Effect of Modifier Agents on Particle Size and Surface Functional Groups of Calcined Eggshell: Test in Adsorption of Remazol Yellow

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Abstract
Calcined eggshell (CES) was modified with Pluronic 123 (P123), Pluronic 127 (F127) and polyethylene glycol (PEG) agents and used in adsorption of Remazol Yellow. The adsorbents were characterized by Fourier transform infrared (FTIR) and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX). FTIR spectrums showed that characteristic peaks corresponding to CES and modifier agents were observed and CES was successfully modified. Modification of CES with PEG having high chain length (or high molecular weight) positively affected particle size. From EDX analysis was determined the carbon content increased from 21.44 % to 36.60 % whereas the calcium content decreased from 21.23 % to 8.69 % with increasing of the molecular weight of modifier agents. Removal percent of Remazol Yellow was found as 68.55, 91.79, 93.09 and 95.69 for CES, CES-P123, CES-F127 and CES-PEG, respectively. CES-PEG adsorbed Remazol Yellow more than other adsorbents and also dye adsorption on it fitted to Freundlich isotherm model. Dye adsorption capacity of CES-PEG was obtained as 133.3 mg/g. Particle size and carbon content of adsorbents was more effective in adsorption of Remazol Yellow.

Keywords: Calcined eggshell, modification, adsorption, Remazol Yellow

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1. INTRODUCTION

The use of synthetic dyes which are in many industrial areas such as textile, leather, medicine, food processing, dyeing and cosmetics are caused to the water pollution problem. Synthetic dyes are toxic, carcinogenic and mutagenic and also discharging of dyes into natural streams without untreated causes a severe environmental problem. This problem results in adverse effects on human and animal health and therefore the removal of dyes from wastewater is important [1-5]. A variety of treatment methods are used such as physical, chemical and biological process to removal of dyes from wastewater. Adsorption is the most of favorable method for removal of dyes because of its simple design, ease of operation and high-performance removal efficiency of toxic substances and low cost as compared to other techniques [6-8]. Using activated carbon as adsorbent for dyes has been widely studied due to their large surface area and high adsorption capacity. However, due to its high cost and the difficulty of regeneration, cheaper, more effective adsorbent such as zeolites, clays, fly ash, natural and biological materials, chitin, and chitosan are being considered as alternative low cost adsorbents [2-5, 8-11].

Eggshell is a bio-waste widely produced from house, restaurant and bakery. Eggshell has a little developed porosity and pure calcium carbonate as an important constituent. On the other hand, eggshell is environmentally friendly and economically feasible an adsorbent [12, 13]. In addition, eggshell is attracting attention due to it has dye removal efficiency often ranging from 94 to 98 %. Literature studies confirm that eggshells are very effective in removing heavy metals, dyestuffs and other contaminants. Approximately 85-95% of the eggshell is calcium carbonate and is confirmed as an adsorbent in which the adsorption takes place mainly by the exchange reaction. Therefore, studying and analyzing the structure of the eggshell is important understand its properties as an adsorbent [2, 5].

The Remazol Yellow is an organic azo dye and a limited number of literature studies have been conducted with Remazol Yellow adsorption [2, 10, 14]. Trujillo-Reyes et al. [14] has been studied adsorption of Remazol Yellow on different composite materials such as Fe-Ni, Fe-Cu, C/Fe-Ni and C/Fe-Cu and it is obtained that maximum adsorption capacity of 157.8 mg/g at 30 h with Fe-Ni nanoscale oxides material. Torres-Pérez et al. [15] obtained Remazol Yellow adsorption capacity as 3.61 and 12.72 mg/g for zeolitic material and carbonaceous material/HCl materials, respectively. In the study performed by Gómez-Treviño et al. [10] adsorption capacity of iron modified montmorillonite to Remazol Yellow observed as 8.08 mg/g. Also in a study used Al-SBA-15 material, the adsorption capacity of Remazol Yellow determined as 670 mg/g. Cestari et al. [16] found that, Remazol Yellow adsorbed 30.26 mg/g on modified mesoporous silica. On the other hand, adsorption studies of Remazol Yellow on calcined eggshells (CES) and also calcined eggshell modified with Pluronic 123 (P123), Pluronic 127 (F127) and polyethylene glycol (PEG) are not included in the literature.

The aim of this study was to test the potential of calcined eggshell as an adsorbent for removal of Remazol Yellow. In the present study, calcined eggshell was modified with P123, F127 and PEG for the improving of surface functional groups and reducing of particle size of CES.

2. EXPERIMENTAL

2.1. Synthesis of adsorbent

The eggshell was collected from household waste. To remove impurities and pollutants, firstly, eggshell samples were rinsed several times with deionized water and dried at 105 °C for 24 h. And then the dried eggshell samples were crushed. Finally, the crushed eggshell was calcined at 800 °C for 4 h for obtain of calcined eggshell.

In the synthesis of adsorbents, 1 g calcined eggshell was dissolved in 15 mL distilled water and then 1 g modification agent (P123 Mw:
5.800 g/mol; F127 Mw: 12.600 g/mol; PEG Mw: 20.200 g/mol) added to synthesis solution. The solution was stirred at room temperature for 1 h. The resulting solid was poured to petri dishes and dried at room temperature. Adsorbents were coded as CES-P123, CES-F127 and CES-PEG. All agents were purchased from Sigma-Aldrich.

2.2. Characterization of adsorbent

FTIR analysis technique was used for the determination of surface functional groups of adsorbents. FTIR analyses were carried out by Bruker Vertex 70/70v instrument a resolution of 4 cm\(^{-1}\) and averaged over 16 scans in the range of 400-4000 cm\(^{-1}\) wavelength. Before analyses, 1 mg of samples was mixed with 99 mg KBr and then samples which are powder form were transferred to DRIFT cell.

The surface morphology, size and elemental analysis of the samples were investigated using a scanning electron microscopy (SEM) equipped with a field emission gun FEI/Quanta 450 FEG at an accelerating voltage of 30 kV equipped with an energy dispersive X-ray spectroscopy (EDX), respectively.

2.3. Adsorption studies

Remazol Yellow (C.I. Reactive Yellow 160) was chosen as a model organic pollutant. The molecular structure of Remazol Yellow is represented in Figure 1.

![Figure 1. Molecular structure of Remazol Yellow](image)

The CES and modified CES adsorbents were tested for the adsorption of Remazol Yellow from aqueous solutions at room temperature and natural pH media using a batch reactor. In experiments, adsorbent dosage of 0.1 g/L was used and dispersed into 100 mL of aqueous solution of Remazol Yellow with an initial concentration of 50 mg/L. During adsorption experiments, 4 mL suspension was withdrawn from the reactor at predetermined time intervals and filtered using 0.45 μm naylon filters (Milipore). The Remazol Yellow concentrations were measured using an UV–VIS spectrophotometer (Genesy 10S UV–VIS, Thermoscientific) at 429 nm wavelength. The dye removal % was calculated by the following equation (1):

\[
\text{Dye removal \%} = \frac{(C_o - C)}{C_o} \times 100
\]

The adsorption capacity of adsorbents q (mg/g) at time t (min) was determined according to the following equation (2):

\[
q = \frac{[(C_o-C) \times V]}{m}
\]

where \(C_o\) and C are the initial and final concentration of Remazol Yellow (mg/L), V is the solution volume (mL) and m is the weight of adsorbent (g).

3. RESULT AND DISCUSSION

3.1. FTIR analyses

The FTIR spectrums of adsorbents are given in Figure 2. The peaks at 713, 875, 1433, 1797 and 2513 cm\(^{-1}\) are characteristics peaks of eggshell which are associated with the vibrations of the carbonate groups. The peak observed at 713 cm\(^{-1}\) is due to C-H and also at 873 cm\(^{-1}\) is due to C-C. The peak at 1433 cm\(^{-1}\) denotes C-O stretching vibration. In addition, appearance of peaks around 713 (also C-H) and 1062 cm\(^{-1}\) are attributed to conversion of carbonate to Ca-O. The sharp peak at 3650 cm\(^{-1}\) and a little peak at 2355 cm\(^{-1}\) were assigned to O-H group in \((\text{CaOH})_2\) resulted from water adsorbed [5, 12, 17-20]. On the other hand, the peaks at 3290 and 1651 cm\(^{-1}\) could be due to presence of amines in the eggshell membrane particle [17]. The obtained peaks at 963, 1103, 1237, 1281, 1342 and 2865 cm\(^{-1}\) were assigned to characteristic
peaks of P123 and F127. Peaks at 1061, 1353, 1456 and 2869 cm\(^{-1}\) were corresponding to PEG. The intensity of characteristic peaks of CES was decreased due to modifier agents interacted with the calcined eggshell. This behavior showed that CaO was well interacted with agents.

![FTIR spectrums of adsorbents](image)

Figure 2. FTIR spectrums of adsorbents

3. 2. SEM/EDX and particle size analyses

SEM images and particle size of CES-P123, CES-F127 and CES-PEG adsorbents are given in Figure 3, 4 and 5, respectively. It was seen that, all adsorbents was exhibited a porous structure and regular and popcorn appearance. Al-Ghouti et al. [5] reported that, this is due to calcination which leads to the formation of pores where the major inorganic composition is CaO.

The effect of modifier agents having different chain length (or molecular weight) on particle size was investigated. It was seen that, increase of chain length was caused to decrease of particle size. The particle size of CES-PEG which synthesized using PEG having highest chain length was observed smaller than that of CES-P123 and CES-F127. The particle size of CES-P123, CES-F127 and CES-PEG was determined as 2.34, 2.24 and 1.70 \(\mu m\), respectively.

![SEM images at different scale](image)

Figure 3. SEM images at different scale (a) 50 \(\mu m\) (b) 2\(\mu m\) and (c) particle size distribution of CES-P123 adsorbent

Table 1 summarizes the elemental composition of CES-P123, CES-F127 and CES-PEG. It was showed that, the carbon content increased from 21.44 % to 36.60 % whereas the calcium content decreased from 21.23 % to 8.69 % with increasing of the molecular weight of modifier agents. The increase of carbon content is associated with an increase in the C/O ratio with
the values being 0.37, 0.44 and 0.67 for CES-P123, CES-F127 and CES-PEG, respectively.

Table 1. Elemental composition of adsorbents determined from EDX.

| Adsorbent | Element (Weight %) | C    | O     | Ca    |
|-----------|--------------------|------|-------|-------|
| CES-P123  |                    | 21.44| 57.33 | 21.23 |
| CES-F127  |                    | 25.32| 58.20 | 16.48 |
| CES-PEG   |                    | 36.60| 54.70 | 8.69  |

3.3. Adsorption studies

The dye removal percent of the adsorbents are given in Figure 6. The dye removal % increased a rapid at the first 30 min and then reached to equilibrium at 180 min. At the first 30 min, the percent of removal of Remazol Yellow was obtained as 57.73, 86.60, 89.20 and 93.09 % and also as 91.79, 93.09 and 95.69 at equilibrium for CES, CES-P123, CES-F127 and CES-PEG, respectively.
Equilibrium adsorption capacities of adsorbents at 50 mg/L dye concentration are tabulated in Table 2.

Table 2. Equilibrium adsorption capacity of adsorbents for 50 mg/L dye concentration

| Adsorbent | Adsorption capacity (mg/g) |
|-----------|---------------------------|
| CES       | 47.5                      |
| CES-P123  | 63.6                      |
| CES-F127  | 64.5                      |
| CES-PEG   | 66.3                      |

While the adsorption capacity of CES was obtained as 47.5 mg/g, it was increased up to 66.3 mg/g by modification of CES for 50 mg/L dye concentration. The adsorption capacity of modified CES adsorbents increased from 63.6 to 66.3 mg/g with increasing carbon content. CES-PEG exhibited the highest dye removal. This might be explained with its high carbon content and smaller particle size according to the other adsorbents. The experimental results showed that, the amount of carbon was more effective than the amount of calcium for adsorption of Remazol Yellow. The effect of initial dye concentration on dye removal percent and adsorption capacity on CES-PEG adsorbent having the highest adsorption capacity was investigated and are given in Figure 7 and 8, respectively. While the percentage of dye removal decreased with an increase in the initial dye concentration, the adsorption capacities increased (Figure 8).

Langmuir and Freundlich isotherm models were used to determine the adsorption mechanism. The linearized form of the Langmuir equation is given by the following equation [4]:

$$
\frac{C_e}{q_e} = \frac{1}{q_{max}K_L} + \frac{C_e}{q_{max}}
$$

where, C_e (mg/L) is the equilibrium dye concentration, q_e (mg/g) is the adsorption capacity at equilibrium, q_{max} (mg/g) is the
maximum adsorption capacity of the sorbent and $K_L$ (L/mg) is the Langmuir adsorption constant.

The Freundlich isotherm model equation is [4]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$  \hspace{1cm} (4)

where, $K_F$ and $n$ are the Freundlich adsorption constant and intensity factor, respectively. The isotherms are given in Figure 9 and results are tabulated in Table 3.

When the isotherm models were compared in terms of the high correlation coefficient values ($R^2$), it was seen that the Langmuir and Freundlich isotherm models fitted well with the experimental data (Figure 9).

Table 3. Langmuir and Freundlich isotherm parameters for dye adsorption on the CES-PEG

| Adsorbent   | Langmuir isotherm | Freundlich isotherm |
|-------------|-------------------|----------------------|
|             | $q_{max}$ | $K_L$ | $R^2$ | $K_F$ | $n$ | $R^2$ |
| CES-PEG     | 133.33   | 0.271  | 0.992  | 58.05  | 5.31  | 0.999  |

The adsorption capacity of CES-PEG was compared with several different adsorbents in the literature studies and is given in Table 4.

Table 4. Comparison of adsorption capacities of Remazol Yellow on various adsorbents

| Adsorbent                        | Adsorption capacity (mg/g) | References |
|----------------------------------|----------------------------|------------|
| Fe-Ni                            | 157.8                      | [14]       |
| Zeolitic material                | 3.61                       | [15]       |
| Carbonaceous material/HCl material | 12.72                     | [15]       |
| Fe-montmorillonite               | 8.08                       | [10]       |
| Modified mesoporous silica      | 30.26                      | [16]       |
| CES-PEG                          | 133.3                      | This study |

4. CONCLUSION

Calcined eggshell was successfully modified with P123, F127 and PEG. The decreasing of intensity of characteristic peaks of CES after modification showed that calcined eggshell and modifier agents interacted very well. The chain length or molecular weight of agents primarily affected particle size. The particle size of CES-PEG was observed smaller than that of CES-P123 and CES-F127. Removal percent of Remazol Yellow was found as 68.55, 91.79, 93.09 and 95.69 for CES, CES-P123, CES-F127 and CES-PEG, respectively. The modified calcined eggshell adsorbents exhibited high dye adsorption capacity as compared with calcined eggshell. Particle size and carbon content according to calcium content of adsorbents was more effective in adsorption of Remazol Yellow. The highest dye removal was achieved by CES-PEG. Dye adsorption capacity of CES-PEG was obtained as 133.3 mg/g. The results indicated that synthesized adsorbents could be considered as potential adsorbents for Remazol Yellow removal from aqueous solution.
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