Peanut shells-based adsorbent for lead removal from batik waste with potassium hydroxide and nitric acid activation

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Abstract. Due to its uniqueness, the demand for batik keeps increasing. Environmental issues arise due to waste from batik production and needs to be taken care of. Adsorption of lead content in batik waste has been done using peanut shells-based adsorbents with potassium hydroxide and nitric acid activation. The peanut shells were heated at 450°C for 2 hours and screened through an 80 mesh filter. Base activation was done by mixing the adsorbent with KOH 50% solution for 30 minutes at 180 rpm. For acid activation, a solution of nitric acid was used instead. It was done at 90°C for 2 hours. The potassium hydroxide-activated adsorbent offered the best performance, reached 99.93%. While nitric acid-activated adsorbents have worse performance than unactivated adsorbent.

1. Introduction

Batik is world-renowned for its unique patterns and characteristic. In Indonesia, batik industry is growing well and contributing to our economy [1]. Higher batik production rates are required to fulfill the demand. While this is improving the economy, on the other hand, this activity generates a considerable amount of waste and causing environmental problems.

Batik waste contains metals such as Pb, Zn, Cd, and Cr, as well as dye and non-biodegradable synthetic materials [2]. Among others, lead is the most noxious heavy metal even in low concentration. Lead can accumulated inside the human body and causing kidney failure, nerve injury, or even death [3]. When batik waste is released to the environment without further treatment, there is a good chance that people will interact with it. Thus, effective waste treatment is needed to overcome this problem.

Different kinds of waste treatment can be applied to address the situation from adsorption, membrane to photocatalysis. Among others, adsorption is easy to use and can be made from various abundant materials, biomass, for instance. A good way to retrieve the biomass is by utilizing organic material waste.

Cilegon, a city in Banten, Indonesia, is both an agricultural and industrial city. Its largest agricultural products are rice and peanuts. Peanuts are sold directly or converted into various kinds of processed foods, leaving a considerable amount of peanut shells waste. According to the Indonesian Central Bureau of Statistics (BPS) in 2018, production rates of peanuts in Cilegon reached 2,488 tons/year and is the largest in Banten province [4]. Mostly, the waste is directly discarded or incinerated and should be utilized further.

Peanut shell contains high cellulose concentration, thus can adsorb waste components. Still, the efficiency of the adsorption process is not only determined by the cellulose content alone. Many
treatments can be done to improve its efficiency. Activation using alkali solution and surface modification by acid solution are known to enhance adsorption capacity.

A study was done by Irdhawati et al. on the adsorption capacity of peanut shells-based adsorbent activated with acid and base to adsorb phosphate ion and its capacity reached 10.4 mg/g [5]. Another study by Wulan et al. about methyl violet adsorption using peanut shells-based adsorbent and its efficiency reached 97.5% [6]. Safrianti et al. reported the adsorption of lead by rice straw-based adsorbent activated with nitric acid [7]. Based on those studies, peanut shells-based adsorbent has the potential to be developed for batik waste treatment, especially removing its lead content. In this study, we report the effect of acid and base activation, specifically KOH and HNO₃, to peanut shells-based adsorbent performance for lead adsorption.

2. Methodology

Peanut shells were obtained from local farmers in Cilegon, Indonesia. They were washed to remove the soil and other impurities followed by sun drying. Analytical grade of KOH and HNO₃ 65% were acquired from Merck chemicals.

2.1. Adsorbent synthesis

Adsorbent was produced by heating the dried peanut shells at 450°C for 2 hours in a furnace and screened using 80 mesh filter. The adsorbent was ready for use and labeled as “non-activation”. Repeat the steps for “non-activation’. Subsequently, a solution of KOH 50% was added and stirred for 30 minutes at 180 rpm. The adsorbent was then washed by aquadest, dried and labeled as “KOH activated”. Repeat the steps for “KOH activated”. An amount of HNO₃ 65% was diluted to 10%. The adsorbent was mixed with the diluted HNO₃ using hotplate stirrer at 90°C for 2 hours, washed with aquadest and dried afterward. The adsorbent was labeled as “KOH + HNO₃ 10% activated”. The steps for “KOH + HNO₃ 10% activated” was repeated for HNO₃ concentration of 20%, 30%, 40% and 50%. They were labeled as “KOH + HNO₃ 20%, 30%, 40% and 50% activated”, subsequently. The adsorbents were analyzed using FTIR analysis.

2.2. Adsorption evaluation

Artificial waste was made by diluting lead acetate. A half gram of adsorbent was added to 50 ml of artificial waste containing 100 ppm of lead. The sample was then agitated at 300 rpm in ambient temperature and filtered to separate the adsorbent from the solution. Later, the lead concentration of the solution was analyzed using Spectrophotometer AAS.

3. Result and Discussion

From FTIR analysis result in Figure 1, it can be seen that adsorbent activation using KOH and HNO₃ altered their functional groups configuration. The interpretation of functional groups recorded is shown in Table 1 [8].
Figure 1. FTIR spectra of peanut shells-based adsorbents.

Table 1. Adsorbent functional groups.

| Wavelength | Range     | Desc  | Wavelength | Range     | Desc  |
|------------|-----------|-------|------------|-----------|-------|
| Without Activation |         |       | KOH activated |         |       |
| 3338.7     | 3200-3550 | OH    | 3350       | 3200-3550 | OH    |
| 2927       | 2840-3000 | C-H   | 1559       | 1566-1650 | C=C   |
| 1578       | 1566-1650 | C=C   | 1375       | 1310-1390 | O-H   |
| 1053       | 1050-1085 | C-O   | 1094       | 1087-1124 | C-O   |
| KOH + HNO_3 10% activated |         |       | KOH + HNO_3 50% activated |         |       |
| 3505.6     | 3200-3550 | OH    | 3250.2     | 3200-3550 | OH    |
| 1595.3     | 1580-1650 | C=C   | 1701.5     | 1685-1710 | C=O   |
| 1241.2     | 1020-1250 | C-N   | 1602.8     | 1580-1650 | N-H   |
|            |           |       | 1528.2     | 1500-1550 | N-O   |
|            |           |       | 1235.6     | 1020-1250 | C-N   |

Functional groups of unactivated adsorbent from FTIR analysis is matched with functional groups of cellulose [9]. An activated adsorbent with KOH 50% has phenol functional group added into the adsorbent, which improves adsorption performance [10]. Phenol is a negative ion, while lead is a positive ion. Attraction force between the opposite charges is leading to a better adsorption efficiency. Generally, activation using HNO_3 produces nitrate functional group, hence good adsorption capacity [10]. When HNO_3 10% is used, the formation of nitrate functional group is not significant, and lower adsorption efficiency is expected.
Table 2. Lead adsorption performance of peanut shells-based adsorbents.

| No. | Type               | C_{final} | %Efficiency | Q (mg/g adsorbent) |
|-----|--------------------|-----------|-------------|--------------------|
| 1   | Without Activation | 0.27      | 99.73%      | 199.46             |
| 2   | KOH 50%            | 0.07      | 99.93%      | 199.85             |
| 3   | KOH 50% + HNO_3 10%| 2.20      | 97.80%      | 195.60             |
| 4   | KOH 50% + HNO_3 20%| 0.25      | 99.75%      | 199.50             |
| 5   | KOH 50% + HNO_3 30%| 0.31      | 99.69%      | 199.38             |
| 6   | KOH 50% + HNO_3 40%| 0.97      | 99.03%      | 198.06             |
| 7   | KOH 50% + HNO_3 50%| 0.23      | 99.77%      | 199.54             |

Figure 2. Effect of adsorbent treatments to pH values of treated waste.

Peanut shells-based adsorbents are effective to lower lead concentration, as shown in Table 2. The final concentration of lead is not significantly different, and the best performance is obtained by adsorbent with activation of KOH 50%. The result is lower than the maximum allowed lead concentration in water (0.1 ppm) based on the Republic of Indonesia Government Regulation [11]. It can be seen that acid treatment reduces the adsorbent performance caused by the influence of pH. When HNO_3 is added as the activator, the pH is as low as 2.87, and the H^+ ion is competing with Pb^{2+} ion to bind with the functional groups on the adsorbent surface thus its adsorption capacity is depleted. When only KOH activation was done, the pH is 7.2 and the OH^- ion on the surface is higher. The addition of OH^- on the adsorbent surface improves the amount of site for binding Pb^{2+} ion, hence the efficiency increase [12].

4. Conclusion
Peanut shells-based adsorbents were successfully synthesized to treat the batik waste effectively. Activation using potassium hydroxide solution could improve the adsorbent performance, while nitric acid solution deprived its performance.

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