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OPTIMISATION OF SULFURIC ACID CONCENTRATION FOR Fe^{2+} ION REMOVAL USING ACTIVATED CHARCOAL FROM BOILED PEANUT SHELLS

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Abstract

Groundwater containing iron(II) (Fe^{2+}) ions causes yellowish-brown discolouration and sediment formation. Since bioadsorbents can remove Fe^{2+} ions, this study investigated the effect of varying H_2SO_4 activator concentrations (5%, 7%, 9%, 11%, and 13%) on adsorption efficiency and identifies the optimal concentration for activated charcoal derived from boiled peanut shells (Arachis hypogaea L.) to remove the metal ions from well groundwater in Punge Jurong Village in Aceh Province of Indonesia. The process included carbonising the peanut shell waste, activating the charcoal, and testing the adsorbent on well groundwater. The results were analysed using SSA, SEM, and FTIR instruments, along with statistical analysis via SPSS 15 for one-way of analysis of variance (ANOVA). The adsorption efficiencies were 60.43%, 55.53%, 59.01%, 61.81%, 61.94%, and 59.10% corresponding to the activated carbons by H_2SO_4 (5%, 7%, 9%, 11%, and 13%) and commercial activated carbon, respectively. The IR-assisted characterisation on the boiled peanut shell waste bioadsorbent suggested that wave number shifting on O–H, C=C and C–O typical regions might be due to protonation affect by the acid activator. Conclusively, the study indicates that 13% H_2SO_4 is the most effective activator concentration for Fe^{2+} ion removal using activated carbon derived from boiled peanut shells.

Keywords: *activated carbon, H_2SO_4 activator, boiled peanut shell, adsorption of iron(II) ions, groundwater*

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1. Introduction

Groundwater with high concentrations of iron(II) (Fe^{2+}) can cause the water to appear brownish-yellow, a change observable through the formation of yellow moss and

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sediment. These visual indicators are evident in the well water of Punge Jurong village, Meuraxa District, Banda Aceh, where water quality has deteriorated following the tsunami. Such contamination poses health risks, as the toxic elements can lead to physiological disorders affecting the liver, kidneys, and nervous system. Therefore, scientific studies are necessary to develop eco-friendly water treatment techniques to reduce Fe^{2+} levels to within permissible limits (Talunoe, Nurhaeni, and Mirzan 2015).

Adsorption is a surface-based process widely utilised for effective water treatment, particularly in the removal of heavy metals (Mandasari and Purnomo 2016). This method is highly popular due to its simplicity and cost-effectiveness, making it an appealing alternative for pollutant removal (Irawan, Dahlan, and Retno 2015). Various studies have explored agricultural waste as potential bioadsorbents, with peanut shells emerging as a viable option (Talunoe, Nurhaeni, and Mirzan 2015). Peanuts are commonly consumed in Indonesia as snacks, either boiled or roasted, leaving the shells as waste (Pratomo et al. 2015). In Aceh alone, peanut production in 2018 was reported to be 3,658 tons by the Indonesian Central Statistics Agency, indicating a significant amount of waste. Utilising this waste, especially from boiled peanuts, as bioadsorbents can effectively address metal contamination in water. This approach is particularly relevant in the Ulee Lheue area, Meuraxa District, Banda Aceh, where boiled peanut shell waste is prevalent.

Bioadsorbents can be produced by heating carbon-rich materials at high temperatures to form charcoal (Nurhasni, Mar'af, and Hendrawati 2018). This transformation involves two stages: carbonisation and activation. Carbonisation is conducted using a furnace at 450°C for one hour. During activation, an activator is used to enhance the charcoal's adsorption capacity. Nunik and Okayadnya (2013) found that activated charcoal from candlenut shells, treated with 9% H_2SO_4, could absorb 91.38% of iron(II) ions from well water. H_2SO_4 is an effective activator due to its dehydrating properties and its ability to open and expand carbon pores by removing contaminants such as metal oxides (Asrijal, Chadijah, and Aisyah 2014). Given this context, research on utilising boiled peanut shell waste as a bioadsorbent is necessary to evaluate its efficiency in absorbing iron(II) ions from well water using various H_2SO_4 concentrations (7%, 9%, 11%, and 13%) for 24 hours of immersion and carbonisation at 450°C for one hour.

2. Method

2.1 Materials

This research employed a 60 mesh sieve (Laboratory test Sieve BBS BA-0710), an oven (Drying Oven/incubator GP-45 BE), beakers (Iwaki 250 mL, Duran 250 mL and 150 mL), test tubes (Duran), desiccator, spatula, hot plate stirrer (AHS-12 A), analytical balance (Matrix AJ602B), volumetric flask (Duran 20 mL), glass funnel (Pyrex), watch glass, Buchner vacuum (Oil Less Pump Model DVP- 3073), dropper pipette, mortar and pestle, Erlenmeyer (Duran 250 mL and 200 mL), atomic absorption spectroscopy (AAS) instrument (Shimadzu AA-6300 Serial No. A305245), furnace (Barnstead Thermolyne Furnace 1300), scanning electron microscopy (SEM) (Hitachi TM 3000 Tabletop Microscope), and fourier transform infra-red (FTIR) (Shimadzu IR Prestige-21).

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The materials were boiled peanut shells, distilled water (H_2O), well water, sulfuric acid (H_2SO4) (Merck), filter paper, commercial activated carbon (Merck), Whatman number 40 filter paper, aluminium foil and potassium, and thiocyanide (KSCN) (Merck).

2.2. Procedure

2.2.1. Sample preparation

Boiled peanut shell waste (1 kg) collected from Ulee Lheu, Meuraxa District, Banda Aceh was washed thoroughly with running water. The sample was cut into pieces (approximately 1 x 1 cm) and sun-dried for 9 h. The sample was then placed in an oven at 105°C for 24 h. Finally, the dried biomass was stored in a container at room temperature.

2.2.2. Formation of activated carbon

The dried sample (100 g) was placed in a furnace at 450°C and carbonised for 1 h. The obtained carbon was left in a desiccator to reach a room temperature, then ground, and sieved using a 60-mesh sieve. The fine sample (1.5 g) was soaked with 7.5 mL of H_2SO_4 solution (5%, 7%, 9%, 11%, 13%) for 24 h. Afterwards, the mixture was then stirred for 2 h using a magnetic stirrer at 100 rpm. The charcoal sample was filtered using a Buchner funnel and washed with distilled water until reaching a neutral pH. The acid-free charcoal was dried in an oven at 105°C for 3 h. The activated charcoal was finally placed in a desiccator to room temperature.

2.2.3. Evaluation of absorbent performance and characterisation of the activated carbon

Well groundwater (100 mL) was mixed with activated carbons (1 g) while well groundwater with and without commercial adsorbent were assigned as positive and negative controls, respectively. Each sample was stirred using a magnetic stirrer (100 rpm, 60 minutes). The samples were then left to settle for 30 minutes at room temperature, followed by filtration using filter paper. The filtrate was collected in an Erlenmeyer flask to be subjected for iron(II) ion content measurement using AAS at a wavelength of 243.3 nm. On the other hand, the carbon residue was then dried in an oven at 105°C for 3 h. The selected activated carbon by 7 % H_2SO_4 and 11% H_2SO_4 representing the poorest and excellent biosorbents, respectively, were characterised using SEM and FTIR. The biosorbent performance was expressed in a percentage of absorption efficiency quantified by the following formula.

$$E\ (\%) = \frac{(C_0 - C_t)}{C_0}\ x\ 100\ \% \qquad \text{(equation 1)}$$

E, C_0, and *Ct* denote efficiency of absorption (%), concentration of Fe^{2+} in untreated groundwater (mg/L), and concentration of Fe^{2+} in treated groundwater (mg/L), respectively.

2.2.4. Statistical analysis

Statistical analysis using the SPSS 15 program tested one way ANOVA to see the significant values of the varied activator concentration and adsorption efficiency.

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3. Result and Discussion

The activation of carbon from boiled peanut shells involved the addition of H_2SO_4 to increase volume, enlarge pore diameters, and create new pores by eliminating residues on the adsorbent's surface. During this activation process, molecular interactions between the activating agents and carbon atoms occur. Subsequently, the carbon is subjected to combustion in an oxidizing atmosphere, which enhances the number of pores and overall surface area through the elimination of volatile byproducts.

The activator can infiltrate the pores between the carbon layers, resulting in enhanced adsorbent activity, as evidenced by its well-distributed hexagonal shape. According to intercalation theory, a compound's structure undergoes modification when ions or atoms are introduced into it (Nunik and Okayadnya 2013). H_2SO_4, compared to other acid activators, has more dehydrating agents and active sites. This activator can open and expand carbon pores by eliminating their coverings, primarily metal oxides (Suhendra and Gunawan 2010), due to its significant reactivity with oxygen (Oktasari 2018).

Table [illegible] er after the

No.	Concentration of H_2SO_4 (%)	Concentration of Fe^{2+} in the groundwater (mg/L)
1.	-	1.142
2.	5	0.452
3.	7	0.508
4.	9	0.468
5.	11	0.437
6.	13	0.435
7.	Commercial activated carbon	0.467

Variations in activator concentration were employed to ascertain their impact on the adsorption capacity of activated carbon derived from boiled peanut shells. Activators can bind water, and during the carbonisation process, tightly bound water within the carbon pores remains intact and is not easily released. Subsequently, the activator penetrates the pores, opening the previously closed charcoal surface. This process enlarges the pores and increases the surface area of the activated carbon, thereby enhancing its adsorption capacity. In this study, untreated well groundwater contained iron(II) ions at a concentration of 1.142 mg/L. As shown in Table 1, the iron(II) ion concentrations in groundwater treated with activated carbons using H_2SO_4

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activators at 5%, 7%, 9%, 11%, and 13% were 0.452, 0.508, 0.468, 0.437, and 0.435 mg/L, respectively. For comparison, the concentration in groundwater treated with commercial activated carbon was 0.467 mg/L. According to ANOVA analysis, the variation in acid concentrations significantly influences adsorption efficiency.

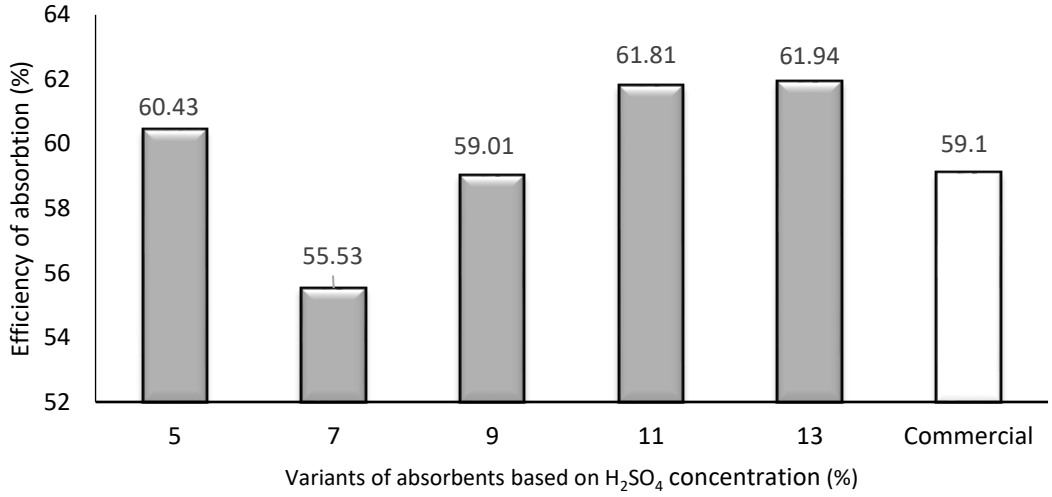

Figure 1: Bar charts representing comparison of estimated performance of activated absorbents in this study

Figure 2 illustrates the morphology of selected activated carbon derived from peanut shells, revealing a rough and irregular pore surface. The formation and enlargement of these pores resulted from the evaporation of degraded cellulose components. The activation process reduced hydrocarbon compounds, progressively clarifying the activated carbon's surface. The pore structure emerged from the evaporation and dissolution of non-carbon compounds in the raw material during the carbonisation process (pyrolysis), creating empty spaces known as pores. The images clearly demonstrate the distinct differences in pore structure before and after activation.

The acid-activated adsorbent derived from boiled peanut shells exhibited significant variations in pore diameter. Initially, the pore diameter of carbon activated with 7% H_2SO_4 ranged between 5 and 12.2 µm, which reduced to 1 to 4.5 µm after adsorption. Conversely, the pore sizes of carbon activated with 11% H_2SO_4 ranged from 2.28 to 8.45 µm initially and expanded to 5 to 17 µm post-adsorption. Notably, the pores in the 7% H_2SO_4-activated carbon were smaller after the adsorption step compared to their initial state. The lower residual Fe^{2+} ions in the well groundwater treated with 11% H_2SO_4-activated carbon suggest a higher capture efficiency (Agboola et al. 2023), indicated by the larger remaining pores compared to the 7% H_2SO_4-activated carbon.

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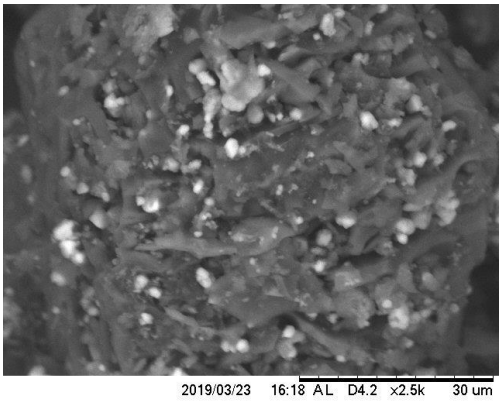
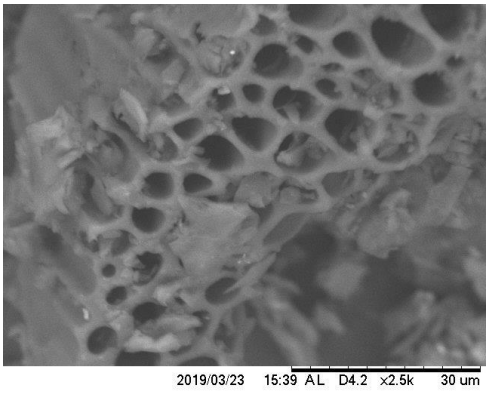


A



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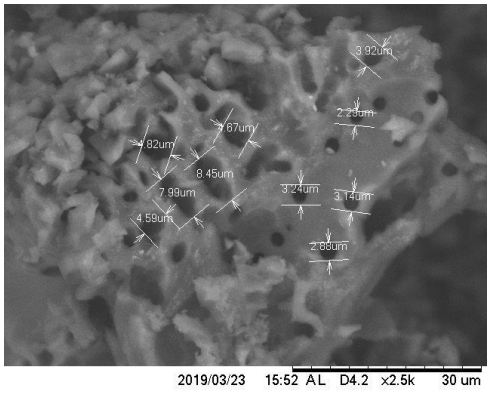

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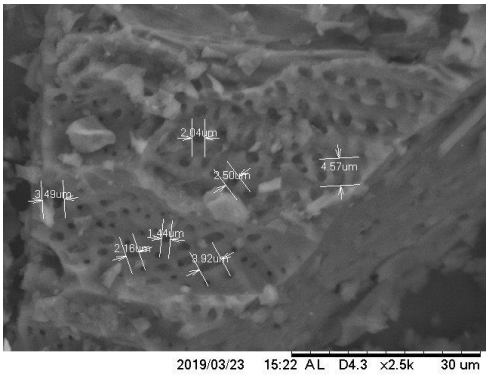

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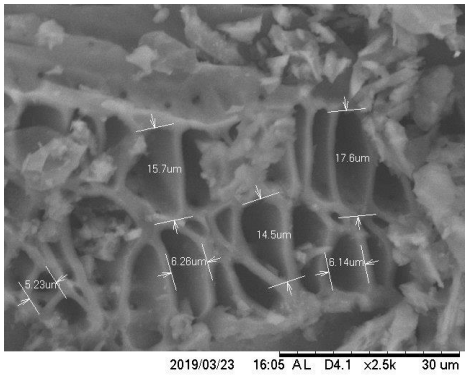

E

Figure 2: Captured images of the carbons by SEM on (A) native carbon and activated carbons with B) 7% H_2SO_4 and (c) 11% H_2SO_4 at pre-adsorption state, (D) 7% H_2SO_4 and (E) 11% H_2SO_4 at post-adsorption state, at the magnifications of 2500x

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Defined vibrations	ers (cm^{-1})				Interpretation of the shifting
	Native carbon	Activated carbon by H_2SO_4 5%	Activated carbon by H_2SO_4 7%	Activated carbon by H_2SO_4 11%	
O – H stretching	3431.36	3404.36	3400.50	3414.00	Decreased vibration due to protonation or molecular interactions
C – H stretching of alkane	2920.23	2914.44	2918.30	2912.51	Decreased vibration due to protonation or molecular interactions
C = C stretching of aromatic	1598.99	1595.13	1604.77*	1597.06	Decreased vibration due to protonation or molecular interactions (activated carbon by H_2SO_4 7% excluded)
C – H bending of alkene	856.39	852.54	831.32	845.47	Decreased vibration due to protonation or molecular interactions

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Peanut shells were utilised as adsorbents due to their high content of cellulose, lignin, and hemicellulose, which provide hydroxyl and carboxyl groups essential for binding with metal cations. These functional groups facilitated molecular interactions with metal ions, commonly referred to as adsorption. FTIR analysis confirmed the presence of these groups in the peanut shells. Upon activation, several absorption peaks shifted compared to their pre-activation states. Notably, the largest shift in the alcohol O-H stretching wave number occurred with the 7% H_2SO_4 activator, surpassing the shifts observed with 5% and 11% H_2SO_4. This reduction in absorption peak and vibration, attributed to hydrogen bonding interactions between hydroxyl groups and water, could diminish the adsorbent's capacity to capture Fe^{2+} ions (Mentari, Handika, and Maulina 2018).

The exceptional adsorption efficiency observed with the 11% H_2SO_4-activated carbon can be linked to lignin loss, as indicated by the shift to a lower wave number region. Detailed wave number shift data are provided in Table 2. The bioadsorbent derived from boiled peanut shell waste contains O–H, C=C, and C–O groups, which are inherently polar. Shifts in the wave number of the –OH functional group post-activation with H_2SO_4 were associated with protonation and molecular interactions with trapped ions, characterised by changed vibration (Nurhasni, Mar'af, and Hendrawati 2018; Wulan, Kusumastuti, and Prasetya 2022).

4. Conclusion

This study successfully determined the optimal H_2SO_4 concentration for activating charcoal derived from boiled peanut shells (*A. hypogaea* L.) for the removal of Fe^{2+} ions from well groundwater in Punge Jurong Village, Aceh Province, Indonesia. Among the tested concentrations (5%, 7%, 9%, 11%, and 13%), the 13% H_2SO_4 activator demonstrated the highest adsorption efficiency at 61.94%, outperforming both lower concentrations and commercial activated carbon. The analysis via SSA, SEM, and FTIR, coupled with statistical validation through ANOVA, revealed significant wave number shifts in O–H, C=C, and C–O regions, suggesting protonation effects due to acid activation or the presence of trapped ions. These findings highlight the potential of using agricultural waste, such as peanut shells, for effective water purification and contribute to sustainable waste management practices.

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