Preparation and characterisation of irradiated waste eggshells as oil adsorbent

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Abstract. Adsorption method had been developed by using natural organic adsorbent for the removal of oil because of its ability to bind the oil molecules into the surface of adsorbent. In this study, chicken eggshells waste was used and it undergoes irradiation process with four different amount of dose which was 0.5 kGy, 1.0 kGy, 1.5 kGy, and 2.0 kGy by using Gamma Cell Irradiator. Three equipment had been used for the characterization process which were the Scanning Electron Microscope (SEM), Energy Dispersive X-ray spectroscopy (EDX), and Fourier-Transform Infrared Spectroscopy (FTIR). The adsorption experiment was conducted to calculate the sorption efficiency by using different mass of samples. The result showed that irradiated chicken eggshells powder with 2.0 kGy amount of radiation dose has a best performance as oil adsorbent.

1. Introduction

The increasing demand and needs for oil by the customers around the world have led to the increasing of shipping activities including the exploration, production, storage, and transportation of oil. These activities have increased the risk of marine pollution by the oil spills. This pollution will give bad impacts on the environment, humans, animals, and plants as it will harm their life [1]. The most affected area of oil pollution in Malaysia is the Straits of Malacca as it is an international route for all the ships [2].

There are various methods that have developed by the researchers in order to clean the ocean from the oil spill which is adsorption, mechanical, chemical and biological. Among all of the methods, adsorption is a most-eco-friendly method where it does not release any harmful gasses or chemicals that affected the environment [3]. Adsorption method is a process where the material called adsorbent is used to attract the oil onto the surface of the material [4]. Among the three types of materials, organic materials are a good adsorbent that can be used to overcome the oil spill problem. Therefore, chicken eggshells waste has been used in order to study their capability as adsorbent that can remove the oil from the surface of the water.

The chicken eggshell waste is a very effective material to remove both dissolved and dispersed oil from produced water. This is because chicken eggshells have an important constituent pure CaCO$_3$ and natural porosity that contribute to the efficiency of the oil adsorption process [5]. In this study, the chicken eggshells undergo the irradiation process by using Gamma Cell Irradiator with four different...
amounts of radiation dose which is 0.5 kGy, 1.0 kGy, 1.5 kGy, and 2.0 kGy. There is study indicated that foaming properties of egg white can be improved by low-dose irradiation [6].

2. **Literature review**

2.1 **Type of methods for the removal of oil from the water**

There are many researches in the studies of low cost and efficient methods for the removal of oil from the water surface. Four methods had been developed for the removal of oil which is mechanical, chemical, biological, and adsorption. Figure 1. illustrates the methods of use for the removal of petroleum products with examples [3].

![Figure 1. Method used for the removal of petroleum products](image)

2.2 **Adsorption method**

Adsorption is the most popular method compared to the other three methods used to remove oil from the surface of the water which involved different types of adsorbents. The adsorbents used consists of several characteristics which is capable to bind the oil molecules on its surface and contains a porous solid with the developed specific surface area. This method is used for the removal of petroleum products in many areas such as on the coastal borders area, on paved roads, and on the surface of the water.

2.3 **Types of adsorbent material**

The adsorbents used for the process to remove oil from the water are categorized by inorganic mineral adsorbents, synthetic organic adsorbent or synthetic polymers adsorbent, and natural organic adsorbents. The development of an adsorbent with high adsorption capacity and low-cost material had been studied using these types of materials in order to obtained efficient material [3].
2.4 Natural organic adsorbents

There are various natural organic adsorbents that have been studied by researchers included kapok, rice husk, various types of plants shells and wastes. This type of material is environmentally friendly adsorbent as they are biodegradable so that they are capable to be disposed of right after the process of oil removal from the surface of the water.

Currently, the utilization of the synthetic products adsorbent is used widely where it is a common adsorbent used to resolve the oil spills problems that occurred on the marine ecosystem. Nevertheless, this type of adsorbents is not biodegradable material which makes it is their major disadvantage [4]. Therefore, chicken eggshells are utilized and modified to become adsorbent that will remove oil from the surface of the water in this study.

3. Methodologies

3.1 Sample preparation

There are two types of samples that were prepared in this study which are chicken eggshells powder for pre and post irradiation process. Both of the samples were needed to study the effect on the physical and chemical properties of the chicken eggshells powder for pre and post irradiation process and the evaluation of the efficiency of both samples to remove the oil from the surface of the water.

3.2 Raw chicken eggshells powder

The chicken eggshells waste was washed with water several times to remove the unwanted impurities. Then, it was dried under the Sun. The dried chicken eggshells waste was crushed into a form of powder by using a blender. Next, the chicken eggshells powder was sieved through 63 microns siever in order to obtain a fine powder. The chicken eggshells powder was washed again with distilled water to remove undesired impurities. Then, chicken eggshells powder was then dried in an oven for 24 hours at the temperature of 70°C [5].

3.3 Irradiated chicken eggshells powder

The raw chicken eggshells powder was undergone irradiation process by using Gamma Cell Irradiator. There were four different amounts of the radiation dose used on the chicken eggshells powder which are 0.5 kGy, 1.0 kGy, 1.5 kGy, and 2.0 kGy. The chicken eggshells powder was irradiated by gamma rays emitted from the Cobalt-60 source.

3.4 Sample characterisation

There are several instruments used to characterise the samples in this study including Scanning Electron Microscope (SEM) to observe the presence of pores, Energy Dispersive X-ray spectroscopy (EDX) to identify the chemical composition, and Fourier-Transform Infrared Spectroscopy (FTIR) to identify the functional groups that presence on the surface of the chicken eggshell powder [5].

3.5 Adsorption efficiency experiment

For the evaluation of the adsorption efficiency of chicken eggshells powder, a synthesized oil-water mixture was produced. In this study, 10 mL of diesel oil was poured into a 250 mL beaker that contains 100 mL distilled water. The adsorption efficiency of both raw and irradiated chicken eggshells powder was measured by using a factor of different amounts of mass for each of the samples [7].
The beaker containing the oil-water mixture was placed on the magnetic stirrer (700 rpm) and it was switched on. One gram of the sample was measured and put into the oil-water mixture. After thirty minutes, all of the substances in the beaker were filtered by using filter paper. This procedure was required to separate the oil and chicken eggshells powder from the water. The amount of oil was obtained by using the syringe and a net fabric with small mesh for one-minute draining process. The residual oil obtained by the process was measured by using a 10 mL measuring cylinder. Therefore, the sorption efficiency was calculated by using the amount of residual oil left and initial mass of oil which was 10 mL. The sorption efficiency can be calculated by using the equation (1) stated by:

\[
\text{Sorption efficiency (%) = } \frac{\text{Mass of oil removed}}{\text{The initial mass of oil}} \times 100 \quad (1)
\]

[1] 4. Results and discussion

4.1 Characterisation by using Fourier-Transform Infrared Spectroscopy (FTIR)

The Fourier-Transform Infrared Spectroscopy (FTIR) spectrum illustrated in Figure 1 displays numbers of absorption peaks that indicate the presence of functional groups on the surface of both the raw and irradiated chicken eggshells powder. It shows the chemical bonding that plays an important role in the chemical structure of chicken eggshells powder. There are three distinct peaks that can be seen on the spectrum. An intense peak of the raw chicken eggshells powder is observed at 1403.76 cm\(^{-1}\) which is assigned to C=C stretching in aromatic ring carbonate ion that can be strongly associated with the presence of carbonate minerals within the chicken eggshell matrix. There are also two observable peaks at 712.12 cm\(^{-1}\) and 872.28 cm\(^{-1}\) which are associated with the out of plane bending C-H or long linear aliphatic chain and vibrations of skeletal C-C respectively, indicating calcium carbonate (CaCO\(_3\)) existence.

![Figure 1. FTIR spectrum of (a) Raw chicken eggshells powder. (b) 0.5 kGy. (c) 1.0 kGy. (d) 1.5 kGy. (e) 2.0 kGy.raw chicken eggshells powder.](image)

It also shows a variety of the FTIR spectrums on the irradiated chicken eggshells powder with different doses of gamma cell irradiation which the blue color lines belong to the raw chicken eggshells powder meanwhile the yellow color for 0.5 kGy, orange color for 1.0 kGy, green for 1.5 kGy, and grey color for 2.0 kGy irradiated chicken eggshells powder. The FTIR spectrums of the irradiated chicken eggshells show similar peaks with the raw chicken eggshells powder. This indicates that there is the
presence of carbonate minerals which is calcium carbonates in both of the raw and irradiated chicken eggshells powder.

4.2 Characterisation by using Scanning Electron Microscope (SEM)

The samples are observed under 2000x magnification in order to observe their surface morphology. The SEM image of raw chicken eggshells powder display a various size of pores and irregular surface structure. The presence of pores on the surface of raw chicken eggshells powder allows the adsorption process of the oil molecules to take place. The measurement of the pores presents in 10 μm x 10 μm of the SEM image of raw chicken eggshells powder shows that there are about 12 pores that can be seen roughly.

The irradiated chicken eggshells powder used in this characterisation is the chicken eggshells powder that undergoes the irradiation process with 1.0 kGy amount of irradiation dose based on the previous FTIR characterization. After the irradiation process, the structure of the chicken eggshells powder changed is also displayed an irregular surface texture but with small sizes of pores. However, the irradiated chicken eggshells powder observed shows the measurement of the pores presents in 10 μm x 10 μm of the SEM are about 17 pores that can be seen roughly. The SEM image for both samples were illustrated in Figure 2.

![Figure 2. The SEM image of (a) raw chicken eggshells powder. (b) 1.0 kGy of irradiated eggshells powder. (Notes: The rectangular shape shows the pores on the irregular surface texture)](image)

4.3 Characterisation by using Energy Dispersive X-Ray Spectroscopy (EDX).

Energy Dispersive X-Ray Spectroscopy (EDX) analysis of both raw and irradiated chicken eggshells powder has been studied to observe the element and chemical composition presented in it. Figure 3(a) shows the EDX spectrum of raw chicken eggshells powder consists of the elements of Carbon, Oxygen, and Calcium. Meanwhile, Figure 3(b) right shows the EDX spectrum for the irradiated chicken eggshells powder with 1.0 kGy of gamma radiation which consists of the same types of elements. It shows there
are three types of elements that contributed to the binding of oil molecules onto the chicken eggshells powder.

![Figure 3. EDX Spectrum for (a) Raw chicken eggshells powder. (b) 1.0 kGy of irradiated chicken eggshells powder.](image)

Table 1 and 2 illustrate the chemical composition of both raw and irradiated chicken eggshells powder respectively. It provided the weight percentage and the atomic percentage of the element existed in the chicken eggshells powder. It can be seen that there was a decreasing amount of both weight and atomic percentage for the element of carbon while oxygen and calcium elements showed an increasing amount for both weight and atomic percentages. Irradiation can cause significant changes in functional properties of egg white due to the oxidation of egg components by hydroxyl radicals produced through the radiolysis of water [8]. Free radicals can cause fragmentation, aggregation, and cross-linking of protein molecules, and induce changes in physicochemical and functional properties.

### Table 1. Chemical composition of raw chicken eggshells powder

| Element | Weight, % | Atomic, % |
|---------|-----------|-----------|
| C       | 27.18     | 39.10     |
| O       | 45.47     | 49.11     |
| Ca      | 27.35     | 11.79     |
| Total   | 100       | 100       |

### Table 2. Chemical composition of irradiated chicken eggshells powder

| Element | Weight, % | Atomic, % |
|---------|-----------|-----------|
| C       | 18.33     | 28.65     |
| O       | 46.93     | 55.07     |
| Ca      | 34.74     | 16.27     |
| Total   | 100       | 100       |
4.4 Adsorption experiment for measurement of adsorption efficiency

The amount of chicken eggshells powder mass used in this experiment is 1 gram, 2 gram, and 3 gram after 30 minutes contact time and a constant volume of diesel oil which is 10 milliliters. Figure 4 illustrates a graph of sorption efficiency against the mass of chicken eggshells powder. Irradiation of eggshell caused substantial changes in turbidity, viscosity, foaming properties, and volatile profiles due to oxidative changes and the extents of the changes were irradiation dose-dependent [9]. It can be concluded that the irradiated chicken eggshells powder with 2.0 kGy amount of radiation dose has higher adsorption efficiency with increasing mass compared to raw. 1 gram of 2.0 kGy irradiated chicken eggshells powder have 40% adsorption efficiency, 2 gram has 60% adsorption efficiency, and 3 gram has 64% adsorption efficiency.

Figure 4. Adsorption efficiency of the different mass of different chicken eggshells powder

5. Conclusion

It can be concluded that the chicken eggshells powder that were irradiated capable to be better adsorbent than the raw chicken eggshells powder for the removal of oil from the surface of the water. Besides that, irradiation method changed the morphology structure of eggshells that supported by EDX spectrum with shows fluctuate amount of elements carbon, calcium and oxygen.

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