Synthesis of nano-porous hydroxyapatite from eggshell by combustion method and application for disperse red dye removal from wastewaters

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Abstract
Industrialization of countries causes the adverse effect on human life due to the eflluent of pollutant, especially synthetic dyes into water resources. This investigation presents the synthesis of hydroxyapatite, the most Important member of calcium phosphate group,by self-combustion method using a solid waste, eggshell as a rich source of calcium, and produce an efficient nanoporous adsorbent to remove the disperse red dye from wastewater. The effect of processing factor such as fuel ratio, calcination temprature and material dosage on dye adsorption have been investigated. The obtained adsorbent have been evaluated by convential analyzes and final adsorption capacity was determined to be 1150 mg/g approximately.

Keywords: Hydroxyapatite, eggshell, combustion synthesis, red disperse dye, adsorption

Introduction
Synthetic dyes have been widely used in different industries, especially in textile units, which discharge the huge quantity of disperse dye into wastewaters[1]. The wastewaters contiminated by disperse dyes contain organic pollutant which make an adverse effect on environment, due to toxcity. In order to remove dyes from wastewaters and increase the quality of water, different method have been represented, recently[2]. Among all of these methods, the adsorption is one of the most effective way to remove dyes from wastewaters by using an efficiant adsorbent[3]. Hydroxyapatite which is well known as an important member of calcium phosphate group is one of the inorganic adsorbent that have been widely used in water treatment[4]. The aim of peresent work is to synthesize the nano-porous hydroxyapatite from eggshell as source of calcium by simple, rapied and ecofriendly route to applly in treatment of wastewaters conteminated by red disperse dye.

Experimental Material and Method
Eggshell was collected from restaurants, washed carefully and dried in the air condition. The dry eggshell was craushed and powdered by lablatory jar mill. Then, the obtained powder was calcinated in furance at 1000°C for 2 h to convert the calcium carbonate to calcium oxide which was used as calcium resource. Nitric acid, di-ammonum hydrogen phosphate as phosporous source, urea were provided all in analytical grade produced by Merck Company. Hydrocholoric acid and ammonium hydroxide were used to controll pH of solution. In order to synthesis

hydroxyapatite from eggshell, 1.12 g of calcium oxide were dissolved in extra nitric acid solution to produce calcium nitrate solution. Also 1.58 g di-ammunium hydrogen phosphate and 0.25 g of urea were dissolved in 10 ml of distilled water, separately. Firstly, the fuel solution was added to calcium nitrate solution and stirred quickly then the di-ammonium hydrogen phosphate solution was added to mixed solution dropwise. The solution pH was controlled by adding ammonium hydroxide at level 7 and solution was heated at 100°C to achieve approperiate gel. Then the obtained gel was transfered into a laboratory furance which preheated at 500°C to obtain the porous powder. The obtained product was used as adsorbent to remove the red disperese dye, industrial grade, from wastewater.
The X-ray diffraction patterns of product was recorded by a diffractometer (Model D-5000, Siemens, Germany). The particle morphology was evaluated by field emmision scanning electron microscopy (FESEM MIRA3, Tescan, Czech Republic).

Results and discussion Effect of fuel ratio on adsorption efficiency

The effect of fuel ratio on red dispese dye removal efficiency is plotted in Figure 1. The strategy is to find optimum fuel ratio to control the adsorption yield. Dye removal efficiency remaines constant approximatly when fuel ratio is changed 0.13-0.75. The further enhancement in efficency was not observed with the arise in fuel ratio. Therefore, the minmum content of urea should be used to achieve adsorbent with yield about 70 %.

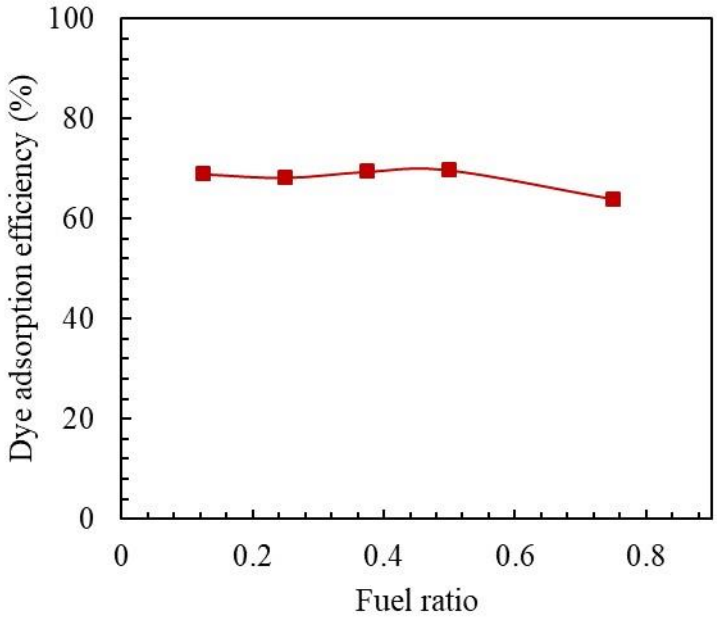

Figure 1. Adsorption efficiency vs. fuel ratio.

Effect of calcination on adsorption effeciency

Figure 2 represents the trend of adsorption yield versus calcination temperature. After heat treatment, a unconsiderable change is observable in efficiency. The increase in efficiency was just about 6 % between 500 and 600 °C remained constant with rise in temperature up to 800 °C. It is evident that the fragile foam contains a higher content of amorphous phase which reduces continuously with rise in calcination temperature. The amorphous phase becomes minimal at temperatures above 800 °C. The powder is drastically transformed to crystalline phase above 800 °C [4]. The obtained powder mainly consists of nano-particles, meaning that

the recrystallization effectively changes the structure. Gradually, the growth of particle becomes slowly at low temperatures, but it rapidly grows at temperatures higher than 800℃.
Hence, the efficiency increases very slowly with the increasing temperature up to 800°C.

Effect of adsorbent dosage on adsorption effeciency

The influnce of adsorbent content on red disperse blue dye removal was indicated in Figure 3 by changing the adsorbent dosage from 8 to 25 mg.

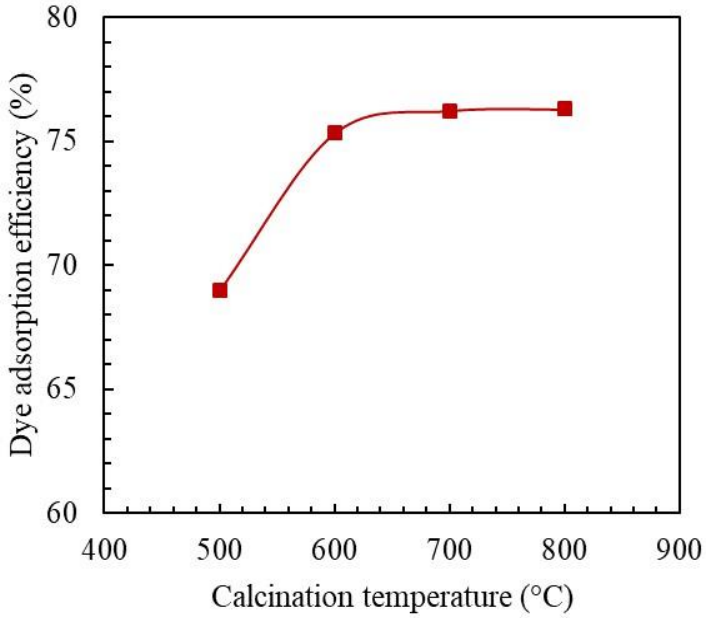

Figure 2. Adsorption efficiency vs. calcination temprature

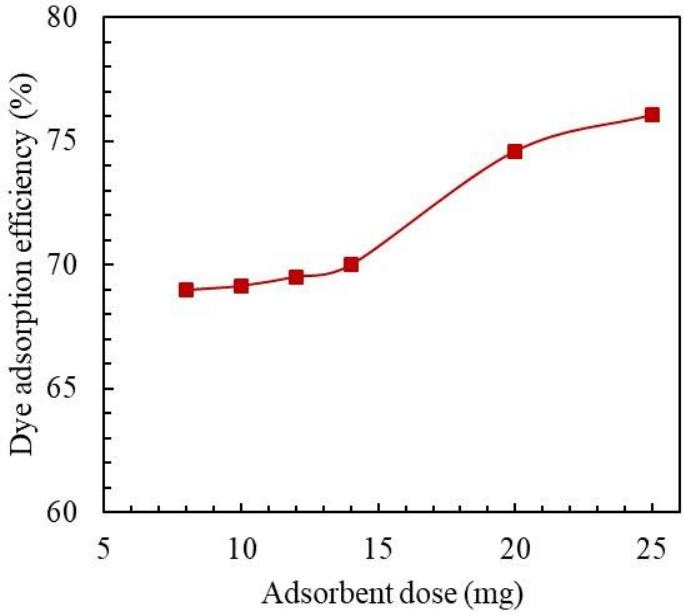

Figure 3. Adsorption efficiency vs. adsorbent dose.

The yield increases with arise in powder dose which is due to the rise in available active sites for adsorption. About 6 % increase in efficiency is observable with 43 wt% rise in adsorbent dose but there is no significant change over 20 mg. Figure 4 shows the image of starting dye solution contiminated with red disperse dye and wastewater treated by 20 mg of hydroxyapatite.

The effective change is observable in color of wastewater, revealing the effectiveness of produced adsorbent in uptake of red dye which cannot efficiently removed by conventional adsorbents.

Adsorption isotherm

Figure 5 indicates the adsorption of red dye onto hydroxyapatite, prepared by fuel ratio of 0.13 in the neutral condition. As the dye concentration rises, the adsorption capacity shows a continuous increase to reach a maximum value. No further enhancement in the adsorption capacity is observed when the equilibrium concentration increases higher than 500 $mg.l^{-1}$. The Langmuir isotherm expressed as a follows to evaluate the adsorption nature.

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \quad (1)$$

where q_e, $mg \cdot g^{-1}$, is the adsorption capacity at equilibrium, C_0 and C_e, $mg \cdot l^{-1}$ are the initial and equilibrium concentrations of dye, respectively. q_m, $mg \cdot g^{-1}$, is the Langmuir monolayer adsorption capacity, 1150 $mg.g^{-1}$. K_L, $l \cdot mg^{-1}$, is the Langmuir constant, 0.008. The high R^2 value, 0.99, of Langmuir isotherm proves that the dye adsorption onto hydroxyapatite is reasonably homogenous.

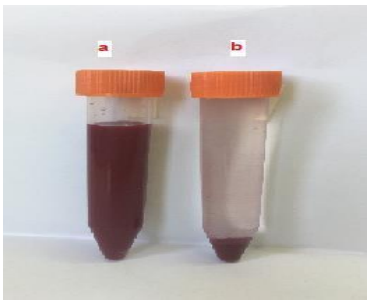

Figure 4. Adsorption of disperse dye with optimum dose of adsorbent, (a) starting solution of red disperse dye, (b) treated by hydroxyapatite.

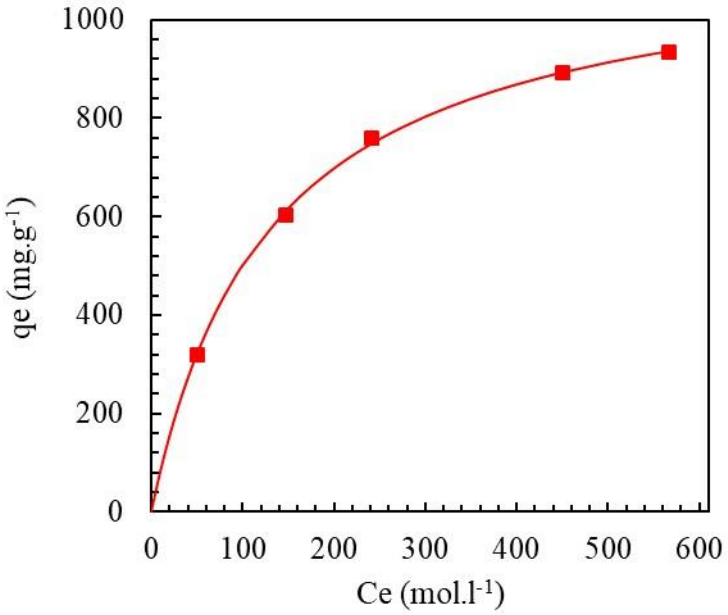

Figure 5. Adsorption isotherm for removal of red disperse dye onto hydroxyapatite.

Srtucture of synthesised adsorbent

Figure 6 indicates the XRD patterns of fragile powder of hydroxyapatite. The patterns exhibit XRD peaks corresponding to (0 0 2), (1 0 2), (1 1 2), (2 1 1), (3 0 0), (2 0 2), (1 3 0), (2 2 2) and (2 1 3) reflections, showing the successfully synthesis of hydroxyapatite by self combution route. The amorphous single phase was formed.

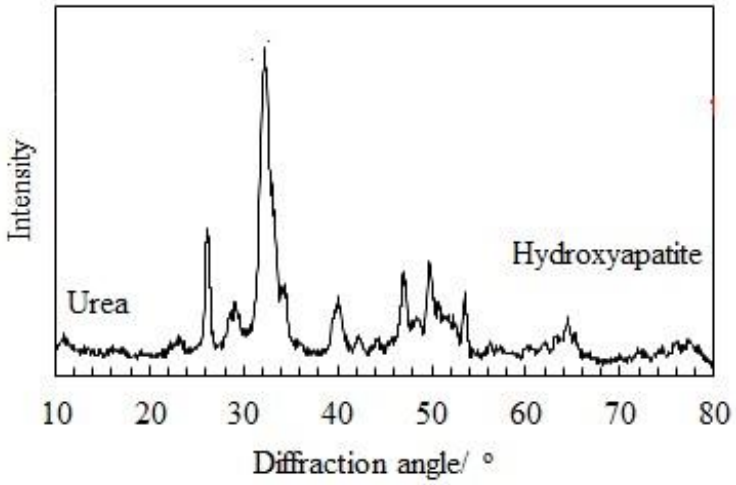

Figure 6. XRD pattern of fragile powder.

Figure 7 shows the morphology of particles synthesized by self combustion route with fuel ratios of 0.13. The fragile agglomerated particles are observed in the FESEM image in which the nano-particles, < 10 nm, are irregularly distributed on the clusters. The FESEM image shows that the nano-particles have the semi-spherical shape when the minimum content of urea is employed in combustion process.

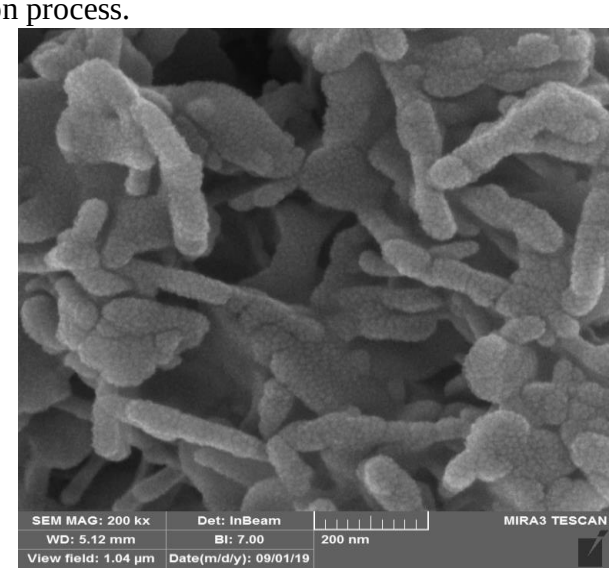

Figure 7. FESEM image of powder prepared by fuel ratio of 0.13 and pH: 7.0.

Conclusions

The poorly crystalline hydroxyapatite nano-particles were prepared by self combustion route from eggshell as efficient adsorbent to remove red disperse dye from wastewater. From engineering point of view, the optimum condition for synthesis of hydroxyapatite to remove disperse dye are found to be: pH of 7.0 and fuel ratio of 0.13. The preparation of appropriate

gel is very critical for synthesis finagle powder in single stage to successfully remove red dye. The dye removal by the as-prepared amorphous hydroxyapatite obeys a monolayer adsorption isotherm, in which the maximum adsorption capacity was determined to be 1150 $mg.g^{-1}$.

References

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