



Contents lists available at ScienceDirect

Environmental Technology & Innovation

journal homepage: www.elsevier.com/locate/eti

Mercury removal using modified activated carbon of peat soil and coal in simulated landfill leachate

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ARTICLE INFO

Article history:

Received 18 April 2021

Received in revised form 7 October 2021

Accepted 10 October 2021

Available online 18 October 2021

Keywords:

Mercury
Activated carbon
Peat soil
Coal
Adsorption

ABSTRACT

This study focuses on the production of activated carbon from peat soil and coal, and the use of CaO from clamshell byproducts as a pH buffer, to reduce mercury content in artificial landfill leachate. Activated carbon from coal and peat soil was characterized according to its water content, ash content, iodine sorption, methylene blue sorption, and by XRD, SEM, and FTIR analysis. Clamshell was characterized using XRF analysis. The results indicate that the equilibrium point for mercury reduction was reached after 100 min of agitation at 500 rpm at different pH levels. These results also suggest that mercury does not undergo precipitation at neutral or near alkaline pH. Mercury content was successfully reduced by 81% during the adsorption process. The adsorption capacities of activated carbon in coal and peat soil are 114 mg/g and 102 mg/g. The Langmuir isotherm model was used as it was most appropriate for mercury adsorption. This study shows that activated carbon from peat soil and coal can be utilized as a low-cost adsorbent for treating landfill leachate.

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1. Introduction

Many studies have been performed on the release of methylmercury into the environment, particularly in Asia. The latest scientific reports indicate that more than 33 regions across Asia have experienced a decrease in environmental quality due to mercury contamination. According to the European Environmental Agency (EEA), mercury has been contaminating more than 46,000 surface water bodies. EEA reported that the current mercury level in the oceans and atmosphere is about 200% and 500% above natural levels (European Environment Agency, 2018). In Indonesia, gold mining in the Talawaan watershed on North Sulawesi Island has resulted in mercury pollution (Li et al., 2009), and various other regions in Indonesia have also experienced very significant decreases in environmental quality a result of mercury contamination from illegal gold mines (Spiegel et al., 2018). This fact is not widely reported, however, because the affected regions are remote and prone to social conflict. Some studies have reported efforts to reduce mercury concentrations in

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polluted water by using activated bentonite (Naswir et al., 2020), while various other studies have employed coconut shells as the primary material for making activated carbon (Heidarinejad et al., 2020). However, the use of coconut shells as core materials for adsorbents has proven to be uneconomical. The market price of coconut shells is relatively high, and there is potential to improve local communities' economies by processing them into other products.

Carbon-rich materials such as peat soil and coal also have great potential for the remediation of soil layers contaminated with mercury. There are two procedures for producing activated carbon from these materials: physical activation and chemical activation (Bello et al., 2017). The materials are treated with activation agents (steam and carbon dioxide) at temperatures of 700–900 °C. During physical activation, the pores of the activated carbon material are formed. In physical activation, the reactor must be in a state without oxygen, so none of the material becomes ash. The impurities formed during the physical activation process are cleaned using a chemical agent during chemical activation, which uses chemical agents such as sodium hydroxide (NaOH), sodium carbonate (Na₂CO₃), zinc chloride (ZnCl₂), potassium hydroxide (KOH), magnesium chloride (MgCl₂), and phosphoric acid (H₃PO₄) (Bergna et al., 2020). Wajima and Sugawara (2011) modified coal using K₂S powder and burning the material in a reactor at 800–1000 °C for 30 min. HCl was used as the chemical agent for activation. Their study demonstrated that coal activated at 900 °C had better sorption at 25 °C.

Several studies have reported on the adsorbent properties of physically and chemically activated peat soil and coal. A Malaysian study by Rosli et al. (2017) suggests that adsorbents derived from peat can be used to successfully remove color and Fe in landfill liners. The combination of activated carbon and peat successfully reduced 75% of color at a ratio of 2:2, and the most effective combination for Fe removal was found to be activated carbon and peat at a ratio of 5:3. A lab-based study using activated carbon from peat soil has successfully reduced Pb and Cd concentrations in artificial solution (Marques et al., 2020). However, the utilization of coal as an adsorbent for landfill liners is rarely found in the literature. Several studies have reported coal to be an effective adsorbent for general wastewater. Most studies on mercury remediation have used coal fly ash (Ochedi et al., 2020). Although research on the utilization of coal for mercury removal is limited, coal has been reported as a potential adsorbent of metal components.

Peat soil and coal are both carbon-rich materials that can be used as alternative materials for creating activated carbon. Peat soil has a high carbon content and pores which can potentially be useful in an adsorbent, and it is widely available in Indonesia. Peat soil and coal are low-cost adsorbents, and more readily available in remote areas than other adsorbent materials such as zeolite, bentonite, and coconut shells (Fazal et al., 2021; Khadiran et al., 2015). Composite liners which combine clay and adsorptive materials are reported to be effective landfill leachate barriers which can prevent the contamination of soil and groundwater (Di Matteo et al., 2020). Studies on the use of low-cost activated carbon from peat soils and coal for treating landfill leachate are interesting and should be developed. Therefore, this research will holistically evaluate activated carbon produced from coal and peat soils, characterizing these materials and assessing their potential as adsorbents. Clamshell waste will also be evaluated as an alternative material for buffering the pH of the landfill leachate. This research could be a baseline study for the further development of low-cost adsorbent materials for removing pollutants from landfill leachate and other wastewater.

2. Materials and methods

2.1. Materials preparation

Coal and peat soil were extracted in Jambi Province, Indonesia. The coal was taken from the Sarolangun area and the peat soil from the West Tanjung Jabung area. The coal and peat soil samples were cleaned, then dried in the sun for 12 h. The coal and peat soil samples were crushed using a jaw crusher (5E-JCA) and sieved through a 100-mesh sieve. The samples were then heated at 500 °C for four hours using a furnace (Naberthem L9/12). The samples were activated using H₃PO₄, H₂SO₄, and 1 M ZnCl₂ for 24 h and washed using distilled water. The activated carbon was then put into a Memmert oven at a temperature of 110 °C and periodically weighed until there was no further weight reduction due to moisture loss. Clamshell was collected from Tanjung Jabung Barat, Jambi Province, Indonesia. The shell samples were cleaned and dried under the sun for 12 h. The shell samples were crushed and sieved using the same procedure as for the coal and peat soil. The sample was calcined at a temperature of 900 °C for 8 h. 200 mg/L Hg(II) solution was obtained by adding 20 mL of 1000 ppm Hg(II) solution to a 100 mL volumetric flask, diluting with distilled water to 100 mL, and mixing until the solution was homogeneous.

2.2. Adsorbent materials characterization

Moisture content was determined by drying the samples in an oven. For each sample, one gram of material was carefully weighed out and placed in a known-weight aluminum plate, then dried in the oven at 105 °C for 3 h until constant weight was reached. The samples were then cooled in a desiccator for 15 min before weighing. Eq. (1) was used to determine the water content of the adsorbent, where C_0 is the initial weight (g), C_e is the final weight (g), and m is the mass of adsorbent (g).

$$\text{Water content (\%)} = \frac{C_0 - C_e}{m} \times 100\% \quad (1)$$

The ash content of the activated carbon was measured in order to determine the metal oxide content of the activated carbon. Indonesian National Standard 06 – 3730 – 1995 states that the ash content must be below 10%. A gravimetric method was used to test ash content by measuring sample weight before and after burning. Total ash content was determined by carefully weighing 2 grams of material into an ash dish, then drying it in an oven at 105 °C for 3 h until it reached a constant weight. The activated carbon was then burned again using a furnace at a temperature of 600 °C for 1 h. The ash obtained was cooled and weighed. The ash content (%) was calculated using Eq. (2), where C_o is the initial weight (g) and C_e is the final weight (g).

$$\text{Ash content (\%)} = \frac{C_e}{C_o} \times 100\% \quad (2)$$

The adsorption process of activated carbon was tested using an iodine solution (Bestani et al., 2008). The activated carbon was placed to an erlenmeyer flask, then a 25 mL pipette of iodine solution was added. The erlenmeyer was closed with a lid moistened with potassium iodide (KI) and kept in a dark place. After 2 h, 10 mL of 20% KI solution and 150 mL of distilled water were added to the flask while it was in the dark, then titrated with 0.4 N sodium thiosulfate solution. The iodine sorption capacity was calculated using Eq. (3), where V_1 is the initial volume of iodine (L), N_1 is the normality of iodine (N), V_2 is the volume of sodium thiosulfate used (L), N_2 is the normality of sodium thiosulfate (N), 126.9 is the weight equivalent of iodine, and F_p is the dilution factor.

$$\text{Iodine sorption} = \frac{((V_1N_1) - (V_2N_2)) \times 126.9 \times F_p}{\text{carbonmass}} \quad (3)$$

Methylene blue was also used to test adsorption. This test used an ultraviolet-visible absorption spectroscopy (UV-VIS) instrument with a wavelength of 560.50 nm. Samples of 1 g of activated carbon material were placed in an erlenmeyer flask, to which 50 mL of methylene blue solution was then added. The flask was then shaken for 30 min. 5 mL of filtrate was pipetted into a 100 mL volumetric flask and diluted with distilled water until the volume of the solution reached 100 mL.

$$\text{Sorption efficiency} = \frac{V(C_o - C_e)}{W} \quad (4)$$

Sorption efficiency was measured with Eq. (4), where V is the volume of solution, C_o is the initial concentration of solution, C_e is the final concentration of the solution, and W is the weight of activated carbon. Surface area can be determined using methylene blue adsorption test data, which is formulated as follows (see Eq. (5)).

$$\text{Surface area (S)} = \frac{X_m N a}{M} \quad (5)$$

Where S is surface area (m^2/mg), X_m is the amount of methylene blue adsorbed by 1 g of carbon, N is the Avogadro value (6.02×10^{23}), a is the particle size of methylene blue (197×10^{-20}), and M is the molecular weight of methylene blue (320.5 g/mol) (Okeola et al., 2012).

A scanning electron microscope (SEM) instrument was used to detect changes in the surface morphologies of each material. Results from the analysis of SEM photos were used to assess the ability of the material to adsorb the pollutants present in landfill leachate. The larger the material's pores, the better the material's ability to reduce pollution in landfill leachate. An X-ray diffraction (XRD) instrument was used to determine the size and crystal structure of the activated carbon material. XRD is commonly used as a destructive method for the analysis of carbon-based materials. A Fourier transform infrared (FTIR) instrument was used to identify compounds, detect functional groups, and analyze the synthesized material.

2.3. Clamshell characterization

An X-ray fluorescence (XRF) instrument was used to analyze the elemental and oxide content of the shells which were utilized for pH buffering. Crystal diameter was determined based on the following Debye-Scherrer equation, where D is crystal size, K is Scherrer constant (0.89), λ is the X-ray wavelength used (1.54056 \AA), β is full width at half maximum (FWHM), and θ is the Bragg diffraction angle (see Eq. (6)) (Hargreaves, 2016).

$$D = \frac{K}{\cos \theta} \quad (6)$$

The FWHM data were calculated based on the highest peak that appeared on the diffractogram. The FWHM value is inversely proportional to crystal diameter.

2.4. Batch adsorption test

A Hg(II) solution with 200 mg/L concentration and 100 mL volume was added to 0.5 mg of peat or coal adsorbent. The sample was then agitated at 500 rpm with time variations of 0-500 min. Adsorption capacity was obtained using Eq. (7),

where C_0 is the initial concentration, C_e is the final concentration in the supernatant after centrifugation, m is the mass of adsorbent, and v is the volume of the suspension (Serunting et al., 2018).

$$Q_e = \frac{C_0 - C_e}{C_e} \times \frac{v}{m} \quad (7)$$

2.5. Isotherm model

Adsorption isotherms can be used to study the mechanism of adsorption. The adsorption isotherm was obtained by conducting experiments on different concentrations (10–500 mg/L) of Hg(II) combined with 0.5 g of coal or peat adsorbent in a 50 mL solution agitated at 150 rpm. This analysis was carried out to calculate the Freundlich and Langmuir isotherm models, which are appropriate for solid–liquid phase adsorption (Serunting et al., 2018). Eq. (8) shows the Freundlich isotherm model.

$$q_e = K.C_e \cdot \frac{1}{n} \quad (8)$$

While the Langmuir isotherm model is shown in Eq. (9).

$$q_e = \frac{(q_{max} \cdot K \cdot C_e)}{(1 + K \cdot C_e)} \quad (9)$$

Relative error analysis was obtained using the average relative error (ARE) and chi-square equations, which are shown in Eqs. (10) and (11).

$$ARE = \frac{100}{N} \sum \frac{q_e - q_{e'm}}{q_e} \quad (10)$$

$$X^2 = \sum \frac{(q_e - q_{e'm})^2}{q_{e'm}} \quad (11)$$

Where q_e , m is the value of q_e obtained from the isotherm model.

3. Results and discussion

3.1. Adsorbent characteristics

The characteristics of activated carbon materials from coal and peat soil are quite similar. The water content of each only differs by 0.2%. However, the effect of water content on the adsorption ability of the material is very high. Material with low water content is a promising adsorbent, while the adsorbent pores of high-water content material are filled with water molecules. When the water content of an adsorbent is very low, the adsorption process is likely to be more successful because more pores can be filled with Hg(II). Materials with water contents of 4% are much better adsorbents than materials with water contents of the maximum permitted by Indonesian National Standard 06 - 3730 - 1995, which states that maximum moisture content for an adsorbent is 15%. In this study, coal and peat adsorbents were found to have water contents of 4.1% and 4.3%, respectively. This successful result is caused by the careful preparation and good source of adsorbent. Physical preparation is a crucial aspect of creating lower water content.

Ash content is influenced by the base material for the adsorbent and the mineral salts it forms during the charring process. The ash content levels measured in this study were lower than those of a similar study on another material (adsorbent derived from *Moringa oliefera* leaf) which measured an ash content of 12.71% (Bello et al., 2017). This study has successfully produced a low-cost adsorbent with a low ash content. A previous study reported that the ash contents of *Sphagna*, *Acutifolia*, *Cuspidata* and *Carex* peats were around 1.2% to 6% (Ringqvist et al., 2002). This result is lower than that of a previous study which reported ash content of 10.10% in an adsorbent derived from bituminous coal (Cuhadaroglu and Uygun, 2008).

The adsorption power of methylene blue is representative of the adsorption capacity of coal and peat soil. The results in this study confirm that methylene blue has higher sorption than other materials, for instance polyaniline hydrogel. A previous study reported that polyaniline hydrogel successfully reduces the methylene blue is only 23 mg/g at 100 mg of adsorbent and 50 mL of methylene blue (Yan et al., 2015). The adsorption power of the iodine adsorbent value also influences adsorption ability. The greater the iodine value, the greater its ability to adsorb the adsorbate. The adsorption iodine value also affects surface area. This study has successfully created an adsorbent with high iodine adsorption value in a solution. A previous study reported an iodine adsorption value of 144 mg/g in a solution using other methods and materials (Li et al., 2020). The greater the adsorbent surface area, the more Hg(II) is able to enter the adsorbent's pores. The surface areas of the peat soil and coal considered in this study are greater than the surface area of adsorbents derived from sludge (28 m²/g), dust (13 m²/g), and slag (4 m²/g) from industrial waste (Bhatnagar and Jain, 2005). The results show that there is no significant difference in surface area between the peat soil and coal samples.

In Fig. 1, all peaks can be identified according to the JCPDS card number data 25-0284 for graphite, which confirms that the synthesized material is graphite-based activated carbon with a plane orientation of 2 theta 26.69° (002); 42.48 (100);

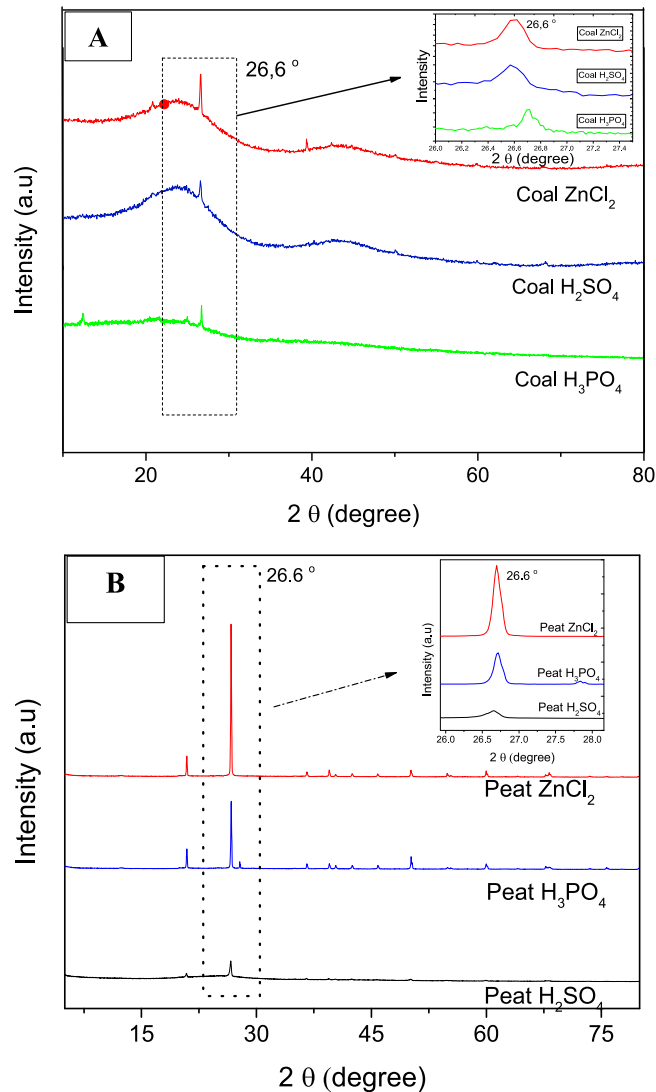


Fig. 1. Diffractogram of activated carbon from coal (a) and peat (b).

45.8 (101); 50.17 (102); 54.9 (004); 59.9 (103) (Sivachidambaram et al., 2017). When ZnCl₂ was used for active solution, the synthesized material had a large peak at 2θ 26.69°. This indicates that the activated carbon that was synthesized had increased levels of graphite content. ZnCl₂ was found to be the most effective chemical used in the activated charcoal synthesis process in this study.

Fig. 2(a) shows the surface morphologies of the non-activated coal sample. At a magnification of 1000x, analysis results indicate that the inactivated coal's particle size was 26.9 μm. The results of characterization using SEM instruments reveal that, even prior to activation, the morphology of the coal sample still had large pores and it is therefore potential adsorbent material. Fig. 2(b), (c), and (d) show the SEM characterization results for coal materials activated using H₃PO₄, H₂SO₄, and ZnCl₂. The results of SEM characterization demonstrate that materials activated using H₃PO₄ and H₂SO₄ had more open pores. SEM photos of the coal material activated using ZnCl₂ do not indicate much change after activation. The particle size of the activated coal samples was 53.7 μm for coal activated using H₃PO₄, 89.5 μm using H₂SO₄, and 269 μm using ZnCl₂. Particle size affects the adsorption capacity: the smaller the particle size, the greater the adsorbent's surface area; and the greater the surface area, the more adsorbent ability the material has.

The structural morphologies of non-activated peat soil are shown in Fig. 3(a). Examination at 1000x magnification shows that the peat soil contains large pores, making it an appropriate material for use as an adsorbent for landfill leachate. The particle size of non-activated peat soil ranges from 26.9 to 53.7, with an energy of 15 kV. The morphology of non-activated peat soil is slightly different from that of non-activated coal. The morphology of non-activated coal has significant and planar pores, while peat soil does not show open pores and has a morphological structure that tends

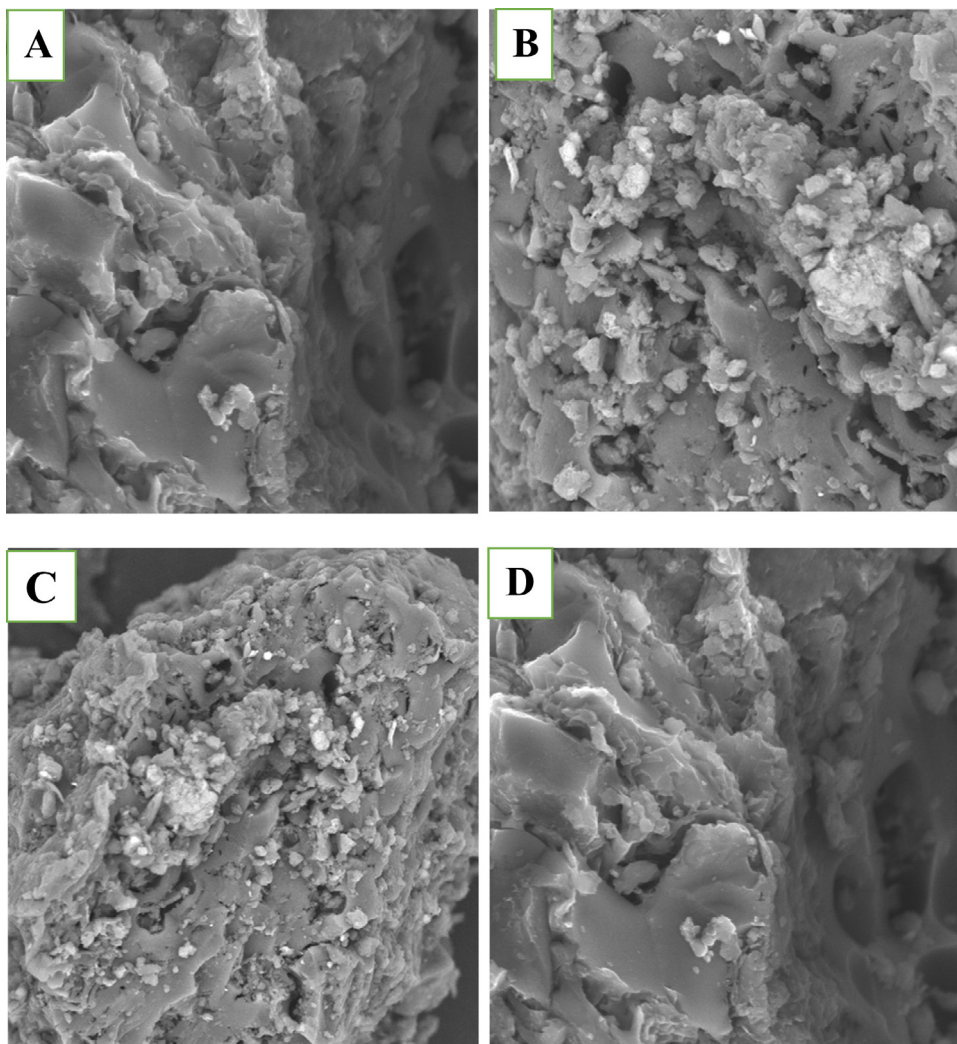


Fig. 2. Surface morphologies of coal before activation (a) and after activation using H_3PO_4 (b), H_2SO_4 (c), and ZnCl_2 (d).

to be rough. Pore characterization and analysis of the morphology of non-activated coal and peat soil indicate that the adsorption ability of non-activated coal is better than that of non-activated peat soil. This is because the pores in the coal sample are more open, and are thus able to adsorb more pollutants from landfill leachate.

Activation using acid and salt solutions removes any inhibitor compounds from the pores in a material, and therefore increases the material's adsorption capacity. The results of SEM characterization of peat soil samples activated using H_2SO_4 , H_3PO_4 , and ZnCl_2 are shown in Fig. 3(b), (c), and (d), respectively. Analysis of the characterization of the morphological structure of the ZnCl_2 -activated peat soil samples indicates that there was no significant change in surface morphology following activation. The results of the characterization of ZnCl_2 -activated peat soil show less change after activation than was apparent in H_3PO_4 - and H_2SO_4 -activated peat soils. These results also confirm that activation using acidic compounds produces better adsorbents than activation using salts. The H_3PO_4 and H_2SO_4 activation results for peat soil are not significantly different from each other, but comparison with the results of characterization in the coal samples demonstrates that the peat soil samples had a surface structure with more open pores and more waves. This confirms that peat soil is potentially a more useful adsorbent material than coal. It must be noted that the size of the pores formed is also influenced by the temperature at the time of physical activation (Saifuddin et al., 2020)

Fig. 4 shows a broad spectrum at wave number 3448 cm^{-1} , which is the vibration of the hydroxyl (O-H) functional group of water molecules or of -OH radicals on the surface of activated carbon after activation. A peak at wave number $2,924.09\text{ cm}^{-1}$ represents the stretching vibration of the functional group C-H; one at $2,368.59\text{ cm}^{-1}$ represents the vibration of $\text{O}=\text{C}=\text{O}$, possibly from carbon dioxide in the measurement process; while a peak at $1,627.92\text{ cm}^{-1}$ represents the stretching vibration of $\text{C}=\text{C}$. In the carbon which was activated using H_3PO_4 , the spectrum that appears is not much different. However, a peak appears at $1,442.75\text{ cm}^{-1}$, indicating a vibration of $\text{S}=\text{O}$ from the sulfate.

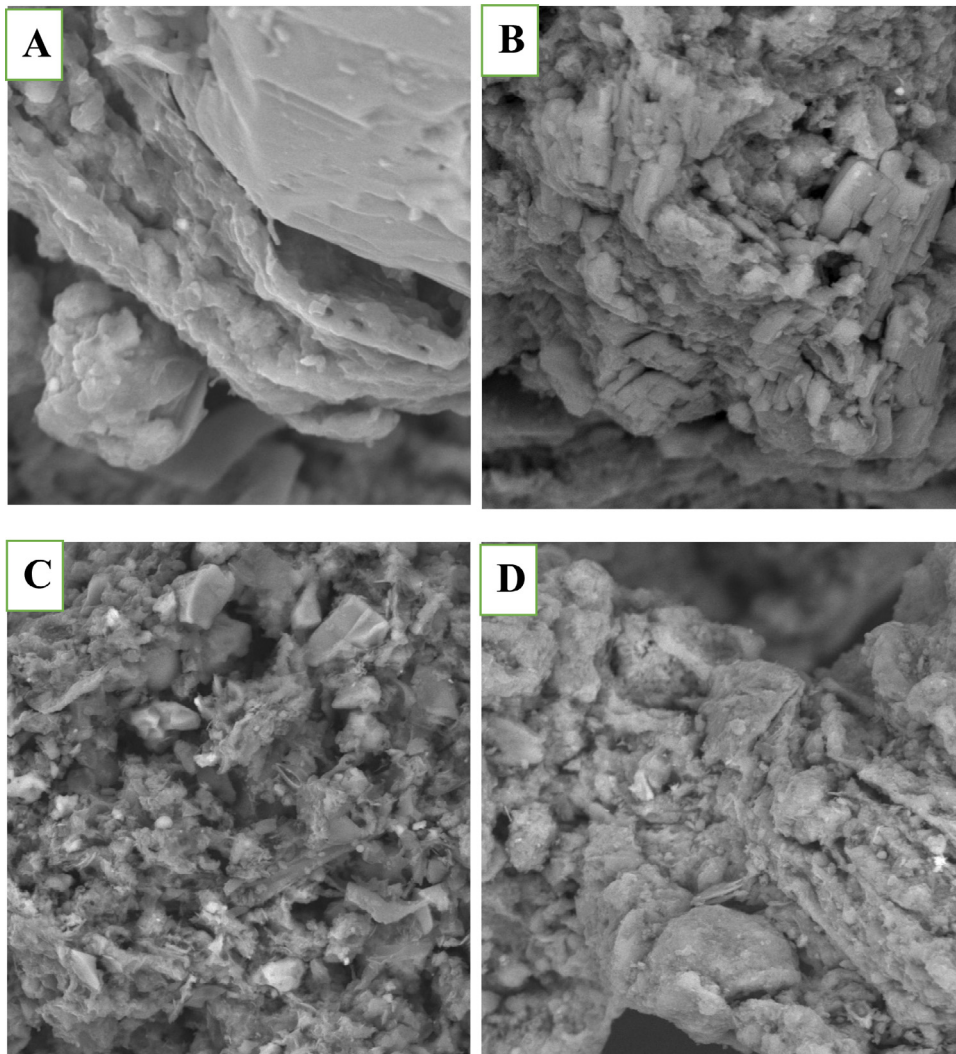


Fig. 3. Characterization of peat soil (a) before activation, and after activation with (b) H_3PO_4 , (c) H_2SO_4 , and (d) ZnCl_2 .

The FTIR spectrum for peat soil gives typical spectrum peaks as follows: at $3,448.72\text{ cm}^{-1}$, a broad peak indicates the hydroxyl functional group (O–H); at $2,924.09\text{ cm}^{-1}$ a peak indicates the stretching vibration of C–H aliphatic hydrocarbons; and at $1,635.64\text{ cm}^{-1}$ a peak indicates the stretching vibration of the C=O carboxylic acid double bond. The peaks at $1,080.14\text{ cm}^{-1}$ and $1,033.85\text{ cm}^{-1}$ represent the stretching vibrations of the C–O polysaccharides. Moreover, 779.24 cm^{-1} represents the stretching vibration of the hydrogen OH bond in the carboxylate group.

3.2. Clamshell characterization

XRF instruments were used to obtain the main composition of oxides and elements in the shell material. This was intended to obtain high levels of CaO, which could then be used to increase the pH to near neutral. At a temperature of $800\text{ }^\circ\text{C}$ for two hours, the pyrolysis process produces CaO from the CaCO_3 in clamshell waste. Clamshell waste has a higher CaO level than other waste materials such as eggshells. Previous research has demonstrated that eggshell has a CaO level of 52.75%, which can be increased to 86.93% in the nano-CaO phase after synthesis (Habte et al., 2019). The chemical process that occurs in this treatment is shown in Eq. (12).



High levels of CaO from the clamshells (97%) can increase the pH of acidic leachate by forming $\text{Ca}(\text{OH})_{2(\text{aq})}$. The complete process that occurs after adding coconut shell to acidic leachate is shown in Eqs. (13)–(16).

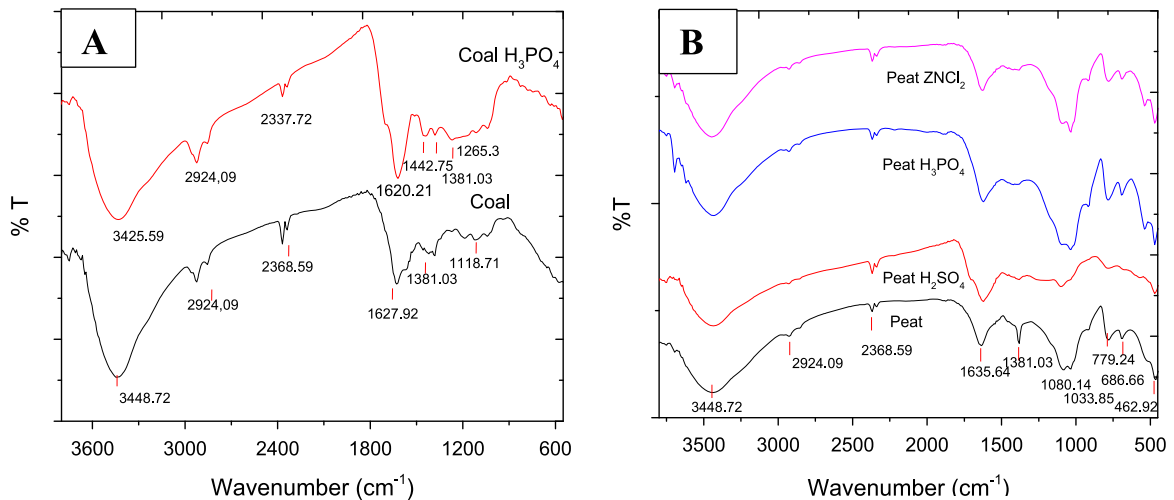


Fig. 4. FTIR spectrum of coal and activated coal-activated carbon using H_3PO_4 solution (a) and peat soil-activated carbon which was activated using a solution of H_2SO_4 , H_3PO_4 , and ZnCl_2 (b).



The addition of clamshell will not only increase the pH of the leachate in the landfill, but this process will also reduce the metal content of the leachate. This decrease in metal content is caused by a precipitation process, in which some metals will undergo precipitation after the water's pH becomes neutral. A recent study has shown that increasing the pH of the water can result in a significant reduction in Fe and Mn levels (Seo et al., 2017). Fe and Mn are metals that are very dangerous to health and can pollute the soil if it is directly contaminated with leachate. If this happens continuously, the pollution will harm the soil biota and groundwater. The test results show that the greater the weight of coconut shell added, the greater the increase in pH.

3.3. Batch adsorption test results

Table 1 shows the effect of agitation time on Hg(II) adsorption by coal and peat at different pH levels. This study confirms that agitation time affects the rate of Hg(II) reduction. The longer the agitation time, the more Hg(II) will be adsorbed into the adsorbent. The results of this study show that each adsorbent reaches the equilibrium point at the 100th minute. The equilibrium point in the test is reached when the pores of the activated carbon material are completely filled with Hg(II) ions. Agitation at a speed of 500 rpm was carried out to speed up the adsorption process. The faster Hg(II) compounds collide with the adsorbent, the faster the adsorption process is. The test results also show that there is no significant difference between the abilities of each material to reduce the Hg(II) content in the solution.

These results also confirm that both peat soil and coal can potentially be used to reduce the mercury content in leachate produced in landfill. Leachate contains various types of heavy metals and has low pH. These results demonstrate that modified coal and peat soil materials can reduce leachate pollutants. The pH variation used in this study was intended to obtain the most effective pH conditions, but the test results show that pH conditions do not significantly affect the decrease in Hg. This result also confirms that leachate can be controlled at neutral pH conditions before adsorption is carried out. In this research, the maximum adsorption of mercury occurred by the 100th minute. The adsorption process is thus faster than it was in a previous study which used granular activated carbon in $\text{Hg}(\text{CN})_2$ solution (Aliprandini et al., 2020).

The results indicate that the maximum adsorption capacity of coal and peat soil adsorbents is 82%, after an agitation process lasting for 100 min. An increase in removal percentage was seen with increased contact time between the adsorbent and artificial leachate. The test results show that contact time significantly affects Hg(II) adsorption in peat soil and coal adsorbents. The adsorbents' ability to adsorb Hg(II) seems to continue to increase from 1 min to 100 min. This significant increase occurs because the adsorbents' pores can still be filled with Hg(II) until the 100th minute. After the 100th minute, it appears that the adsorbents' ability to adsorb Hg(II) remains constant. An increase of 1% occurs between 100 min and 500 min. This shows that the maximum adsorption capacity of the adsorbents is limited to the

Table 1
Effect of pH on mercury removal.

Time (min)	Coal (mg/L)			Peat (mg/L)		
	pH 5	pH 7	pH 8	pH 5	pH 7	pH 8
0	200	200	200	200	200	200
10	180	170	179	180	175	178
20	150	149	147	158	149	150
30	130	128	123	140	138	135
50	115	113	114	118	125	123
70	75	65	71	80	69	75
100	40	39	41	45	50	41
150	39	39	38	40	43	38
200	39	39	38	37	39	38
300	39	38	38	37	38	38
400	38	38	37	35	36	37
500	38	38	37	35	36	37

100th minute. There is no process to release Hg(II) from the visible adsorbent pores. This result proves that adsorbents made from peat soil and coal have a stable adsorption ability. Another study has reported the higher removal efficacy of other materials, such as fuller earth powder. However, more of that adsorbent (9.5 g) was required to adsorb 90% mercury in a solution (Oubagaranadin et al., 2007).

The results also demonstrate that Hg(II) does not precipitate at neutral pH, due to the specific characteristics of Hg(II) as compared to other pollutants. There is an increase in adsorption ability when the Hg(II) solution is close to neutral pH (Kadirvelu et al., 2004). Among the pollutants in leachate which are known to precipitate at neutral pH are several heavy metals such as Zn, Co, Fe, Ni, and Mn (Lewis, 2010). The results of this study also show that the removal of Hg(II) contamination in leachate cannot be performed simply by neutralizing the pH of the water in the leachate. Although there is a slight difference in adsorption ability when the leachate is at neutral pH (7) and when it is closer to alkaline (8), the Hg(II) reduction percentage of leachate at neutral pH is higher than it is in acidic conditions (pH 5). In acidic conditions, the parameters of water pollutant mobilization are very high, so it is more challenging to adsorb pollutants in these conditions. These results are better than those of an adsorbent produced using iron oxide nanoparticles, which could only reduce Hg(II) by 70% (Vélez et al., 2016). Another study has reported that other materials, such as gold (Au) nanoparticles, could only reduce Hg(Cl₂) by 54.87% (Kamarudin and Mohamad, 2010). Moreover, peat soil and coal adsorbents are easier to produce and use, because of their abundance.

3.4. Sorption capacity

The analysis results show that the adsorption capacity of the materials used in this study reached 141 mg/g. These results are better than those obtained with some commonly used materials, such as activated carbon produced from agricultural waste (maximum adsorption capacity is 25.88 mg/g) (Rao et al., 2009). The adsorption capacity is reached when all the material's pores have been filled by Hg(II). The isotherm model analysis results indicate that the adsorption pattern that occurs is monolayer (following the Langmuir isotherm model). This explains that at maximum absorption Hg(II) in the adsorbent only adheres to one adsorbent layer. Maximum adsorption capacity was reached when the adsorbent and leachate (artificial solution of Hg(II)) were agitated for 200 min at a speed of 500 rpm. The agitation process was carried out to accelerate the collision rate between the adsorbent and the Hg(II). The faster the collision rate, the faster the rate at which the adsorption process occurs. The equilibrium phase, which was reached at the 200th minute, did not increase even when the agitation process was continued for more than 500 min. This is because all the adsorbent pores were completely filled with Hg(II). A different phenomenon might occur if the isotherm model obtained in this study was the Freundlich model, where adsorption occurs in a multilayer. If this condition occurred, there would be a possibility that adsorption would increase despite reaching the equilibrium point at the 200th minute. This condition would occur because Hg(II) could still be adsorbed in other layers of the adsorbent.

The bond occurs between the adsorbate molecule and the surface of the adsorbent. This is a result of both physical sorption and chemisorption. Data on adsorption capacity and the concentration of adsorbent residue in the solution were used in determining the isotherm. The Langmuir adsorption isotherm model assumes that maximum adsorption capacity occurs due to a single layer (monolayer) of adsorbate on the adsorbent surface, and all parts of the surface are homogeneous because each part of the surface can only adsorb one adsorbate molecule. In contrast, the Freundlich isotherm model assumes that there is more than one layer (multilayer) and the surface is heterogeneous, with differences in binding energy at each part of the surface during the adsorption process that takes place. The linearity value (R^2) of the Langmuir isotherm model approaches 1 with the linear line equation, namely $y = 0.0283x + 1.1271$ with $R^2 = 0.9949$. In addition to calculating the linearity, it is necessary to calculate the average relative error as another criterion to determine which isotherm model is most appropriate for this adsorption process. This method attempts to make corrections to the data obtained. The methods used to obtain a correction for linearity were ARE and chi-square. The ARE and chi-square results show that the Langmuir isotherm model has a smaller relative error value than the Freundlich isotherm model.

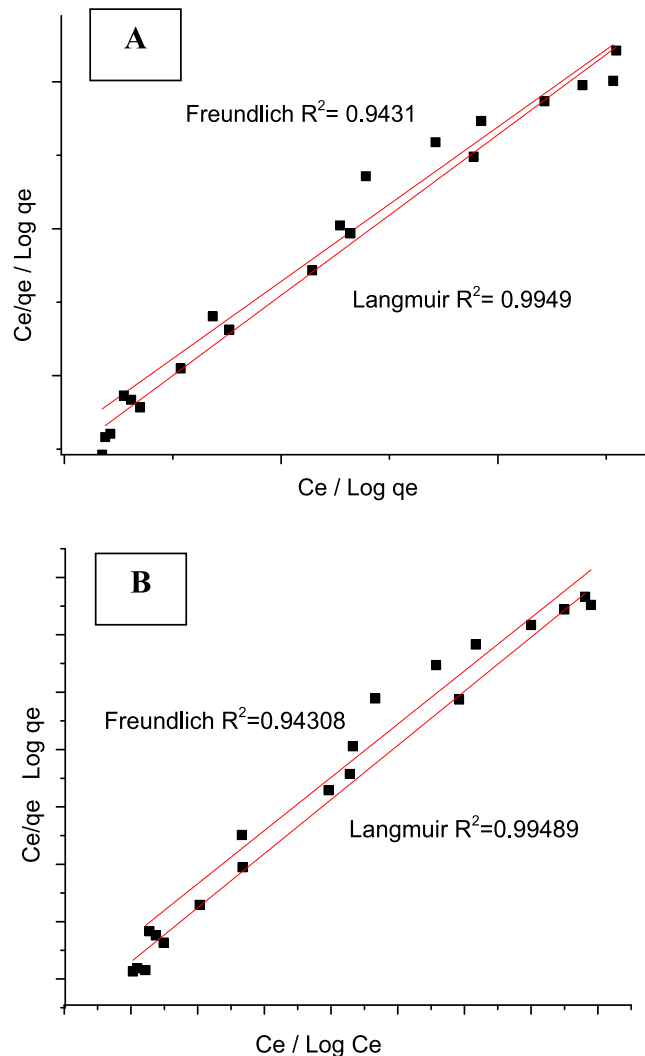


Fig. 5. Isotherm models of coal (a) and peat (b).

This indicates that the data obtained in this study are valid. These results confirm that the adsorption pattern of the coal adsorbent follows the Langmuir isotherm model (see Fig. 5(b)). The Langmuir model assumes that maximum adsorption capacity occurs due to the presence of a single layer (monolayer) of adsorbate on the adsorbent surface, and that all parts of the surface are homogeneous because each part of the surface can only adsorb one adsorbate molecule.

The Langmuir isotherm model is most suitable for Hg(II) adsorption by peat soil (see Fig. 5(b)). These results also confirm that the two Hg(II) adsorption phenomena occur in a monolayer. Based on the results of several previous studies, the adsorption that occurs in carbon materials almost always occurs in Langmuir isotherms. This is because the carbon material is amorphous. As a result, the adsorption pattern is not as good as that of materials that have a crystalline crystal structure. The Langmuir isotherm model used in this study is taken to be valid because the ARE and chi-square values are relatively minor compared to the ARE and chi-square values of the Freundlich isotherm model.

4. Conclusion

This research succeeded in producing an adsorbent material which can reduce mercury content at different pH conditions. The specifications for the activated carbon produced follow the standards set by the Government of the Republic of Indonesia for ash content, water content, methylene blue sorption, iodine number and surface area. The adsorbent material produced showed better characteristics than other materials found in previous studies. The results of XRD characterization show that the synthesized material is graphite-based activated carbon. The results of FTIR characterization show $-\text{OH}$ radicals on the surface of the activated carbon. There is a stretch vibration of the functional

group C–H, which is possibly from carbon dioxide in the measurement process. XRF characterization demonstrates that clamshell is 97% CaO in composition. This high concentration of CaO was successfully transformed into Ca(OH)₂ in order to increase the pH of leachate. This study also demonstrates that the adsorbents produced were able to reduce mercury content by up to 81% after 100 min of agitation. The Langmuir isotherm model was found to be suitable. This model assumes that maximum adsorption capacity occurs due to a single layer (monolayer) of adsorbate on the adsorbent surface. All parts of the surface are homogeneous, as each part of the surface can only adsorb one adsorbate molecule. This study also reports that the best adsorbent material is activated peat soil in acid conditions.

CRediT authorship contribution statement

Mochammad Arief Budihardjo: Conceptualization, Supervision, Writing – review & editing, Validation. **Yudha Gusti Wibowo:** Investigation, Formal analysis, Visualization, Data curation. **Bimastyaji Surya Ramadan:** Writing – original draft, Resources, Software, Project administration. **Muhamad Allan Serunting:** Formal analysis, Resources, Software, Data curation. **Eflita Yohana:** Formal analysis, Visualization. **Syafrudin:** Writing – original draft, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This research was funded by SAPBN Universitas Diponegoro 2021 Number 329-119/UN7.6.1/PP/2021. The authors would like to acknowledge the blind reviewers and editors who improved the scientific quality of this manuscripts.

Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.eti.2021.102022>.

References

- Aliprandini, P., Veiga, M.M., Marshall, B.G., Scarazzato, T., Espinosa, D.C.R., 2020. Investigation of mercury cyanide adsorption from synthetic wastewater aqueous solution on granular activated carbon. *J. Water Process Eng.* 34, 101154. <http://dx.doi.org/10.1016/j.jwpe.2020.101154>.
- Bello, O.S., Adegoke, K.A., Akinyunni, O.O., 2017. Preparation and characterization of a novel adsorbent from Moringa oleifera leaf. *Appl. Water Sci.* 7 (3), 1295–1305. <http://dx.doi.org/10.1007/s13201-015-0345-4>.
- Bergna, D., Hu, T., Prokkola, H., Romar, H., Lassi, U., 2020. Effect of some process parameters on the main properties of activated carbon produced from peat in a lab-scale process. *Waste Biomass Valoriz.* 11 (6), 2837–2848. <http://dx.doi.org/10.1007/s12649-019-00584-2>.
- Bestani, B., Benderdouche, N., Benstaali, B., Belhakem, M., Addou, A., et al., 2008. Methylene blue and iodine adsorption onto an activated desert plant. *Bioresour. Technol.* 99 (17), 8441–8444. <http://dx.doi.org/10.1016/j.biortech.2008.02.053>.
- Bhatnagar, A., Jain, A.K., 2005. A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water. *J. Colloid Interface Sci.* 281 (1), 49–55. <http://dx.doi.org/10.1016/j.jcis.2004.08.076>.
- Cuhadaroglu, D., Uygun, O.A., 2008. Production and characterization of activated carbon from bituminous coal by chemical activation. *Afr. J. Biotechnol.* 7 (20), 3703–3710.
- Di Matteo, L., Bulletti, L., Capecci, E., Viola, A. La, Piccinino, D., Piscopo, V., 2020. Perspectives of using lignin as additive to improve the permeability of in-situ soils for barrier materials in landfills. *Sustainability* 12 (12), <http://dx.doi.org/10.3390/su12125197>.
- European Environment Agency, 2018. Mercury pollution remains a problem in Europe and globally. Retrieved from <https://www.eea.europa.eu/highlights/mercury-pollution-remains-a-problem>. (Accessed 01 October 2021).
- Fazal, T., Faisal, A., Mushtaq, A., Hafeez, A., Javed, F., Din, A.A., Rashid, N., Aslam, M., Rehman, M.S.U., Rehman, F., et al., 2021. Macroalgae and coal-based biochar as a sustainable bioresource reuse for treatment of textile wastewater. *Biomass Conv. Bioref.* 11, 1491–1506. <http://dx.doi.org/10.1007/s13399-019-00555-6>.
- Habte, L., Shiferaw, N., Mulatu, D., Thenepalli, T., 2019. Synthesis of nano-calcium oxide from waste eggshell by sol-gel method. *Sustainability* 11 (11), 1–10.
- Hargreaves, J.S.J., 2016. Some considerations related to the use of the scherrer equation in powder X-ray diffraction as applied to heterogeneous catalysts. *Catal. Struct. React.* 2 (1–4), 33–37. <http://dx.doi.org/10.1080/2055074X.2016.1252548>.
- Heidarinejad, Z., Dehghani, M.H., Heidari, M., Javedan, G., Ali, I., Sillanpää, M., 2020. Methods for preparation and activation of activated carbon: a review. *Environ. Chem. Lett.* 18, 393–415. <http://dx.doi.org/10.1007/s10311-019-00955-0>.
- Kadirvelu, K., Kavipriya, M., Karthika, C., Vennilamani, N., Pattabhi, S., 2004. Mercury (II) adsorption by activated carbon made from sago waste. *Carbon* 42 (4), 745–752. <http://dx.doi.org/10.1016/j.carbon.2003.12.089>.
- Kamarudin, K.S.N., Mohamad, M.F., 2010. Synthesis of gold (Au) nanoparticles for mercury adsorption. *Am. J. Appl. Sci.* 7 (6), 835–839. <http://dx.doi.org/10.3844/ajassp.2010.835.839>.
- Khadiran, T., Hussein, M.Z., Zainal, Z., Rusli, R., et al., 2015. Activated carbon derived from peat soil as a framework for the preparation of shape-stabilized phase change material. *Energy* 82, 468–478. <http://dx.doi.org/10.1016/j.energy.2015.01.057>.
- Lewis, A.E., 2010. Review of metal sulphide precipitation. *Hydrometallurgy* 104 (2), 222–234. <http://dx.doi.org/10.1016/j.hydromet.2010.06.010>.
- Li, P., Feng, X.B., Qiu, G.L., Shang, L.H., Li, Z.G., 2009. Mercury pollution in Asia: A review of the contaminated sites. *J. Hard Mater.* 168 (2–3), 591–601. <http://dx.doi.org/10.1016/j.jhazmat.2009.03.031>.
- Li, M., Yuan, G., Zeng, Y., Yang, Y., Liao, J., Yang, J., Liu, N., 2020. Flexible surface-supported MOF membrane via a convenient approach for efficient iodine adsorption. *J. Radioanal. Nucl. Chem.* 324 (3), 1167–1177. <http://dx.doi.org/10.1007/s10967-020-07135-3>.

- Marques, J.P., Rodrigues, V.G.S., Raimondi, I.M., Lima, J.Z., 2020. Increase in Pb and Cd adsorption by the application of peat in a tropical soil. *Water Air Soil Pollut.* 231 (3), <http://dx.doi.org/10.1007/s11270-020-04507-z>.
- Naswir, M., Natalia, D., Arita, S., Wibowo, Y.G., 2020. Adsorption of mercury using different types of activated bentonite: a study of sorption, kinetics, and isotherm models. *J. Rekayasa Kimia Dan Lingkungan (J. Chem. Eng. Environ.)* 15 (2), 123–131.
- Ochedi, F.O., Liu, Y., Hussain, A., 2020. A review on coal fly ash-based adsorbents for mercury and arsenic removal. *J. Cleaner Prod.* 267, 122143. <http://dx.doi.org/10.1016/j.jclepro.2020.122143>.
- Okeola, O.F., Odebunmi, E.O., Ameen, O.M., et al., 2012. Comparison of sorption capacity and surface area of activated carbon prepared from jatropha curcas fruit pericarp and seed coat. *Bull. Chem. Soc. Ethiop.* 26 (2), 171–180. <http://dx.doi.org/10.4314/bcse.v26i2.2>.
- Oubagaranadin, J.U.K., Sathyamurthy, N., Murthy, Z.V.P., 2007. Evaluation of Fuller's earth for the adsorption of mercury from aqueous solutions: A comparative study with activated carbon. *J. Hard Mater.* 142 (1–2), 165–174. <http://dx.doi.org/10.1016/j.jhazmat.2006.08.001>.
- Rao, M.M., Reddy, D.H.K.K., Venkateswarlu, P., Seshaiiah, K., 2009. Removal of mercury from aqueous solutions using activated carbon prepared from agricultural by-product/waste. *J. Environ. Manag.* 90 (1), 634–643. <http://dx.doi.org/10.1016/j.jenvman.2007.12.019>.
- Ringqvist, L., Holmgren, A., Öborn, I., 2002. Poorly humified peat as an adsorbent for metals in wastewater. *Water Res.* 36 (9), 2394–2404. [http://dx.doi.org/10.1016/S0043-1354\(01\)00430-4](http://dx.doi.org/10.1016/S0043-1354(01)00430-4).
- Rosli, M.A., Daud, Z., Latiff, A.A.A., Rahman, S.E.A., Oyekanmi, A.A., Zainorabidin, A., Awang, H., Halim, A.A., 2017. The effectiveness of peat-AC composite adsorbent in removing color and Fe from landfill leachate. *Int. J. Integr. Eng.* 9 (3), 35–38.
- Saifuddin, S., Lisa, A., Amalia, Z., Faridah, F., Elfiana, E., 2020. Applications of micro size anorganic membrane of clay, zeolite and active carbon as filters for peat water purification. *J. Phys. Conf. Ser.* 1450 (1), <http://dx.doi.org/10.1088/1742-6596/1450/1/012010>.
- Seo, E.Y., Cheong, Y.W., Yim, G.J., Min, K.W., Geroni, J.N., 2017. Recovery of Fe, Al and Mn in acid coal mine drainage by sequential selective precipitation with control of pH. *Catena* 148, 11–16. <http://dx.doi.org/10.1016/j.catena.2016.07.022>.
- Serunting, M.A., Rusnadi, R., Setyorini, D.A., Ramadan, B.S., 2018. An effective cerium (iii) ions removal method using sodium alginate-coated magnetite (Al-Fe₃O₄) nanoparticles. *J. Water Supply: Res. Technol. - AQUA* 67 (8), 754–765. <http://dx.doi.org/10.2166/aqua.2018.086>.
- Sivachidambaram, M., Vijaya, J.J., Kennedy, L.J., Jothiramalingam, R., Al-Lohedan, H.A., Munusamy, M.A., Elanthamilan, E., Merlin, J.P., 2017. Preparation and characterization of activated carbon derived from the: *Borassus flabellifer* flower as an electrode material for supercapacitor applications. *New J. Chem.* 41 (10), 3939–3949. <http://dx.doi.org/10.1039/c6nj03867k>.
- Spiegel, S.J., Agrawal, S., Mikha, D., Vitamerry, K., Le Billon, P., Veiga, M., Konolius, K., Paul, B., et al., 2018. Phasing out mercury? ecological economics and Indonesia's small-scale gold mining sector. *Ecol. Econ.* 144, 1–11. <http://dx.doi.org/10.1016/j.ecolecon.2017.07.025>.
- Vélez, E., Campillo, G.E., Morales, G., Hincapié, C., Osorio, J., Arnache, O., Uribe, J.I., Jaramillo, F., 2016. Mercury removal in wastewater by iron oxide nanoparticles. *J. Phys. Conf. Ser.* 687 (1), <http://dx.doi.org/10.1088/1742-6596/687/1/012050>.
- Wajima, T., Sugawara, K., 2011. Adsorption behaviors of mercury from aqueous solution using sulfur-impregnated adsorbent developed from coal. *Fuel Process. Technol.* 92 (7), 1322–1327. <http://dx.doi.org/10.1016/j.fuproc.2011.02.008>.
- Yan, B., Chen, Z., Cai, L., Chen, Z., Fu, J., Xu, Q., 2015. Fabrication of polyaniline hydrogel: Synthesis, characterization and adsorption of methylene blue. *Appl. Surf. Sci.* 356, 39–47. <http://dx.doi.org/10.1016/j.apsusc.2015.08.024>.