Experimental study of the effect of pH on the adsorption capacity of H_2S from waste water by using calcination of eggshell as an adsorbent.

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Abstract— Many agro-based waste products are found to be very good adsorbents for industrial and domestic wastewater containing hydrogen sulfide. This is due to their lignin and cellulose contents containing structures such as aldehydes, ketones and alcohols as factional groups. This study employs a batch process to investigate the impact of pH on the adsorption capacity of eggshell for the removal of hydrogen sulfide from wastewater. The sample is characterized by using approaches such as SEM, EDX, and particle size distribution test. Thermal analysis is conducted by using Instrument Thermal Analyzer. In the current work, the eggshell is grounded and modified to calcite by using the calcination process. The optimum conditions for the removal of hydrogen sulfide at an initial concentration of 250 mg/L are dosage of 0.1 g/L and agitation speed of 160 rpm. These conditions lead to an adsorption capacity of 21.2 mg $H_2S.g^{-1}$ with an equilibrium time of 400 minutes. The calcination process facilitates the conversion of $CaCO_3$ to CaO. Also, the current study shows that the optimum pH value for effective H_2S removal by using eggshell is ~7.

Keywords— *Eggshell, hydrogen sulfide, calcite, adsorption*

1. INTRODUCTION

Modern industrial activities have produced incredible amounts of waste products which are polluting our environment. For example, wastewaters containing hazardous substances such as hydrogen sulfide (H_2S) produced by petroleum refineries would cause serious environmental, economic and human health problems. H_2S is a very hazardous, corrosive and flammable substance [1]. In Japan, H_2S caused deaths of four workers [2]. In Finland, an accident was reported in mines due to H_2S [3]. H_2S is the principal form of sulfur and sulfur may volatilize to become H_2S gas [4]. H_2S depletes the dissolved oxygen content in an ecosystem which is fatal to benthic aquatic lives. In fact, all forms of H_2S are harmful to organisms [5]. Also, H_2S may cause the formation of acid rain. Therefore, according to the Safe Drinking Water Act (SDWA), the petroleum industry must treat the wastewater by removing the dissolved H_2S before the wastewater is released to the environment. Generally, conventional methods such as physical, chemical, and biological methods have been used to treat wastewaters [6]. However, many agricultural wastes are good adsorbents as well due to their lignin and cellulose contents containing structures such as aldehydes, ketones and alcohols as factional groups [6]. Many researchers have studied various agricultural wastes as low-cost bio adsorbents such as rice husks [7], banana and orange peels [6]. This research focuses on the use of eggshells as the source of calcium oxide to adsorb the dissolved H_2S from wastewaters. It is important to note that agricultural wastes can reduce chemical residues as well [8]. The objective of this work is to study the effect of pH on the adsorption capacity of dissolved H_2S from wastewater by using calcium oxide derived from eggshells.

2. MATERIALS AND METHODS

A. Materials

Here, the calcite content from eggshells is used as an adsorbent of hydrogen sulfide dissolved in wastewater. The eggshells were collected from various restaurants in Kajang, Malaysia. The eggshells were rinsed by using deionized water to remove impurities and the eggshells were dried at 105°C for eight hours. The dried eggshells were ground into powder consisting of particles of mean size 0.5mm. The calcination of eggshells was performed at 900℃ with two hours of soaking time. This was carried out with the nitrogen (N_2) flow rate of 30 cm^3 min^{-1} at a fixed heating rate of 10°C min^{-1}. The pyrolysis treatments were conducted in a horizontal furnace.

B. Preparation of Hydrogen Sulfide solution

In this work, the synthetic wastewater was prepared by relying on the chemical reaction between hydrochloric acid (HCl) and ferrous sulfide (FeS). The experiment was conducted by using a Kipp generator to produce hydrogen sulfide (H_2S) which was then passed through the distilled water. The concentration of the dissolved H_2S in water is ~ 4-6 g/L [9].

C. Characterization measurements

Instrument Thermal Analyzer (TA) was used to conduct the thermal analysis. The measurement was carried out by heating ~25 mg of eggshell at a rate of 10°C/min (with nitrogen flow rate 100 mL/min). Moreover, the Scanning Electron Microscope (SEM) and Energy-Dispersive X-ray spectroscopy (EDX) methods were used to measure the surface morphology of the sample and the chemical compositions, respectively.

D. Adsorption of hydrogen sulfide

The adsorption experiment was conducted by using a batch process. The adsorption process was carried out by using 0.1g of adsorbent in 100mL of synthetic wastewater. After that, the mixture was agitated at a speed of 160 rpm performed at 27℃ for 10 hours. The pH of the samples was adjusted to 7.0 by using NaOH and HCL. Upon screening the suspension, the residual solution was used to measure the concentration of the adsorbent by using a UV–vis spectrophotometer. The standard calibration curve was used to get the final concentrations of the pollutants. All the measurements and experiments were performed at fume hood.The adsorption capacity of the pollutants can be determined by:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where C_e and C_o and are the initial and final concentrations in the pollutants, respective, V is the volume of solution (L), m is the mass of the adsorbent (g), and q_e is the adsorption capacity ($mg.g^{-1}$). The adsorbent sample yield can be calculated by using Equation (2):

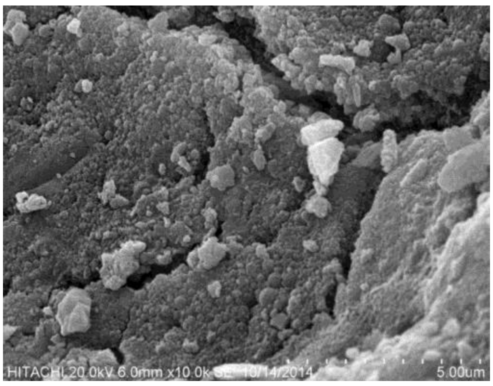
$$Yield(\%) = \frac{W_C}{W_\circ} \times 100\% \tag{2}$$

where W_c is the dry weight of final sample (g) and $W_\circ$ is the dry weight of precursor (g).

3. RESULTS AND DISCUSSION

A. Characterization of the adsorbent.

The adsorbent was characterized by the Energy Dispersive X-ray (EDX) and Scanning Electron Microscopy (SEM) methods. The former was used in the elemental analysis, while the latter was employed in the morphology and porosity analyses of the adsorbent. The surface of the raw material was morphologically analyzed and the result is shown in Fig.1 which indicates that the porosity is poor. The remarkable improvement in the pores properties of the eggshell after the calcination process is demonstrated in Fig. 2. Figs 3&4 reports the results of the EDX test, showing the compositions of the raw material and the adsorbent. As shown in Fig 4, H_2S is converted to elemental sulfur which is then adsorbed by the porous calcite eggshell.



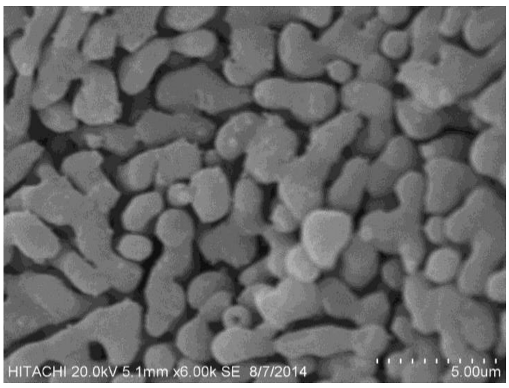


Figure 1: SEM of eggshell

Figure 2: SEM of calcite of eggshell under 900 °C.

The chemical reaction of the absorption process is given in Eq. (4), showing the dissociation of calcium oxide in water to form calcium hydroxide on the adsorbent surface. Eq.(5) shows the reaction between calcium hydroxide and H_2S to yield $Ca(HS)_2$. $Ca(HS)_2$ is then oxidized to become $Ca(OH)_2$ and sulfur as shown in Eq.(6).

$$CaCO_3 \rightarrow CaO + CO_2 \quad (3)$$
$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (4)$$
$$Ca(OH)_2 + H_2S \rightarrow Ca\ (HS)_2 + 2H_2O \quad (5)$$
$$Ca(HS)_2 + O_2 \rightarrow Ca(OH)_2 + 2S \quad (6)$$

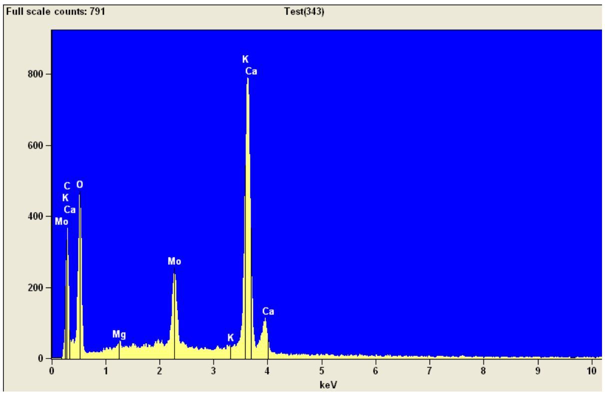


Figure 3: EDX composition of eggshell.

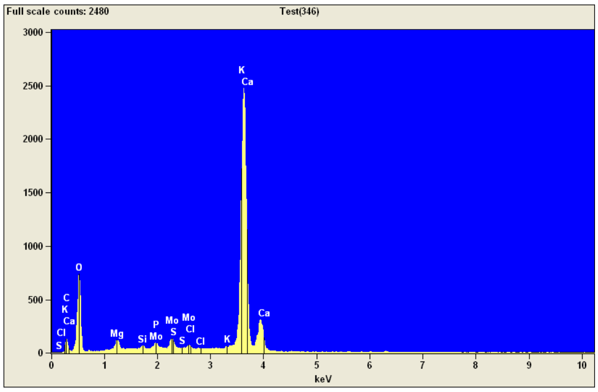


Figure 4: EDX calcite of eggshell after adsorption process.

B. Effect of pH on adsorption capacity

The average adsorption capacities have been calculated by using Equation 1. Fig 5 shows the adsorption capacities at pH values ranging from 2 to 12. It is observed that the adsorption efficiency is the lowest in acidic media, which may be attributed to the competition between metal ions and protons for the adsorption sites. Initially, the adsorption capacity increases as the pH increases. Later, it peaks at pH=7 and declines thereafter. Our result is somehow different from that of Heinonen [10], who has reported that the highest adsorption capacity occurs at pH=6. According to Rahman [10], the adsorption capacity is influenced by the pH fluctuations in the solutions. This is because pH value affects the surface charge of adsorbent, the degree of ionization as well as the speciation of adsorbate.

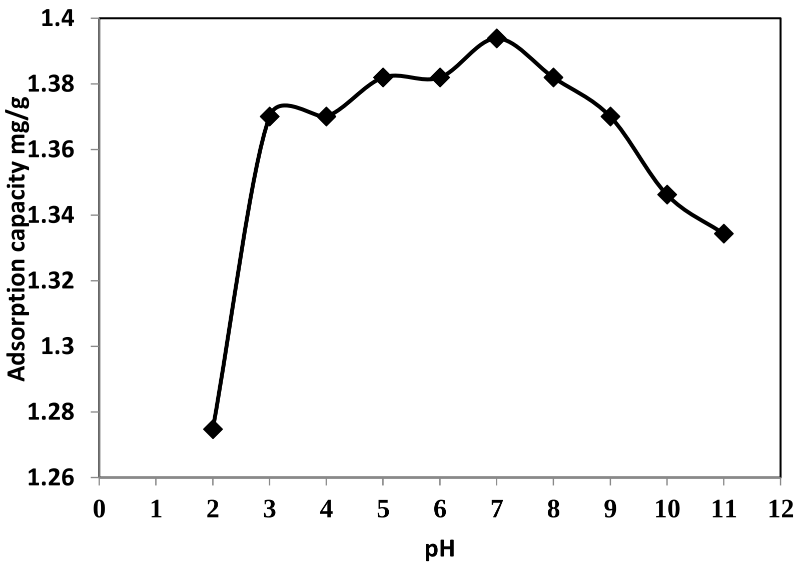


Figure 5: Effect of pH on adsorption capacity of hydrogen sulfide by using calcite of eggshell

Hydrogen sulfide is a very dangerous gas. Thus, many cost-effective solutions have been proposed to convert H_2S into harmless substance. Table 1 compares the absorbent capacities of various waste materials. It shows that eggshell reports the highest adsorption capacity amongst all adsorbents proposed in the literatures.

Table1: Comparison of adsorption capacity of dissolved hydrogen sulfide on various adsorbents

Adsorbents	Adsorbate	Adsorption capacity (mg g-1)	References
Calcite of eggshell	H_2S	21.2	This work
IAC under anaerobic conditions	H_2S	9.4	[11]
Fine rubber particle media (FRPM)	H_2S	0.12	[12]
Crushed oyster shell	H_2S	12	[13]
Red mud	H_2S	17	[14]
Carbonated steel slag	H_2S	7.5	[15]
AC from sawdust pellets	H_2S	6.2	[16]

5. CONCLUSION

This research work reports on the use of eggshell as an alternative adsorbent to remove dissolved H_2S from synthetic wastewater. Maximum adsorption capacity occurs at pH 7. The removal capacity in the batch container reveals that the adsorption capacity is 21.2 mg $H_2S.g^{-1}$ with equilibrium time of 400 minutes. There is no hazardous emission from the calcination process. Thus, eggshell is a very potential and economical alternative to remove H_2S from wastewater.

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