

MINI REVIEW OF ADSORPTION METHOD USING CONVENTIONAL MATERIALS FOR ACID MINE DRAINAGE TREATMENT

TINJAUAN SINGKAT TENTANG METODE ADSORPSI MENGGUNAKAN BAHAN KONVENSIONAL UNTUK PENGOLAHAN AIR ASAM TAMBANG

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ABSTRACT

Acid mine drainage (AMD) is a highly dangerous form of water pollution results from coal mining activities. AMD is characterized by its high concentration of heavy metals and low pH levels, which have been linked to various health problems, including skin disease, cancer, and poisoning. This paper presents a comprehensive review of the available information on the AMD and its alternative low-cost treatment methods. One such method is adsorption, an eco-friendly and cost-effective approach to treating the AMD. This review draws on 99 published papers as the sources that provide a comprehensive overview of the AMD sources and problems worldwide. This study explores the potential of conventional materials, such as activated carbon, biochar, and other materials for treating the AMD. A special section on conventional materials is well-detailed and provides valuable insights into their effectiveness. It is essential to explore the alternative treatment methods that are both environmentally friendly and cost-effective. This review provides valuable insights in this regard. By using the low-cost and sustainable methods, we can effectively treat AMD and reduce its impact on the environment and human health.

Keywords: acid mine drainage, adsorption, activated carbon, biochar, conventional materials.

ABSTRAK

Air Asam Tambang (AAT) merupakan air tercemar berbahaya yang diakibatkan oleh aktivitas pertambangan batubara. AAT memiliki karakteristik konsentrasi logam berat yang tinggi dan nilai pH rendah. Kondisi ini dapat menyebabkan berbagai masalah kesehatan, seperti penyakit kulit, kanker, dan keracunan. Artikel ini menyajikan tinjauan ilmiah yang komprehensif tentang pengelolaan AAT menggunakan metode sederhana dan berbiaya rendah. Salah satu metode yang ramah lingkungan dan ekonomis dalam pengelolaan AAT adalah adsorpsi. Artikel ini meninjau 99 publikasi ilmiah untuk memperoleh informasi mengenai permasalahan AAT di seluruh dunia. Selain itu, penelitian ini mengeksplorasi potensi bahan konvensional, seperti karbon aktif, biochar, dan bahan lainnya, dalam menurunkan parameter pencemar pada AAT. Bagian khusus mengenai bahan konvensional dijelaskan dengan mendalam dan mendiskusikan efektivitasnya. Eksplorasi metode pengolahan alternatif yang ramah lingkungan dan berbiaya rendah sangat penting. Tinjauan ini memberikan wawasan berharga dalam konteks tersebut. Menggunakan metode yang ekonomis dan berkelanjutan, pengolahan AAT dapat dilakukan secara efektif sehingga mengurangi dampaknya terhadap lingkungan dan kesehatan manusia.

Kata kunci: air asam tambang, adsorpsi, karbon aktif, biochar, material konvensional.

INTRODUCTION

AMD is a polluted water caused by mining activities. This wastewater contained high heavy metals and low pH. Due to the high heavy metals content, the AMD was reported as the source of several diseases, such as cancer, skin disease, cardiovascular, brain problem, and other negative ecological impacts (Johnson and Hallberg, 2005; Kumar, Borah and Devi, 2020; Rahaman *et al.*, 2021). Several studies reported that the heavy metals in the AMD are Cu, Pb, Zn, Cd, As, Fe, and Al (Luo *et al.*, 2020; Vélez-Pérez *et al.*, 2020; Gammons *et al.*, 2021). AMD was found in several places, such as tunnels, mine workings, open pits, waste rock piles, and mill tailings (Simate and Ndlovu, 2014). AMD caused by metal sulfides i.e., pyrite, marcasite, pyrrhotite, chalcocite, chalcopyrite, covellite, molybdenite, millerite galena, sphalerite arsenopyrite (Cánovas *et al.*, 2021; Chen, 2022).

Recent studies reported several methods for the AMD treatment for active (adsorption (Motsi, Rowson and Simmons, 2009), phytoremediation (Wibowo, Safitri, Malik, *et al.*, 2022; Wibowo, Nugraha and Rohman, 2023), bioremediation (Rosanti *et al.*, 2020) and filtration (Menzel *et al.*, 2021)). On the other side, passive treatment is also reported in treating the AMD, such as constructed the wetlands (Wibowo, Candra Wijaya, Halomoan, Yudhoyono, *et al.*, 2022). Adsorption is one of the low-cost and effective methods for the AMD treatment. A recent study reported that the adsorption method using biochar derived from coconut shell, coal, and peat can remove heavy metals from the AMD up to 90% (Wibowo, Safitri, Ramadan, *et al.*, 2022). Not only for a single type of adsorbent, a combination of different materials also recently reported successful removal of pollutant parameters from the AMD in different pH conditions (Wibowo, Sudibyo, Naswir and Ramadan, 2022). Adsorption method is a better treatment for treating AMD if compared with other studies. A recent study reported that phytoremediation (as a low-cost treatment for the AMD) can only reduce up to 69% after five weeks of time contact (Wibowo, Safitri, Malik, *et al.*, 2022) meanwhile, the adsorption method can reduce more significant only in 120 minutes for ionic and anionic pollutants (Taher *et al.*, 2023).

Despite some existing research on the benefits of the adsorption method for the AMD treatment, comprehensive reviews of recent advancements in this area are still needed. This study represents a continuation and further development from previous investigations about novel and conventional materials for treating the AMD (Wibowo *et al.*, 2024), with a specific focus on conventional materials used in the AMD treatment. This indicates a significant shift towards exploring the efficiency and applicability of traditional adsorbents under new or improved conditions.

Moreover, the landscape of the AMD treatment strategies continues to evolve. For instance, a study from Japan reviewed recent strategies for the AMD prevention, while another study focused on biological treatment for the AMD (Park *et al.*, 2019). Adsorption is a surface phenomenon where molecules or particles adhere to the surface of a solid or liquid material. It's a crucial process in various fields, especially in environmental science, purification processes, and chemical engineering. Given the widespread occurrence of coal mining activities globally, it is crucial to explore effective and sustainable methods for treating the AMD. This study is important to publish due to the large number of coal mining activities worldwide. In the USA alone, there were 1192 legal coal mining activities between 2011 and 2018, not including the artisanal small-scale and the illegal mining activities. These mining activities had significant negative impacts on the environment, including changes to sediment and substrate morphology, increased stream velocity, metals adsorbed onto sediments, decreased pH levels, increased acidity, and reduced bicarbonate buffering systems (Acharya and Kharel, 2020).

While some studies have reported general information about the AMD treatment, including active and passive methods, there is a lack of specific reviews on the adsorption method for AMD treatment using conventional materials. This paper is therefore important for sharing rare information about the use of conventional materials, such as bentonite, clay, activated carbon, biochar, and others, for treating the AMD. In addition, this study provides a comprehensive overview of the AMD problems worldwide and the potential of the adsorption method as a sustainable and effective treatment option.

This review used both national and international journals. The inclusion of both national and international journals is a strength of this review, as it ensures a broad and diverse range of perspectives on the topic. Additionally, by including highly reputable journals, we can ensure that this reviewed paper was subject to rigorous peer-review processes. The use of Google Scholar as a search engine is a limitation of this review, as it may have missed relevant studies that are not indexed by this platform. However, this paper inclusion of multiple search terms and filters, as well as the comprehensive nature of the review, mitigates this limitation to some extent. Overall, the inclusion of multiple sources and a diverse range of perspectives is critical for generating policy recommendations that can be effectively implemented. Thus, this review provides a strong foundation for future policy recommendations related to the use of conventional materials for the AMD treatment.

METHOD

This review provides a comprehensive overview of acid mine drainage and the use of adsorption methods for its treatment, focusing on conventional materials such as activated carbon and biochar. In order to ensure a thorough and up-to-date analysis, a rigorous search strategy was employed. Specifically, the data in this paper searched both national (indexed by SINTA Indonesia) and international journals, including reputable publishers like Elsevier and Springer Nature, using the search terms acid mine drainage, acid mine drainage impact, human health impact in acid mine drainage, adsorption method for acid mine drainage treatment, activated carbon, biochar, and conventional materials for acid mine drainage adsorption. A total of 99 published papers were reviewed to inform our analysis.

ACID MINE DRAINAGE

The AMD is a polluted water that comes from mining activities. The waste can be formed when there is an oxidation process of pyrite minerals (FeS_2) and other sulfide minerals found on the surface of the soil where mining occurs. These materials can produce sulfates with high acidity levels (Wahyudin, Widodo and Nurwaskito, 2018). The AMD can also be interpreted as the water formed from exposed

sulfide minerals caused by excavation and stockpiling of overburden and will react with oxygen in the air in a watery environment (Wati *et al.*, 2003). In principle, the formation of AMD is due to a reaction to the formation of H^+ ions, which causes acid formation. Indeed, the H^+ ions are formed by the oxidation of sulfide minerals that react with water. The result of the mineral oxidation process is sulfuric acid and metal dioxide deposition, which can be seen in a chemical process, while from the biological process, the process of the AMD is due to the influence of certain bacteria such as *Thiobacillus ferrooxidans*, which functions as a catalyst for the oxidation of sulfide minerals and iron oxidation. While the bacteria *Thiobacillus thiooxidans* functions as a catalyst for the oxidation of sulfide minerals and the oxidation of sulfur. The color of AMD can be recognized by orange or red water that comes from iron hydroxide (ferric hydroxide) deposits at the bottom of the stream or by the smell of sulfur. However, this is not always the case because there are some AMD instances that appear bluish-green due to the presence of high copper in the water. In the AMD process, several factors cause AMD, such as physical, chemical, and biological factors. These three factors can be grouped into three main factors, namely tertiary, secondary, and primary factors. The tertiary factors that cause the AMD due to the physical environment can form oxide minerals through oxidation process, such as the physical condition of the material. Secondary factors play a role in consuming oxidized sulfide minerals that neutralize the AMD.

In contrast, the primary factors have a direct role in forming the sulfide mineral oxidation process, which is an important component in forming the AMD. Mining locations are the most potential places in the AMD formation, because the AMD that occurs at mining sites is usually located in the mining water storage ponds (sludge deposition ponds and water ponds) and the dumping sites for dumped sulfide materials (Wijaya, 2010).

AMD occurs due to the mixing of rainwater or groundwater with rocks containing sulfide minerals cause the water to be acidic. The formed AMD will affect the groundwater quality around the mining area. The occurrence of conditions that decrease the groundwater quality, such as cloudy, smelly, and tasteless well water can endanger the health of

residents and workers if the water is consumed (Said, 2018). In determining the status of water quality standards in mining areas, the Pollution Index Method is used, which has been regulated in the Minister of Environment Decree No. 115 of 2003 concerning Guidelines for Determining Water Quality Status. The pollution index must be 0 to 1.0 to be said to meet the quality standard or not be polluted (Wati *et al.*, 2003).

As a result of low pH, there will be an increase in the solubility of microelements in the form of dissolved metallic elements. If those are at high concentrations, they will poison plants which can inhibit plant growth (Widyati, Widyastuti and Lantifasari, 2010). Water is said to be unpolluted if it meets the established water quality standards. Coal mining AMD quality standards have been regulated in the Minister of Environment Decree No. 113 of 2003 concerning Wastewater Quality Standards. Coal mining businesses and/or activities have determined that the quality standard for pH is between 6-9, TSS with a maximum quality standard of 400 Mg/L, Fe (Iron) has a maximum quality standard of 7 mg/L, and Mn (Manganese) a maximum quality standard of 4 mg/L (Wati *et al.*, 2003). In general, two methods can be used for AMD processing, namely active and passive processing technologies (Said, 2018). Handling the AMD can be carried out in several stages, namely the AMD in the pit is carried out to the sump, trenches are made to facilitate the drainage of the AMD to the sump, or pumping can also be done. After entering the sump, the AMD will be pumped to the sediment pond. The sediment pond functions as a catcher and retainer, a lot of soil and dirt settles into the sediment (Wahyudin, Widodo and Nurwaskito, 2018).

Many mines are abandoned, causing acid water to form, polluting and damaging the environment. Table 1 summarizes the AMD problems around the world. AMD has a bad impact on life. If not treated, AMD can interfere with the lives of living things. In 2019, the US Bureau of Soil Management reported that AMD could increase the risk because 500,000 ex-mining sites resulted in AMD being abandoned and left unattended, which makes very dangerous problems such as radiation, groundwater contamination, and poisoning of life in the water (Ojonimi *et al.*, 2019). Heavy metals contained in AMD produce metal toxicity that has the potential to poison all living things and interfere with the metabolism of microorganisms and plants. The toxic effect of AMD on soil microorganisms causes soil quality to decrease due to microbial growth and enzyme activity being inhibited. This makes it difficult for plants to grow. Apart from plants that cannot grow, animals cannot live in an ecosystem that has been damaged (Ferreira *et al.*, 2021).

The main problem caused by heavy metals in AMD is human health. The content of copper ions causes damage to the liver. Mercury can interfere with nerves and blood circulation in humans. Headaches, diarrhea, and seizures caused by chromium and lead poisoning can cause kidney failure, muscle damage, brain damage in infants, and damaging internal organs. The disease is also in the form of skin irritation, the most common. Preventing AMD is almost impossible because the miners and the government have different point of view. Natural forces such as weather factors can affect sulfur rock, and on the other hand, once started, it will happen forever after mining closes (Ojonimi *et al.*, 2019). Table 1 informs the AMD problems around the world.

Table 1. Worldwide AMD problems

No	Location/Country	pH	Parameters	Reference
1	South Borneo, Indonesia	3.92	Mn, Fe, Cd	(Utami, Susanto and Cahyono, 2020)
2	Southwestern Colorado	2.9 - 3.1	Cu, Fe, Pb, Zn, Al, Cd, Mn, As	(White <i>et al.</i> , 2017)
3	Dogie-up, Samchoek, Gangwon Province, about 300 km away from Seoul, the capital of the Republic of Korea	3.28	Fe, Al, Mn, SO_4^{2-}	(Seo <i>et al.</i> , 2017)
4	Jiangxi Province, Southern China	2.50 - 2.64	Fe, Al, Ca, Cu, Mg, Mn, SO_4^{2-}	(Pei <i>et al.</i> , 2019)
5	Elazığ, Turkey	3.04	Fe, Cu, Co, Ni, Cd, Mn	(Yilmaz <i>et al.</i> , 2019)

No	Location/Country	pH	Parameters	Reference
6	Southwestern Spain	2.65	Al, As, Cl-, Co, Cu, Fe, K, Mg, Ca, Mn, Na, Ni, Sb, Si, Zn, SO_4^{2-} , HPO_4^{2-} , HCO_3^-	(León-Venegas <i>et al.</i> , 2023)
7	Mpumalanga Province, South Africa	2.9 ± 0.2	Al^{3+} , As^{3+} , Cd^{3+} , Cu^{3+} , Cr^{3+} , Fe^{3+} , Mg^{3+} , Mn^{3+} , Ni^{3+} , Pb^{3+} , Sr^{3+} , Zn^{3+}	(Akinpelu <i>et al.</i> , 2021)
8	North China	4.9	Cu, Zn, Pb, As	(Hu <i>et al.</i> , 2022)
9	Tab-Simco site from the sulfate-reducing bioreactor (SRB)	2.46	Fe, Al, Mn, Zn, Ni, Cu, Pb, Cr	(Kiiskila <i>et al.</i> , 2019)
10	Perry Canyon	2.81 ± 0.18	Cu, Fe, Mn, Zn, SO_4^{2-}	(Ruehl and Hiibel, 2020)
11	Tinto and Odiel rivers are located in Southwest Spain in the province of Huelva	2.5-3.0	FeS_2 , ZnS, Cu, Cu FeS_2 , PbS	(Guerrero <i>et al.</i> , 2021)
12	Brunkunga mine in South Australia	2.8	SO_4^{2-} , Fe	(Sephton, Webb and McKnight, 2019)
13	Municipality of Caldas, Minas, Gerais, Brazil	2.5 - 3.6	Fe, Cl, SO_4^{2-} , Na, K, Mg, Ca, P, Al, Si, Mn, Fe, Zn, U, Y, La, Ce, Pr, Nd, Sn, Eu, Gd, Tb, Dy, Er, Yb	(Moraes and Ladeira, 2021)
14	The Chelopech deposit is located within the southern part of the Panagyurishte Metallogenic district in the central part of the Srednogie zone-Bulgaria	1.8 ± 0.02	Fe, Mn, Al	(Mafta <i>et al.</i> , 2020)
15	Sierra Minera of Cartagena-La Unión (South-east of Spain)	2.3	Fe, Cu, Zn, As, Cd, Pb	(García-Valero <i>et al.</i> , 2020)
16	Mount Morgan mine, Central Queensland	1.9 - 3.8	Al, Mn, Cu, Zn	(Kaur, Couperthwaite and Millar, 2018)
17	Santa Catarina, Brazil	< 4.0	Fe, Al, Mn, Cu, Zn, Pb	(Myagkaya <i>et al.</i> , 2020)
18	The Novo-Ursk complex ore deposit, in the northern Salair Ridge of The AltaSayan fold area	1.9	Cu, Zn, Pb, As, Se, Te, Hg, Cd, Au, Ag	(Núñez-Gómez <i>et al.</i> , 2019)
19	Andean Mountains of Central Chile	2.95	SO_4^{2-} , Cu, Fe, Zn, Ni	(Hurtado, Viedma and Cotoras, 2018)
20	Podwiśniówka quarry	2.4–2.6	Fe, Al, As, Co, Cr, Cu, Ni and REE	(Migaszewski, Gałuszka and Dołęgowska, 2019)

CONVENTIONAL MATERIALS IN HEAVY METALS REMOVAL

Adsorption is a robust process that will enable companies to meet their obligations regarding water reuse and meet stringent runoff regulations. Efficiency, affordability, and environmental friendliness make adsorption one of the best technologies for water decontamination (Abdel-Raouf and Abdel-Rahim, 2016). Adsorption is a process that occurs when a liquid solute (adsorbate) accumulates on the surface of a solid to form molecules or atoms (Burakov *et al.*, 2018). Removes harmful heavy metal ions from wastewater. Some adsorbents are of natural origin. These materials can be used in either unmodified or modified configurations (Chai *et*

al., 2021). Adsorption has several types based on the attractive forces between the molecules. In physical adsorption, hydrogen bonds or van der Waals forces are used to bind the adsorbate to the surface of the adsorbent, only in a low-temperature environment with a proper pH balance. Chemical adsorption is a chemical reaction between adsorbent and adsorbate, leading to high interaction requirements (Abdel-Raouf and Abdel-Rahim, 2016). However, all adsorbents have weaknesses and limitations, such as low adsorption capacity, effectiveness, and low heavy metal removal efficiency.

The most common adsorbent is activated carbon, often produced in small pellets or powder and is a highly porous amorphous

solid made of microcrystals with a graphite lattice (Lakherwal, 2014). Activated carbon is the most widely used in the world but is expensive, so it cannot be used on a large scale due to cost efficiency (Ahmad and Azam, 2019). An alternative to activated carbon is clay which contributes significantly to the inorganic composition of the soil. Clay can be a biosorbent for water treatment plants because of its larger surface area, which can bind pollutants in water. The negative charges on clay minerals can attract positive toxic heavy metal ions (Liu *et al.*, 2014).

Biochar is a substance produced without oxygen by heating the biomass through the pyrolysis process. The biochar is also known as the carbon-rich material. Graphene-like carbon matrix, high porosity, increased surface area, and high cation and anion exchange capacity, and high surface area make the biochar capable of blocking contaminants and pollutants from entering water or soil and further reduce the bioavailability of pollutants through adsorption into wastewater treatment processes. Biochar has been widely used in anaerobic digestion to remove pathogens, suspended particles, and trace metals (Tan *et al.*, 2020). Compared with traditional adsorbents such as activated carbon, biochar is the best for removing heavy metal (Chai *et al.*, 2021). Several adsorbents can remove toxic heavy metal ions from wastewater in their original or modified form. Industrial solid waste, activated carbon, zeolite, clay minerals, and biomaterials are the most common. The following describes some nano-sized manganese oxide (MnO_2) modified with Fe_3O_4 . Without needing templates or organic surfactants, a simple hydrothermal approach produced MnO_2 -coated magnetic nanocomposites with a 3D flower-like structure. Within seconds, $\text{Fe}_3\text{O}_4/\text{MnO}_2$ can quickly and effectively remove several heavy metals from water, including Cu(II) , Pb(II) , Zn(II) , and Cd(II) . Certain hydrochemical conditions, particularly low pH, high ionic strength, and the presence of calcium ions, will affect the adsorption properties. $\text{Fe}_3\text{O}_4/\text{MnO}_2$ can also be recycled up to five times without losing its adsorption capacity (Kim *et al.*, 2013).

Laboratory-scale tests on a single system revealed that the extracellular polymeric substance (EPS) extracted from *Klebsiella sp.*

has a larger equilibrium Cu^{2+} adsorption capacity than Zn^{2+} in a single system. The absorption efficiency in the binary system can be described accurately by the Langmuir-Freundlich isotherm. The presence of Cu^{2+} has a significant adverse effect on the Zn^{2+} absorption, but the interference of Zn^{2+} with Cu^{2+} absorption is not good. Zn^{2+} is not adsorbed on EPS as well as Cu^{2+} . Cu^{2+} has adsorption sites that overlap with Zn^{2+} , and Cu^{2+} has a greater affinity for protein binding in EPS (Yang *et al.*, 2015). Clay is believed to function as a filter and cleanser of pollutants. The results of this study indicate that Jebel Chakir (JCK) smectic clay can be used as an effective adsorbent at an affordable price. The increased adsorption capacity was observed as the pH of the chromium increased in the single-element system. Pure JCK has the ability to adsorb Cr (III) and Cd (II). This study reaffirms that when clay is used as a contaminant barrier in waste storage facilities, it becomes an effective weapon in combating heavy metal pollutants in the landfills (Ghorbel-Abid and Trabelsi-Ayadi, 2015). Wood-based or granular activated carbon (GAC) is modified with nanofibrous sodium titanate (TNF). In the table, the cumulative amount adsorbed by GAC is arranged in the order $\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd} > \text{Ni}$, while the cumulative amount adsorbed by GAC+TNF is arranged in the order $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni}$. In single and mixed metal systems, the use of TNF (4%) combined with the GAC (96%) revealed that the amount of metal removed by adsorption varied widely and could be up to 80 times the amount of metal obtained with GAC alone. This shows that the TNF can significantly reduce the amount of the heavy metals in contaminated water. The TNF can also be used with the GAC to improve the hydraulic properties while effectively removing the heavy metals due to their smaller size (Sountharajah *et al.*, 2015).

Zeolite is a hydrated crystalline aluminosilicate that can be produced on a large scale industrially or naturally and is one of the largest adsorbents for removing heavy metal ions. Zeolites are made of hydrated aluminosilicate minerals, which are made of interconnected tetrahedral parts of alumina (Al_2O_3) and silica (SiO_4) (Tseng, Tseng and Wu, 2006). Compared with the original zeolite, the modified zeolite has a greater adsorption capacity. Zeolite alteration can be done by various techniques. For example, nano-sized zeolites are more suitable for removing heavy

metals because the pores are more accessible. Nax-type Zeolite is one of the most widely used nano-sized zeolite adsorbents for heavy metal removal from wastewater, especially Cd^{2+} (Zwain, Vakili and Dahlan, 2014).

A relatively new and promising method for removing the heavy metal pollutants is the biosorption of heavy metals from aqueous media. Its main advantages are the use of expensive materials and high biosorption efficiency in adsorbing heavy metal ions. This method is ideal, especially for treating diluted wastewater (Burakov *et al.*, 2018). Many inexpensive, non-living plant materials have been extensively studied as potential heavy metal adsorbents, including cashew shells (Coelho *et al.*, 2014). Industrial solid waste can adsorb heavy metals from the waste and be used for this purpose. Industrial effluents may enhanced heavy metals absorption after minor physical and chemical changes (Burakov *et al.*, 2018). Zn^{2+} is removed from wastewater by various adsorbents. The maximum adsorption capacity of Zn^{2+} was determined to be 168 mg/g for powdered sludge waste, 73.2 mg/g for lignin, and 55.82 mg/g for cassava waste, higher in adsorption capacity of 52.91 mg/g achieved for bentonite, clay, and in most cases, lower than 128.8 mg/g obtained from dried marine green algae macrobiomaterials (Zwain, Vakili and Dahlan, 2014).

Activated carbon

In nature, various adsorbents can be used to remove heavy metal ions from wastewater. The adsorbent often used in the water treatment plants is activated carbon because of its specific surface area, microporous structure, and chemical complexity. Activated carbon is a primarily amorphous solid and has a large pore volume and surface area (Baker *et al.*, 2000).

Agricultural waste is one of the low-cost raw materials that can be used to produce activated carbon. Agricultural wastes that can be utilized include coconut shells, oil palm shells, corn cobs, and rice husks (Qu, 2002). The previous studies stated that the activated carbon from pistachio nuts and coconut shells with KOH activation and CO_2 gasification increased the high surface area (Tseng, Tseng and Wu, 2006). Several types of documents refer to the preparation and characterization of activated carbon from the

cashew shells. However, it is rare to find literature explaining how to prepare activated carbon from the cashew shells with high specific surface area. Monkey cashew, or cashew with the Latin name *Anacardium occidentale* is a plant belonging to the *Anacardiaceae* tribe originating from Brazil, then introduced to other tropical countries such as Africa, India, and Indonesia in the 16th century. Cashew nuts are the main product of cashew nuts often used as snacks and in the baking industry (Mulyono, 2007). The cashew shells are often forgotten and become agricultural waste. Therefore, several studies have developed cashew shells as an activated carbon product with high specific surface area using KOH activation and CO_2 gasification to remove lead(II) and copper(II) content, in aqueous solution by batch method. The parameters include the activated carbon dosage, the effect of the initial pH of the heavy metal solution, the initial concentration of the heavy metals, and the contact time (Tangjuank *et al.*, 2009).

A study reported that cashew shells could be pyrolyzed to become an adsorbent. The Cashew shells undergo carbonization when exposed to ambient air conditions, then put in a beaker glass, and then added with water and KOH with a ratio of KOH: charcoal equal to 1: 4. The resulting charcoal mixture is then dried in an oven at 120 °C for 24 hours to obtain a dry mixture of charcoal and KOH. The dry mixture was then reheated in an oven from room temperature to 850 °C for 20-150 minutes. After 150 minutes, the nitrogen gas was turned off, and the CO_2 was immediately supplied into the oven. The obtained activated carbon was then washed several times with distilled water, dried at 110 °C, cooled to room temperature, and stored in a desiccator to determine the properties of activated carbon. The presence of surface functional groups in the sample was determined by an FT-IR spectrometer. Crystal structure changes were characterized by X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation (Siemens, D-500). Scanning electron microscope is used to investigate the microstructure of activated carbon. The specific surface area of the activated carbon was obtained from the adsorption isotherm of N_2 at 77K using an adsorption meter (Tangjuank *et al.*, 2009).

Besides cashew shells, carbon-rich materials such as coal and peat can also be used as

activated carbon products to remediate mercury-contaminated soil layers. There are two procedures for producing the activated carbon from coal and peat soil: physical activation and chemical activation (Bello, Adegoke and Akinyunni, 2017). Coal and peat were activated by steam and carbon dioxide at a temperature of 700-900 °C, and pores of will form in the activated carbon material during the physical activation period. In the physical activation process, the reactor material must be clean and without oxygen so that no material turns into ashes. In contrast, the impurities formed during the physical activation process will be cleaned using chemicals such as sodium hydroxide (NaOH), zinc chloride (ZnCl₂), potassium hydroxide (KOH), magnesium chloride (MgCl₂), and phosphoric acid (H₃PO₄) during chemical activation period (Bergna *et al.*, 2020).

Biochar

Biochar is a carbon-rich material that undergoes a certain thermal combustion process with a limited amount of oxygen from raw organic waste, such as agricultural waste and municipal sewage sludge. Biochar is a solid biomass product that has been produced and used for thousands of years and is commonly referred to charcoal (when produced from woody biomass) (Weber and Quicker, 2018). Biochar has several advantages, such as rich carbon content, high cation exchange capacity, large surface area, and structural stability. Adsorption is the biochar's main mechanism in removing heavy metals and organic pollutants. The biochar is a biomass pyrolysis process that produces solid products. Biochar is an efficient adsorbent for remediation because of its low production cost and is derived from readily available biomass waste. Chemical modification of the biochar can use acids, bases, and polymers. This provides adsorption efficiency because it can increase its surface area and chemical functionality (Wang and Wang, 2019).

Carbonization process can produce the biochar. Carbonization, including pyrolysis, gasification, and hydrothermal carbonization, are part of the biochar manufacturing processes. The common process for producing the biochar is pyrolysis, while hydrothermal gasification and carbonization generally need to meet the definition of biochar. Pyrolysis is the thermal

decomposition of organic materials at high temperatures without the addition of external oxygen. Pyrolysis takes place in the absence of oxygen, at temperatures around 300 to 900°C. The solid product is called biochar, the liquid one is called bio-oil, and the gas is called syngas (synthetic natural gas), which contains carbon dioxide, hydrogen, and nitric oxide. Pyrolysis can be divided into several types, namely fast, slow, intermediate, and flaked pyrolysis processes. Fast pyrolysis is the raw material introduced into the reactor when the temperature reaches the desired value, usually involving high temperatures (10 - 1000 °C) for the duration of only a few seconds (0.5 - 2 seconds). Slow pyrolysis takes place as raw materials are introduced into the reactor from the pyrolysis process, starting with a longer duration of several hours at moderate temperatures (300-550 °C). From both processes, slow pyrolysis produces better biochar due to its slow heating rate and longer residence time than fast pyrolysis. Intermediate pyrolysis occurs at temperature between 450-550 °C. The flaked pyrolysis process is mild, with temperature of 200-300 °C at a slow heating rate.

Torrefaction can remove excess water and volatiles as well as biopolymers (cellulose, hemicellulose and lignin) by releasing organic volatiles. The result of the disintegration process cannot be called biochar because the ratio of oxygen to carbon in the biochar itself is high. Pyrolysis requires a fairly dry raw material with a moisture content of below 30%. Producing biochar by pyrolysis is easier and cheaper than other processes. The gasification process requires air, oxygen, and steam to oxidize the biochar raw materials. This process requires high temperatures above 700 °C and little oxygen and steam.

Similar to the pyrolysis, solid, liquid, and gaseous products are formed. However, the yield of biochar is lower than that of the pyrolysis process because the gas product is the most produced product in the gasification process. The pyrolysis and gasification processes are dry, unlike the hydrothermal carbonization one. The hydrothermal carbonization process is wet because when the raw material is introduced into the reactor, it is mixed with water. Then the temperature and pressure will be increased to 250 °C. The biochar produced from this process has a higher carbon content than the pyrolysis and gasification processes.

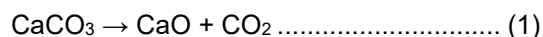
Biochar adsorbs hydrocarbons, other organics, and some inorganic metal ions, indicating the potential for water purification and soil improvement. The biochar can replace coal-based activated carbon, coconut shell, and wood as a cheap adsorbent for contaminants and pathogens. Biochar can remove pollutants from water by containing certain nutrients as soil conditioners and fertilizers (Mohan *et al.*, 2014). Different raw materials have different elemental compositions, so the resulted biochar has different performances. For example, the biochar from the rice straw has a higher potassium content (961 mg/kg) and pH (9.5) than biochar from wood (349 mg/kg, pH 8.0). In addition, rice straw biochar has a higher volatile content, which can be removed more easily than the non-volatile content during the pyrolysis process. Therefore, raw materials containing high volatile content can produce low biochar yields. In addition, pig and cow dung also show different proportions of elemental composition. Therefore, raw material type affects biochar's physiochemical properties (Wang and Wang, 2019). Raw material characteristics can affect the finished product's conversion process and properties. Biomass is a raw material for producing the biochar, which consists of three organic compounds, cellulose, hemicellulose, and lignin, which can produce biochar with unique physicochemical properties. The raw materials for biochar production are biomass, municipal waste, animal manure, and field residues. These raw materials can be divided into lignocellulosic and non-lignocellulosic biomass. Lignocellulosic biomass is derived from biological resources: parts of plants, animals, and others (Li and Jiang, 2017; Daful and Chandraratne, 2020).

Other materials

Bioremediation, especially the use of biosorption to treat heavy metals in wastewater, has become popular due to its low economic cost and the effectiveness in adsorbing heavy metals. Biosorption using everyday waste such as eggshell, has a potentially high chance, due to its easy gain the materials in surrounding. The high demand for egg leads to egg waste in the form of eggshell accumulation, causing bio-pollution for the environment. Therefore, utilizing the material for heavy metals treatment is a brilliant step for pollution mitigation.

Other biomass, such as fungi, also shows the possibility of bioremediation. Fungi have been reported to be simultaneously effective in the metal-contaminated water and soils remediation. Various fungi specimens can hide contaminants in their bodies, making it easier to isolate metal contaminants from the environment (Zhang *et al.*, 2020). The green algae bio-pellets combined with *A. niger* fungi have been reported to increase the Cd removal capacity by 40 to 56% compared to bio-pellets consisting of algae alone (Chugh *et al.*, 2022). According to Badan Pusat Statistik Indonesia (BPS), the average domestic hen egg produced from 2019 – 2021 in Indonesia reached 5,016,983.41 tons, and the waste in the form of eggshells is still not utilized thoroughly. The main material in eggshells is CaCO_3 which reaches around 90% (Choi and Lee, 2015). Due to eggshells' porous nature, they have been widely used for contaminant removal. This ability is the main consideration for using eggshells as natural biosorbent material for heavy metals in water (Lin *et al.*, 2021).

The eggshell waste could be collected either in local restaurants or surrounding neighborhoods. It is then cleaned using deionized water to remove impurities, including the residual egg membrane. The eggshell should be dried completely and then crushed until it reaches fine powder or desired sizes (Pettinato *et al.*, 2015; Zhang *et al.*, 2017; Harripersadth *et al.*, 2020; Sankaran *et al.*, 2020; Lin *et al.*, 2021). Calcination is strongly recommended to maximize its potential as a biosorbent. Heating the eggshell at a high temperature (700-900°C) is expected to neutralize the remaining major organic and inorganic materials, which are undesired, and turn the eggshell into a calcined eggshell (Table 2), indicated by its color that turns into a white powder. CaCO_3 , the main material in eggshells, turns chemically into CaO through reaction (1) when the eggshells are calcined (Choi and Lee, 2015).



The eggshell's adsorption occurs mainly through ion exchange reactions. The smaller adsorber particle diameter results in better heavy metals adsorption due to increased surface area. With different sizes of eggshell powder, smaller particles will yield higher solubility and durability value (Pettinato *et al.*, 2015).

Table 2. Composition of eggshell

Compound	Natural (%)	Calcined (%)
CaCO ₃ (Calcium Carbonate)	91.86	-
CaO (Calcium Oxide)	-	99.54
SiO ₂ (Silicon Dioxide)	4.32	-
Al ₂ O ₃ (Aluminum Oxide)	1.45	-
Na ₂ O (Sodium Oxide)	0.51	-
K ₂ O (Potassium Oxide)	0.52	0.24
F (Fluorine)	0.44	-
P ₂ O ₅ (Phosphorus Pentoxide)	0.30	0.08
Cl (Chlorine)	0.22	-
SO ₃ (Sulfur Trioxide)	0.19	0.14
Fe ₂ O ₃ (Iron Oxide)	0.08	-
ZnO (Zinc Oxide)	0.09	-
ZrO ₂ (Zirconium Dioxide)	0.02	-

Source: Choi and Lee (2015)

Eggshell waste is cheap but easy to obtain because the daily worldwide egg consumption is huge. The adsorption capacity of calcium carbonate as the main compound of eggshells is expected to make the eggshells favourable for the heavy metals treatment in AMD. Fungi are another excellent biosorbent for heavy metals contaminated water. Fungi exhibit high metal-binding capacity due to the large amount of cell-wall material. Various fungi species have been reported to be effective in reducing metals such as Pb and Cd from wastewater (Table 3) (Rozman *et al.*, 2020). Compared with other biosorbents, fungi can easily grow on a large scale and in a short time using simple methods and economical substrates, thereby obtaining a large amount of biomass (Dhankhar and Hooda, 2011).

To prepare the biomass, the fungi are boiled with chemical solutions such as HNO₃ and NaOH to remove the unwanted materials or substances. The biomass was then washed with distilled water and dried completely, leaving the moisture content at around 5%. It

is then pulverized into specific sizes (Akar and Tunali, 2005; Kumar *et al.*, 2008; Bhainsa and D'Souza, 2009). In conclusion, biomaterials are economical and easy to manufacture because they have been shown to be practically effective in reducing heavy metals in wastewater. He suggested chemical and physical action will enhance the capacity of biosorbents by increasing the surface area of biomaterials (Chai *et al.*, 2021).

ECONOMIC ANALYSIS

The use of conventional materials for the adsorption of the acid mine drainage (AMD) presents a potential economic benefit for the mining industry, especially for those who are looking for low-cost and sustainable solutions to treat their wastewater. In this discussion, the economic feasibility of using conventional materials for AMD treatment, focusing on the costs and benefits of using these materials, will be analyzed as well as the potential revenue streams.

Table 3. Removal efficiencies of different fungal biosorbents for artificial Pb(II) and Cd(II)

Metal	Biomass	Removal Efficiency (%)
Pb(II)	Live <i>A. alternate</i>	80
	Dry <i>A. flavus</i>	88
	Fruit body <i>A. bisporus</i>	92
Cd(II)	Live <i>B. bassiana</i>	63
	Dry <i>S. halophilu</i>	95
	Fruit body <i>P. platypus</i>	91

Source: Rozman *et al.* (2020)

One of the key benefits using conventional materials for the AMD treatment is their low cost, which can make them an attractive option for small and medium-sized mining companies that have limited financial resources. For example, bentonite and clay are relatively cheap and abundant materials that can be easily sourced from local suppliers, while biochar can be produced from agricultural waste, which is usually disposed in the landfills, making it a cost-effective alternative for commercial adsorbents. In addition, activated carbon, a widely used adsorbent material, can be produced from renewable sources, such as coconut shells, which makes it an eco-friendly and sustainable solution for the AMD treatment. Another economic benefit of using conventional materials for the AMD treatment is their high adsorption capacity, which can help reduce the volume of the wastewater that needs to be treated, thus lowering the costs associated with the disposal of wastewater. In addition, some of these materials, such as biochar, have been shown to have other beneficial properties, such as soil enhancement and carbon sequestration, which can provide additional revenue streams for mining companies.

However, it is important to note that the economic feasibility of using conventional materials for the AMD treatment depends on several factors, such as the size of the mining operation, the volume and the quality of the wastewater, and the availability and cost of the adsorbent material. In addition, the cost-effectiveness of using conventional materials can be influenced by the type of treatment method used, such as batch or continuous flow systems, as well as the operating and maintenance costs associated with the treatment process.

Moreover, the disposal of the spent adsorbent material is also a crucial economic factor that needs to be considered. While some conventional materials, such as bentonite and clay, can be disposed in the landfills or reused in other applications, others, such as biochar, may require specialized disposal methods, which can increase the overall cost of the treatment process. Despite these economic considerations, the use of conventional materials for the AMD treatment has potential to provide significant cost savings for the mining industry. For example, a study conducted in South Africa showed that the use of activated carbon as an adsorbent material

for the AMD treatment resulted in a 70% reduction in the treatment costs compared to other methods, such as lime treatment (Akinwekomi *et al.*, 2020). In addition, the use of biochar for the AMD treatment has been shown to reduce the costs associated with soil remediation, as it can enhance soil fertility and reduce the need for chemical fertilizers.

RECOMMENDATION AND FUTURE PROSPECT

One of the main recommendations for the future development of conventional materials in the AMD treatment is to continue researching and optimizing the adsorption process. While conventional materials have shown great potential in removing heavy metals from the AMD, their efficiency can still be improved. Future studies should focus in finding the novel materials that could produce significant with low-cost and could be optimizing factors such as pH, contact time, and adsorbent dosage to achieve the highest removal efficiency possible. Additionally, further research should be conducted to identify and develop new materials that may be more effective at adsorbing heavy metals. Another recommendation for the future development of the conventional materials in the AMD treatment is to explore new methods of material modification. The modification of conventional materials, such as clay and activated carbon, has been shown to improve their adsorption capacity. For example, the modification of clay with iron oxide nanoparticles has been shown to significantly increase its adsorption capacity for heavy metals. Further research should be conducted to explore new methods of material modification that can enhance the adsorption capacity of conventional materials.

Furthermore, the use of conventional materials in the AMD treatment should be coupled with other treatment methods to achieve optimal results. For example, the combination of adsorption with biological treatment has been shown to improve the removal efficiency of heavy metals from the AMD. Additionally, the use of conventional materials should be complemented by the implementation of best management practices in mining operations to reduce the generation of the AMD. Finally, the future development of the conventional materials in the AMD treatment should take into account the economic viability of the

process. While conventional materials are generally low-cost, the cost of their transportation and disposal should be taken into consideration. Therefore, future studies should focus on developing methods of material recovery and reuse to reduce the overall cost of the treatment process.

Another recommendation is the analysis of circular economy in adsorption methods for treating heavy metals from the AMD. Circular economy is an economic system where waste is minimized and resources are used efficiently and effectively. The concept of the circular economy is gaining the popularity worldwide as it promises sustainable development and environmental protection. Conventional materials used in adsorption of the acid mine drainage (AMD) have the potential to be integrated into a circular economy system. In this discussion, we will explore the potential of circular economy for conventional materials used in the AMD treatment.

Conventional materials such as activated carbon, biochar, and clay are widely used in the adsorption process of the AMD. These materials have high adsorption capacity, low cost, and are readily available. The circular economy can be applied to these materials by ensuring that they are reused and recycled after their initial use. The conventional materials can be regenerated and reused, and their waste products can be repurposed, creating a closed-loop system that reduces waste and improves resource efficiency.

One potential way of implementing circular economy principles in the use of conventional materials in the AMD treatment is through a closed-loop adsorption system. In this system, the conventional materials are used to adsorb heavy metals from the AMD. Once the materials are saturated with the heavy metals, they can be regenerated and reused. The regeneration process can be done by washing the materials with acid or heat treatment, which removes the heavy metals from the material, making it available for reusing. The regenerated materials can then be used for further the AMD treatment or repurposed for other applications. Another way to integrate circular economy principles in conventional materials used in the AMD treatment is through the use of waste materials as a source of raw materials. For instance, the waste materials from the agricultural industry, such as rice

husks and coconut shells, can be converted into activated carbon and used for the AMD treatment. This approach reduces waste and turns waste materials into valuable resources.

In addition, the circular economy can be applied to the disposal of waste products from the AMD treatment process. The waste products can be repurposed for other applications. For example, the waste products from the regeneration of conventional materials can be used as soil amendments or construction materials. This approach not only reduces waste but also creates value from waste products. The circular economy approach to conventional materials used in the AMD treatment can provide economic benefits as well. The reuse and regeneration of conventional materials can reduce the need for new material production, reducing costs associated with mining and extraction of new materials. In addition, the repurposing of waste products can create new economic opportunities and markets for waste products, promoting job creation and economic growth.

One of the key policy recommendations for promoting the use of conventional materials in the AMD treatment is the development of regulatory frameworks that set environmental standards for the discharge of mine wastewater. These standards should incorporate the use of conventional materials for the AMD treatment and encourage mining companies to adopt this method as a way of meeting the regulatory requirements. Governments should work with stakeholders to create regulations that require mining companies to use conventional materials for the AMD treatment and to monitor their performance.

Another important policy recommendation is the establishment of a regulatory framework for the disposal of spent conventional materials after use. The conventional materials used in the AMD treatment may become contaminated with heavy metals and other pollutants. Therefore, it is necessary to have regulations in place for the proper disposal of these materials after use. Governments should work with the stakeholders to develop regulations that require mining companies to dispose of spent conventional materials in an environmentally responsible manner, such as by recycling them in other industrial processes or by using them as a source of energy.

Another policy recommendation is the promotion of public-private partnerships (PPPs) to support the utilization of conventional materials for the AMD treatment. The governments can work with the mining companies, the academia, and the private sector to form the PPPs in promoting the research and development of new and innovative conventional materials for the AMD treatment. PPPs can also help to promote the use of conventional materials for the AMD treatment by providing incentives to mining companies that adopt this method. Lastly, the government can provide a financial support for research and development of new and innovative conventional materials for the AMD treatment. The governments can provide funding for research institutions and companies to develop new materials or improve existing ones for the AMD treatment. The financial support can also be provided to the mining companies to adopt the use of conventional materials for the AMD treatment. This can be done through subsidies or tax incentives.

In conclusion, the utilization of conventional materials for the AMD treatment is a promising solution to address the environmental issues associated with the mining activities. However, the successful implementation of this method requires supportive policies that promote its adoption and use. The governments should work with the stakeholders to develop the regulatory frameworks, promote the PPPs, and provide financial support for research and development of new and innovative conventional materials for the AMD treatment. These policy recommendations can help to promote the adoption and use of conventional materials for the AMD treatment, leading to a more sustainable and environmentally friendly mining industry.

Conclusion

The AMD poses a significant threat to both environmental and human health due to its high concentrations of heavy metals and low pH levels, which are linked to serious health issues such as skin diseases, cancer, and poisoning. This comprehensive review highlights the urgent need for effective treatment methods, focusing particularly on low-cost and eco-friendly alternatives. Among these, adsorption using conventional materials like activated carbon and biochar emerges as a promising solution. Drawing on an extensive

analysis of 99 published studies, the review provides a thorough understanding of AMD sources, impacts, and treatment efficacy. Detailed examination of conventional materials offers valuable insights into their potential in mitigating the adverse effects of the AMD. The findings underscore the importance of developing and implementing sustainable treatment strategies to protect both the environment and the public health from the harmful consequences of the AMD.

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