes due to less time of reaction and requirement of trace amount of catalyst (Jaiswal *et al.,* 2020). But preparations of such metal oxides involve hazardous and toxic chemicals, high temperature, high energy and huge cost (Honarmand *et al*., 2019).

Emphasis has been given to explore eco-friendly, low-cost catalyst derived from earth-abundant and waste materials (Jaiswal *et al.*, 2020). The present work comprises valorisation of waste eggshell to degrade cationic dyes under optimized condition followed by mechanistic study using LC-MS.

EXPERIMENTAL SECTION

Materials and chemicals

Malachite green, MG ($C_{23}H_{25}N_2Cl$) and Brilliant green, BG ($C_{27}H_{34}N_2O_4S$) were procured from commercial source (Loba Chemie Pvt. Ltd., Mumbai, India) and used as received. Double distilled water was used for the preparation of all stock solutions.

Preparation of urea modified eggshell (UES)

Waste eggshell collected from hostels, canteens and fast-food shops of the university campus, was cleaned to remove impurities, boiled for 30 min to separate the membrane and then crushed in the mortar pestle, sieved to 75 microns and coded as ES-75. The ES-75 (15.0 g) was well mixed with urea (6.0 g) and a little amount of distilled water was added to the mixture to prepare a paste of ES-75. It was placed in a muffle furnace at a constant temperature of 850 ° ± 20 °C for 120 min. After cooling, urea modified eggshell (UES) was crushed and sealed in a closed container for further use.

Characterization of urea modified eggshell (UES)

The UES was characterized by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) studies. In order to characterize the crystallinity of UES, XRD analysis was performed using Cu Kα radiation beam (λ = 1.5406 Å), operating at 30 kV and 30 mA with a copper target. Data were collected between 2θ angles in the range of 10° and 80°. The size of material was evaluated using the Scherrer equation, equation (1),

$$crystal\ size, D = \frac{\kappa\lambda}{\beta\cos(\theta)} \quad (1)$$

where, k was Scherrer constant (0.9), λ was wavelength of X-ray (1.5406 Å for Cu-Kα), β was full width half maxima, FWHM (radians), θ was angle of diffraction (degree).

Degradation study of dyes

The study was conducted by UES (10.0 mg) on MG and BG (1.0, 5.0, 10.0, 20.0 and 30.0 mg/l, 10 ml double distilled water) with constant shaking of 115 rpm at 25 °C in borosil capped culture tubes. In each experiment, the mixed solution was kept under sunlight for 30 min.

The pH of the medium was adjusted by the addition of the required amount of 0.1 (N) NaOH/HCl. After addition of UES, the suspension was sampled at a regular time interval and centrifuged immediately at 2500 rpm for concentration measurement by the UV-Vis spectrophotometer. The degradation efficiency (D) was calculated by the equation (2)

$$D = \frac{A_0 - A_t}{A_0} \times 100 \quad (2)$$

where, A_0 was the initial absorbance of the dye solution and A_t was the absorbance at time 't'.
Removal efficiency (% R) was calculated by the equation (3)

$$\% R = \frac{(C_0 - C_f)}{C_0} x100 \quad (3)$$

where, C_0 was the initial dye concentration (mg/l), and C_f was the dye concentration at equilibrium (mg/l).

The chemical oxygen demand (COD) of dyes before and after the degradation were determined by potassium dichromate reflux method (Kopp, 1979). All experiments were carried out in triplicate and the mean value was used for the estimation.

RESULTS AND DISCUSSION

Characterization of UES

SEM study

The micrographs, obtained from SEM study, showed (Fig. 1a and 1b) that the surfaces of UES contained pores with well-developed cavities and exhibited crystallinity and irregular angular pattern of fractures (Khan *et al.*, 2019).

XRD study

The diffractogram (Fig. 2) indicated that UES possessed calcite structures with a similarity to calcium carbonate mineral (2θ = 29.305 nm) (Khan et al. 2019) and particle size was found in the range 40-50 nm (D = 44.822 nm) from the Scherrer formula.

Effect of several parameters on dye degradation

Initial dye concentration

Initial dye concertation was varied from 1.0 mg/l to 30.0 mg/l with a fixed catalyst loading (10.0 mg). At the low concentration (1.0 mg/l), degradation

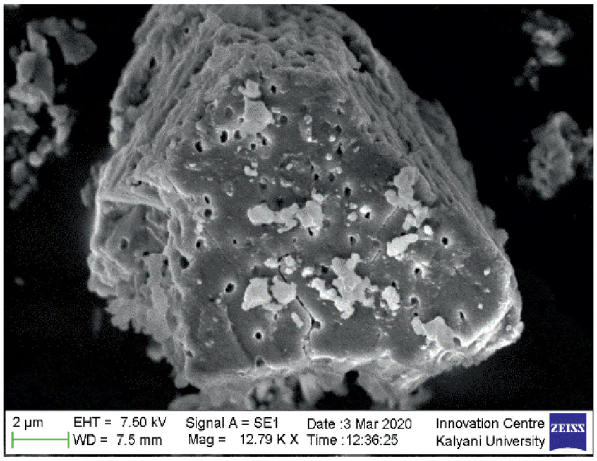


Fig. 1a. SEM image of UES.

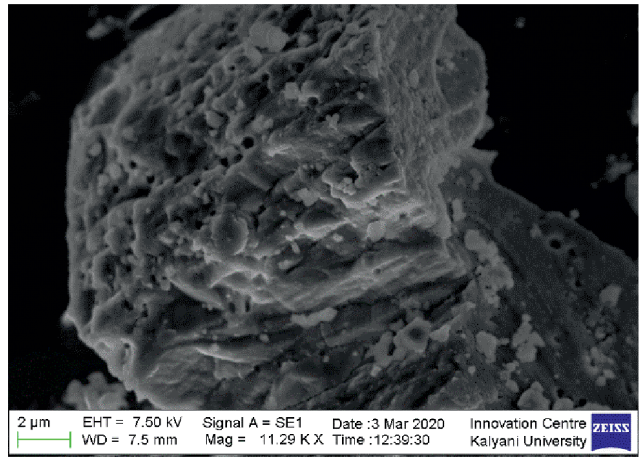


Fig. 1b. SEM image of UES.

percentages were found to be 82.61% for BG and 79.1% for MG and reached maximum (97.04% for BG and 98.9% for MG) at dose of 20 mg of UES. But at higher concentration of dye, degradation percentages decreased from 97.04% (20.0 mg/l) to 90.32% (30.0 mg/l) for BG and remain unaltered (~ 99.0 %) for MG (Fig. 3).

Catalyst dose

Varied concentrations of UES (5.0 mg, 10.0 mg, 20.0 mg and 30.0 mg) and fixed concentration of (50.0 mg/l) dyes were used for degradation study. The percentages of degradation were ~90.0% for all dosages of UES (Fig. 4). The maximum percentages of degradation were found to be 95.0% for MG and 93.0% for BG at 20.0 mg of UES. Thus, optimum dose was 20 mg for degradation of dyes.

pH

The pH was varied from 2 to 10 with the help of 0.1 (N) HCl/NaOH to avoid the dissolution of eggshell above pH 10 (Fig. 5). The degradation rate of both dyes increased from 50% (52.2% for MG and 58.96% for BG) to 97% (97.7% for MG and 95.1% for BG) from pH 2 to pH 10 in 90 minutes. The maximum degradation rate of dyes by UES was achieved at pH 10. This may be due to cationic nature of dyes which facilitated adsorption on the surface of catalyst at higher pH.

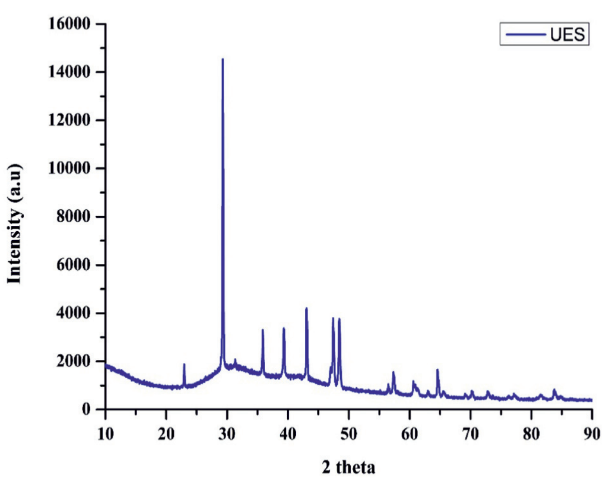


Fig. 2. XRD pattern of UES.

Mineralization study by COD removal

In case of BG and MG, mineralization study was carried out by COD removal in water using fixed concentration of dyes (30 mg/l) and UES (20 mg) under constant stirring (120 rpm) for 120 min at 25 °C. The COD values were significantly decreased for both dyes (92% for MG and 82.76% for BG).

Kinetic study

Initially BG and MG exhibited major absorption peaks at 627 nm and 619 nm respectively in aqueous medium (Fig. 6a and 6b; inset). After addition of UES, two new peaks were observed in the UV region at 274 nm and 321 nm in the case of BG dye and the absorption intensity increases with time (Fig. 6a) and a new peak was observed at 368 nm after disappearance of original distinct peak for MG (Fig. 6b).

The effect of time of contact with two different dyes, BG and MG, was studied at different time interval with a fixed dye concentration (30 mg/l) and UES (10 mg). The first-order rate kinetics (simplification form of Langmuir-Hinshelwood kinetic model) was fitted (-ln (C_t/C_0) vs time) to obtain almost linear plot following the equation (4).

$$-\ln\left(\frac{C_t}{C_0}\right) = kt \qquad (4)$$

where, C_t and C_0 represented the concentration of dye at time t = t and t = 0, k represented the rate constant and t was time in min. It was found that UES effectively degraded BG and MG within 90 min and the first order rate constants were $1.62 \times 10^{-2}\ S^{-1}$ for MG and $1.76 \times 10^{-2}\ S^{-1}$ for BG.

Degradation pathway of malachite green by LC-MS

The LC-MS study was performed after degradation of malachite green (10 mg/l in 10 ml double distilled water) by UES (20 mg). The structures of degradation by products (DPs) were obtained from their chemical formulas, degree of protonation and m/z values. The intermediates with lowering m/z values, 421.14, 329.2, 315.19, 301.17, 182.07, 179.03, 146.0, 145.05, 106.04, 103.06, 101.05, 78.05 with

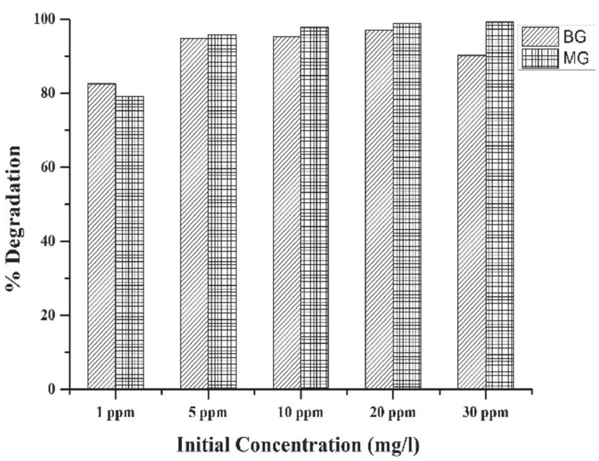


Fig. 3. Effect of initial dye concentrations on degradation.

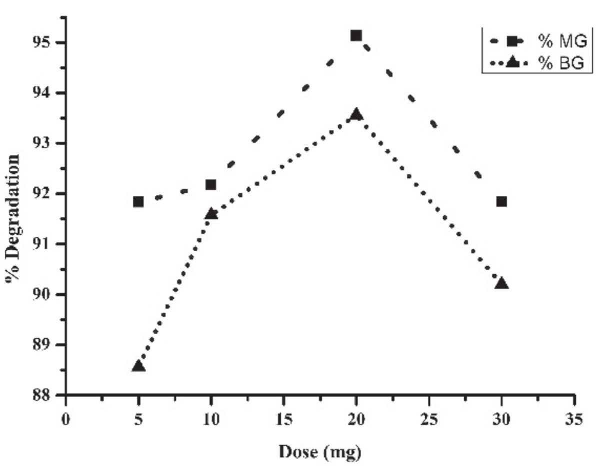


Fig. 4. Effect of UES dosages for degradation of dyes.

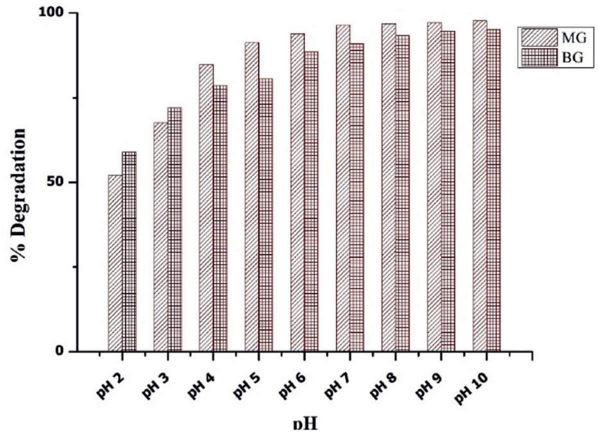


Fig. 5. Effect of pH on degradation of dyes by UES.

probable molecular structures were depicted in Scheme 1 (Fig S1).

(i) The byproducts from MG-DP-I to MG-DP-III, may be generated via N-dealkylation reactions and compared with reported references: MG, m/z = 329.2 (Wang *et al.,* 2012, Ju *et al.,* 2009). The other DPs were MG-DP-I, m/z = 315.19, MG-DP-II, m/z = 315.2 (Wang *et al.,* 2012, Ju *et al.,* 2009), MG-DP-III, m/z = 301.17 (Wang *et al.,* 2012).

(ii) The byproducts from MG-DP-IV to MG-DP-XII, may be produced either through hydroxylation of N-de-methylated products or through hydroxylation reactions of MG, followed by N-de-methylation: MG-DP-IV, m/z = 421.14, MG-DP-V, m/z = 182.07, MG-DP-VI, m/z = 179.03, MG-DP-VII, m/z = 146.0, MG-DP-VIII, m/z = 106.04, MG-DP-IX, m/z = 78.05, MG-DP-X, m/z = 145.05, MG-DP-XI, m/z = 103.06 (Riaz and Ashraf, 2015), MG-DP-XII, m/z = 101.05.

Toxicity assay of degraded compounds of dyes by seed germination test

Seed germination test was conducted by seed of peas and compared with control experiment. Here, dyes (10 ml) of varied concentrations (1 mg/l, 5 mg/l, 10 mg/l, 20 mg/l and 30 mg/l) were degraded by UES (20 mg, 120 min) and the seeds were soaked in above solutions for one hour. Then the seeds were allowed to germinate in the laboratory condition for three days. The results showed that seeds were germinated (60-80%) in all the cases depending on concentration of dyes.

CONCLUSION

The present study deals with the valorisation of

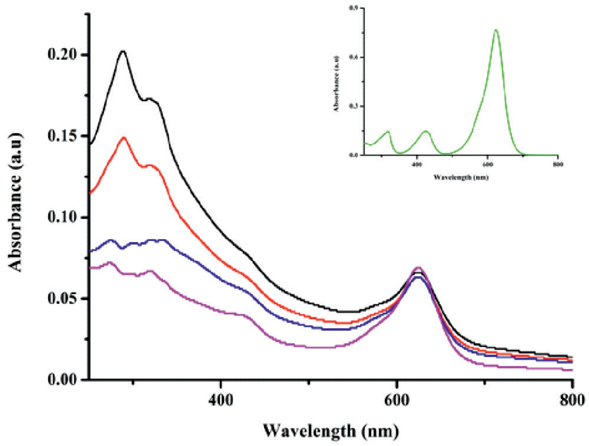


Fig. 6a. Time dependent (60 min, 75 min, 90 min, 120 min) UV-Vis spectra of BG dye (30 mg/l) in presence of UES (20 mg) and standard curve of BG (inset).

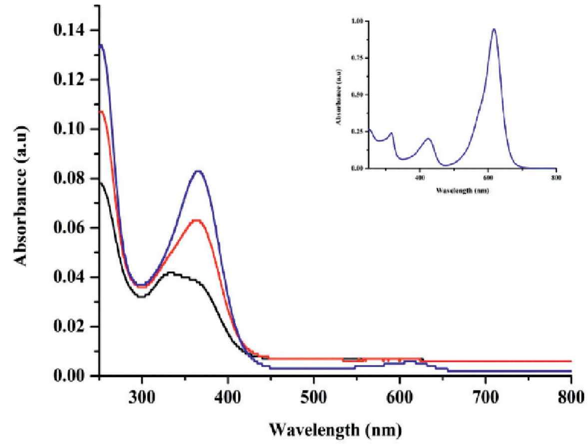
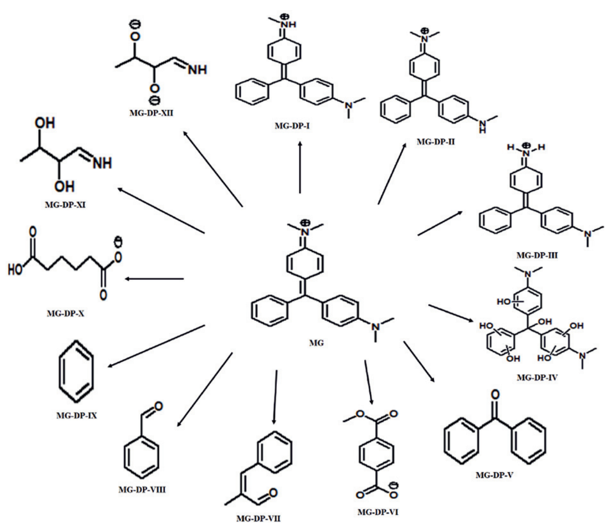


Fig. 6b. Time dependent (60 min, 90 min, 20 min) UV-Vis spectra of MG dye (30 mg/l) in presence of UES (20 mg) and standard curve of MG (inset).

waste eggshell for degradation of selected cationic dyes. Malachite green and Brilliant green dyes were effectively degraded by urea modified eggshell in laboratory conditions. Both dyes followed first-order kinetics and the degradation was dependent upon dye concentration, time of contact, pH of the media, catalyst amount etc. The dyes were almost mineralized in the aqueous environment. Interestingly, the mechanistic study by LC-MS indicated the formation of several degraded byproducts via (a) dealkylation, (b) ring opening, (c) hydroxylation pathways. These by products may not have significant adverse impact as revealed from seed germination test. Hence, the present investigation might be helpful for removal of dyes from the environment using waste eggshell



Scheme 1. Probable degradation pathway of malachite green by UES via LC-MS study.

following an eco-friendly approach.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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