



Pillared Interlayered Clays (PILCs): Harnessing Their Potential as Adsorbents and Catalysts - A Mini Review

Restu Kartiko Widi¹

¹ University of Surabaya, Surabaya 60293, Indonesia
restu@staff.ubaya.ac.id

Abstract. The Pillared Interlayered Clays (PILCs) have attracted significant attention in recent years due to their versatile applications as adsorbents and catalysts in various environmental and industrial processes. This mini review presents a comprehensive overview of the recent researches conducted on PILCs and highlights their potential as effective materials for pollutant removal and catalytic reactions, with a particular focus on the principles of green chemistry. The review begins by introducing the basic concept of PILCs, emphasizing the importance of interlayer pillaring to enhance their structural stability and surface area. PILCs offer a greener alternative to traditional adsorbents and catalysts by providing high adsorption capacity and catalytic activity with lower environmental impacts. The catalytic applications of PILCs in green chemistry are also explored. Their unique structural features, such as tunable acidity and porosity, enable efficient catalytic reactions while minimizing the use of toxic or harmful substances. This mini review provides a concise yet comprehensive summary of the recent advancements in the research on PILCs as adsorbents and catalysts, with a focus on green chemistry principles. PILCs offer great potential as sustainable alternatives for pollutant removal and catalytic reactions, aligning with the goals of green chemistry to minimize environmental impact and promote sustainable development. Further research and development efforts are required to fully harness the green potential of PILCs and facilitate their practical and commercial applications in various industries.

Keywords: Pillared Interlayered Clays, Bentonite, Adsorbent, Catalyst.

1 Introduction

Green chemistry is an approach and application of chemistry that seeks to minimize the negative impact of chemical processes on the human environment. One of the main principles of green chemistry is the utilization of renewable and environmentally friendly materials.

Clay, which is easy to find in Indonesia, is an example of a renewable natural material. The use of clay as an adsorbent, catalyst and ion exchange has been widely used. This is because clay has a large porosity. One of the disadvantages of using clay is that it easily swells in an aqueous environment, but can quickly shrink back when it is dehydrated or heated, which can damage the structure of the clay. To maintain the stability of the porosity of this clay is a challenge. One of the efforts to prevent swelling and shrinkage is to stabilize the clay interlayer area to obtain a large pore volume, and

© The Author(s) 2023

M. Hartono et al. (eds.), *Proceedings of the 4th International Conference on Informatics, Technology and Engineering 2023 (IncITE 2023)*, Atlantis Highlights in Engineering 21,
https://doi.org/10.2991/978-94-6463-288-0_37

ensure that the clay retains its porosity when it is hydrated and dehydrated. This process is known as pillarization and the resulting material is referred to as PILCs, or pillared interlayered clays. PILCs are clay materials known as layered double hydroxides (LDHs). They consist of two-dimensional layers of positively charged metal hydroxide sheets with interlayer spaces that can accommodate a variety of guest species. These unique properties resulting from PILC make them extremely valuable in a variety of applications, including adsorption and catalysis.

PILC has the basic structure of a sheet metal hydroxide layer, which is usually composed of metal cations, such as aluminum (Al) or magnesium (Mg) and coordinated to hydroxide ions (OH⁻). Expansion of the interlayer space between hydroxide sheets in PILC can be accomplished by inserting pillar ions or molecules, usually inorganic species such as metal oxides or organic molecules. This process can create a larger interlayer space and prevent swelling and shrinkage of the layers.

In Pillared Interlayered the material that is often used in PILCs is clay which is a member of the smectite clay family. This clay is a type of phyllosilicate mineral composed of stacked layers of tetrahedral and octahedral sheets, with a high specific surface area and a negative charge on the surface. The most widely used smectite clays in PILC are bentonite and montmorillonite. Bentonite and montmorillonite are types of clay that have a similar structure, consisting of a 2:1 layer, which is composed of two tetrahedral silica sheets covered with sand and an octahedral alumina sheet. Both bentonite and montmorillonite have excellent swelling properties due to their ability to adsorb water and other polar molecules in their interlayer space, so they have excellent swelling and adsorption capacities. Both types of smectite have been widely used in various industrial applications because of their unique properties, such as high surface area and cation exchange capacity.

Several bentonite/clay modification techniques have been carried out to improve the properties of bentonite-clay, including acid modification [1], polymer modification [2], alcohol modification [3], surfactant modification [4], organic matter modification [5], nanocomposite modification [6], and metal doping modification [7]. Bentonite/clay that has been modified through several of the above techniques is able to show better properties, such as increased stability, increased reactivity, and increased adsorption capacity, making it more effective in its application.

This article presents and evaluates the utilization of pillared interlayered-bentonite/clays in the context of green chemistry, focusing on adsorption and catalysis to reduce waste. The main objective of this article is to attempt to provide researchers with valuable information on clay pillarisation and its performance tests as adsorbents and catalysts. For this purposes, after a brief introduction, several applications of PILCs as adsorbents and catalysts are illustrated.

2 Utilization of PILCs as Adsorbent

Adsorption is the ability of a particular solid to adsorb a component in a mixture of gases or liquid into the surface of a solid. This process occurs due to the tendency of molecules in the surface of the solid to attract other molecules in the gas or liquid mixture due to the forces acting on it.

The most popular method for removing dyes from wastewater is adsorption, which can be achieved through the use of activated carbon [8] or ion-exchange resin [9]. Activated carbon is particularly efficient in adsorbing various types of colorants or dyes with fairly to very high capacity, but its high price and regeneration cost make it an impractical choice.

Heavy metals represent a significant group of inorganic pollutants with a profound impact on the environment. The release of these heavy metals has emerged as one of the most pressing environmental issues of our time. The release of these heavy metals can pose a threat to the water and soil environment, and pose potential hazards to plant, animal and human life. What makes these metals particularly concerning is their non-biodegradable nature, which allows them to accumulate in living tissues as they traverse through the food chain. Several noteworthy heavy metals commonly found in wastewater treatment include chromium, nickel, cadmium, copper, zinc, lead, mercury, and arsenic [10,11,12].

Clay, along with its modified forms such as pillared clays, has demonstrated considerable potential for effectively adsorbing heavy metals from aqueous solutions. The adsorption ability of clays such as bentonite or montmorillonite to adsorb metal cations from aqueous solutions has been known for a long time. The bentonite found in East Java, Indonesia, is predominantly of the Ca-Mg type. However, the hydrophilicity caused by the exchangeable metal cations in bentonite means that bentonite is usually ineffective in adsorbing organic compounds such as dyes. To overcome this, surface modifications have been carried out to improve the adsorption capacity of bentonite. In general, the capture of heavy metal ions onto natural clays involves two main mechanisms: cation exchange within the pores of the clays, and complex formation on the surface and outer pore sites of the clays [13].

Although it is known that there are many studies on heavy metal adsorption with various types of pillared clays, the main attention in research related to metal-metal adsorption using pillared clays has started to increase in the last two decades. However, the main problem related to this research is that when metal oxide pillars are inserted between the clay layers, the cation exchange capacity of the clay is reduced resulting in a decrease in metal adsorption through the cation exchange mechanism. On the other hand, efforts to improve the properties of specific surface area of clay, functional groups, clay porosity, and adsorption sites are known to increase the adsorption ability for these metal ions [14].

The utilization of organic materials into the clay structure to produce organoclays has received less attention from researchers in heavy metal adsorption applications. This is because the formation of organoclays turns out to cause sorption competition between organic cations as pollutants and heavy metal ions on adsorption sites [15]. It is also known that the presence of organic species in the clay structure causes the organophilic nature of the clay to increase, resulting in decreased heavy metal adsorption capacity because usually heavy metal adsorption mostly occurs on hydrophilic sites [16].

Related to the synthesis of these pillared clays, many studies have been conducted to explore various modifications to further enhance their adsorption capacity. One of

the most popular early studies was conducted by Yu et al. which involved the use of carbon modification of aluminum-pillared clays for cadmium adsorption [17]. Table 1 provides a summary of some of the research conducted in the last fifteen years that focused on utilizing pillared clays and modified pillared clays for heavy metal adsorption. Some of the key parameters affecting these studies are initial metal concentration, initial pH of the solution, amount of adsorbent, and contact time.

Table 1. Some adsorption of heavy metals on pillared interlayered clays

Material	SSA (m ² /g)	Adsorbate	Qmax (mg/g)	% removal	Ref.
Al-PILC	267	Pb(II)	75.35	-	[18]
		Zn(II)	31.55	-	
		Cd(II)	13.14	-	
		Cu(II)	61.35	-	
	678	Cu(II)	61.35	99	[19]
		Zn(II)	32.26	-	
		Ni(II)	50.25	-	
	191	Cu(II)	19.06	-	[7]
		Cd(II)	17.5	-	
		Co(II)	10	-	
		Cu(II)	139.78	-	[10]
		Ni(II)	99.8	-	
		Zn(II)	91.53	-	
		Si-PILC	162	Cd(II)	101.16
Pb(II)	145.04			-	
Al-Zr-PILC	162	Cr(VI)	183.2-296	-	[7]
		Cu(II)	22.23	65-98	
		Cd(II)	26	-	
Cr-PILC	184.3	Co(II)	16	-	[21]
		Pb(II)	199.65	99.82	
Al-Fe-PILC	184.3	Cr (III)	65	-	[22]
		phosphate	11.4	-	[23]

In the research that the author has done, modifications are carried out, among others, by the addition of surfactant molecules and certain metal ions. The larger the pore of a particle, the higher the adsorption capacity of the material. Bentonite that has been modified with the addition of surfactants will have a larger pore volume when compared to bentonite that is not modified with the addition of surfactants.

Based on the data in the table above, it can be seen that generally an increase in BET surface area, which also means the greater number and size of the pillared clay pores, will also be followed by an increase in sorption capacity. However, this is not the only factor that affects the adsorption ability, because the adsorption capacity of pillared clays is also strongly influenced by other parameters such as the pH of the initial solution, the initial metal concentration, the amount of adsorbent and so on. In addition,

what is also very influential is the type of metal used as a pillar material that is included in the clay structure and the type of pollutant heavy metal ions.

The ability of pillared clays to adsorb adsorbates, similar to commercially available porous adsorbents, is determined by the availability of a large number of pores and empty interlayer spaces in their structure. When chemical characteristics are fixed or unchanged, larger porous parameters often correspond to higher adsorption capacity [22].

In addition, cations residing in the structure of pillared clays are responsible for adsorbing cationic contaminants through ion exchange mechanisms. Thus the selectivity of pillared clays towards different pollutants also depends on their chemical interaction-based mechanisms.

Some researchers have proposed several adsorption mechanisms of heavy metal cations and oxyanions on modified pillared clays, such as: (1) Metal anions replace hydroxide anions on the hydrolyzed metal oxide surface, while cation exchange occurs through the exchange of cations already available on the surface and interlamellar clay sites [7]; (2) heavy metal ions undergo pseudo chemical reactions with functional groups on the surface of pillared clays to form stable complexes. This is referred to as surface complexation. Complexes formed from hydroxyl functional groups and metal oxide pillars present in the pillared clay structure are usually quite stable due to strong interactions with heavy metals [21]. Metal cations that bind to these adsorbed groups further form ternary surface complexes [24]; (3) Adsorption of metal species is also strongly influenced by electrostatic driving forces. This force occurs due to the protonation and deprotonation of the pillared clay surface which can vary at various pH levels. At acidic pH, usually metal oxyanions migrate to the positively charged surface of the pillared clay [7]. On the other hand, metal cations will interact with negative charges at high pH [21]. The presence of hydroxyl groups is one of the functional attributes that plays a crucial role in these electrostatic interactions.

3 Utilization of PILCs as Catalyst

Similar as PILCs find application as adsorbents, they have also garnered attention in the realm of catalysis. However, similar challenges have emerged; particularly concerning the preservation of their porosity stability. PILC has also been used in environmental processes in advanced oxidation processes (AOPs). The versatility of advanced oxidation processes (AOPs) is enhanced by their ability to generate radicals through various mechanisms [25, 26]. Currently, the three most extensively studied AOPs are heterogeneous photocatalysis using TiO_2 , the photo-Fenton process, and $\text{H}_2\text{O}_2/\text{UV}$ treatment [27]. However, the catalytic wet peroxide oxidation (CWPO) process is considered as the most cost-effective method among other AOPs processes,

to remove pollutants in order to overcome the limitations of homogeneous processes [28]. CWPO can allow the degradation of firm organic compounds under mild conditions because it can utilize hydrogen peroxide (H_2O_2) and solid catalysts through redox bonding to the decomposition of H_2O_2 [29]. Various types of catalysts have been used in the CWPO process, including zeolites, and PILCs.

Table 2 provides a summary of several studies conducted in the past ten years that focused on the application of pillared clays and modified pillared clays as a catalyst. The key factors influencing these studies include the reaction process and initial pollutant

Table 2. Some applications of pillared interlayered clays as catalyst

Material	Pollutans	Reaction process	% conversion	Ref.
Al-Cr PILC	phenol	Catalytic Wet Air Oxidation	-	[30]
TiO ₂ -ZnO/clay	acetaminophen	Photocatalytic degradation	90	[31]
Co/Al-PILCs	Azo dyes	oxidation	69	[32]
Fe/Al-PILC	NOx	reduction	90	[33]
Fe/Ti-PILCs	NOx, propene	reduction	95	[34]
Fe ₂ Zn ₂ Al-PILCs	Orange II	catalytic oxidation wet peroxide	77	[35]
Ti-PILCs	Toluene	oxidation	90	[36]
Co-Al-PILCs	oxone	degradation	100	[37]
Fe Zn-PILCs	Palmitic acid	esterification	80	[38]
Ti-Fe-PILCs	Basic blue	photodegradation	90	[39],[40]
	Phenolic	Degradation	16	[41]
	E.Coli	Degradation of bacteria	99	[42],[43]
Al-Fe-PILCs	Phenol	hydroxylation	75	[44],[45]

The catalytic process using modified clays by pillarization of clays involves the utilization of clay materials that have been chemically or physically modified to enhance their catalytic properties. These modified clays act as catalysts in various chemical reactions, facilitating the conversion of reactants into desired products.

The mechanism of catalytic reactions in pillared layered clays can take place through a variety of processes depending on the element used as the pillifying agent. It also depends on the specific modification technique used and the nature of the reaction. However, in general there are some basic principles and mechanisms that are usually involved.

One mechanism is the interaction between reactant molecules and active sites on the surface of modified clay catalysts (PILC). This is because clay modification can introduce additional active sites, such as functional groups or metal species capable of increasing catalytic activity. Reactant molecules are adsorbed onto these active sites, leading to the formation of intermediate species and subsequent chemical transformations.

In addition to these mechanisms, other processes involve increased mass transfer and diffusion in the modified clay catalyst. The modified clay structure (among others through the pillarisation process) can provide a more favorable environment for reactant molecules to reach the active sites, thus capable of increasing the overall efficiency of the catalytic process [46], [47].

Pillarisation process on PILCs is also able to increase selectivity towards certain reactions or products. This selectivity arises due to the unique properties generated during the modification process through pillarisation and clay intercalation, such as the presence of certain functional groups or metal ions. These properties can influence adsorption and reaction pathways, leading to the formation of specific product preferences [48].

Overall, the mechanism of catalytic processes using modified clays involves a combination of surface interactions, mass transfer improvements, and selectivity enhancements. The specific details of the mechanism depend on the nature of the modification and the targeted reaction, making it a versatile approach in various catalytic applications.

Photocatalytic or photodegradation mechanisms using Pillared Interlayered Clays (PILCs) involve the utilization of light energy to induce chemical reactions that result in the degradation or transformation of pollutants. PILCs, with their unique structural features and catalytic properties, offer excellent potential as photocatalysts for environmentally friendly applications.

The mechanism of photocatalytic or photodegradation using PILCs typically involves the following steps:

1. Light absorption: PILCs possess semiconducting properties, enabling them to absorb light energy across a broad range of the electromagnetic spectrum, including UV, visible, and even infrared light. This light absorption initiates the photocatalytic process by exciting electrons from the valence band to the conduction band, creating electron-hole pairs.
2. Redox reactions: The photoexcited electrons (e^-) in the conduction band and the corresponding holes (h^+) in the valence band of PILCs play a crucial role in redox reactions. The photogenerated electrons are available for electron transfer reactions, while the holes act as strong oxidizing agents.
3. Adsorption of pollutants: The PILCs' large surface area and interlayer spacing provide ample sites for the adsorption of pollutants onto their surfaces. This step involves the physical or chemical interaction between the pollutant molecules and the active sites on the PILCs, facilitating their subsequent degradation.

4. Charge separation and migration: Once the pollutant molecules are adsorbed onto the PILC surface, the photoexcited electrons and holes undergo charge separation and migration. The electrons migrate to the surface or to specific active sites, while the holes may react with water or hydroxyl groups on the PILC surface to generate hydroxyl radicals ($\bullet\text{OH}$) or other reactive oxygen species (ROS).
5. Reactive species generation: The photoinduced electrons on the PILC surface react with molecular oxygen (O_2) adsorbed on the surface to produce superoxide radicals ($\bullet\text{O}_2^-$) or other ROS. These highly reactive species play a crucial role in the subsequent degradation of adsorbed pollutants through oxidation reactions.
6. Pollutant degradation: The generated reactive species, including hydroxyl radicals and superoxide radicals, attack the adsorbed pollutants, initiating various degradation pathways. The pollutants undergo oxidative reactions, leading to the formation of smaller, less harmful intermediates and eventually mineralization into simpler and non-toxic end products such as carbon dioxide (CO_2) and water (H_2O).

The efficiency and selectivity of the photocatalytic or photodegradation process using PILCs can be influenced by various factors, including the PILC composition, interlayer spacing, surface functionalization, light intensity, wavelength, and the nature of the targeted pollutants. Optimizing these parameters can enhance the overall photocatalytic activity and improve the degradation efficiency of PILCs for specific pollutants [49][50].

Overall, the photocatalytic or photodegradation mechanism using PILCs involves the absorption of light energy, charge separation and migration, generation of reactive species, and subsequent degradation of pollutants through oxidation reactions. PILCs' unique structural characteristics and catalytic properties make them promising candidates for eco-friendly applications aimed at addressing environmental pollution [51][52].

The catalytic process using modified clays (PILCs) offers several advantages and disadvantages, which are outlined below:

Advantages:

1. Enhanced Catalytic Activity: Modification of clays can significantly increase their catalytic activity by introducing active sites or altering the surface properties. This allows for improved reaction rates and higher conversion efficiencies compared to unmodified clays.
2. Selectivity Control: PILCs can exhibit selective catalytic properties, enabling control over reaction pathways and product distributions. This selectivity is often achieved by incorporating specific functional groups or metal species during the modification process.
3. Abundant and Cost-effective: Clays are naturally abundant minerals, making them a cost-effective choice for catalysts. The widespread availability of clays reduces production costs and makes them attractive for large-scale applications.

4. Environmentally Friendly: PILCs can serve as greener alternatives to traditional catalysts, as they often operate under milder reaction conditions, reducing energy consumption and minimizing waste generation.
5. Stability and Reusability: PILCs can possess improved stability under harsh reaction conditions, maintaining their catalytic activity over extended periods. Additionally, they can be easily separated from reaction mixtures and reused multiple times, contributing to cost-effectiveness and sustainability.

Disadvantages:

1. Limited Catalytic Sites: PILCs may result in a limited number of active catalytic sites compared to other catalysts. This limitation can affect the overall catalytic performance and may require higher catalyst loadings or longer reaction times.
2. Specific Reaction Requirements: Some PILCs exhibit optimal catalytic activity under specific reaction conditions, such as temperature, pressure, or pH. Deviating from these optimal conditions can lead to reduced catalytic efficiency.
3. Diffusion Limitations: In some cases, the PILCs may have restricted mass transfer properties, limiting the accessibility of reactants to the catalytic sites. This can result in diffusion limitations and reduced reaction rates, especially for bulky or large molecules.
4. Catalyst Deactivation: Depending on the reaction environment, PILCs can be susceptible to deactivation through processes such as fouling, leaching of active species, or sintering. Catalyst deactivation can reduce the catalytic efficiency and require additional steps for catalyst regeneration.
5. Limited Scope of Applications: The applicability of PILCs as catalysts may be limited to certain types of reactions or specific classes of compounds. Some modifications may be more effective for certain reactions, while others may not exhibit the desired catalytic performance in different applications.

It is important to note that the advantages and disadvantages can vary depending on the specific modification method, clay type, and targeted catalytic process. Careful consideration of these factors is necessary when designing and utilizing modified clays as catalysts in various applications [22],[14],[53].

4 Conclusion

In conclusion, the application of PILCs as adsorbents and catalysts presents a promising approach in various fields, aligning with the principles of green chemistry. PILCs, formed by introducing inorganic pillars into the interlayer spaces of clay minerals, exhibit unique properties that make them excellent candidates for a wide range of applications in green chemistry.

The mini-review highlights how PILCs offer a sustainable and eco-friendly approach to green chemistry. As adsorbents, PILCs demonstrate high efficiency in

removing organic pollutants and heavy metal ions from water and soil, mitigating environmental contamination. Their increased surface area and tunable pore size enable selective adsorption, ensuring the targeted removal of contaminants without generating harmful waste streams.

Moreover, PILCs serve as solid acid and base catalysts, facilitating various acid-base catalyzed reactions. Their shape-selective catalytic properties enhance the specificity and yield of desired products while minimizing undesired by-products. The use of inorganic pillars further reduces the need for hazardous or expensive metal complexes, contributing to greener and more sustainable catalytic processes.

The article underscores the importance of choosing appropriate clay minerals and inorganic precursors during the pillaring process to tailor PILCs for specific applications. The ability to optimize their properties allows for the design of efficient and highly selective catalysts, reducing energy consumption and increasing reaction yields, thus promoting the principles of green chemistry.

Overall, PILCs hold significant potential in advancing green chemistry initiatives. As environmentally friendly materials, they pave the way for greener and more sustainable chemical processes by offering efficient adsorption and catalysis capabilities. As research in this area continues to progress, PILCs are expected to play an increasingly vital role in promoting environmentally conscious practices and facilitating the transition towards a more sustainable and eco-friendly future.

References

1. Kabdrakhmanova, S., Aryp, K., Shaimardan, E., Kanat, E., Selenova, B., Nurgamit, K., Kerimkulova, A., Amitova, A., Maussumbayeva, A.: Acid modification of clays from the Kalzhat, Orta Tentek deposits and study their physical-chemical properties. *Materials Today: Proceedings* (2023).
2. Kotal, M., Bhowmick, A. K.: Polymer nanocomposites from modified clays: Recent advances and challenges. *Progress in Polymer Science* 51 127-187 (2015).
3. Seydibeyoğlu, M., Demiroğlu Mustafafov, S., Atagür, M., Ocaktan, S.: Modification of Clay Crystal Structure with Different Alcohols. *Natural Resources* 08 709-715 (2017).
4. Jiang, T., Zhang, W., Ilango, A. K., Feldblyum, J. I., Wei, Z., Efstathiadis, H., Yigit, M. V., Liang, Y.: Surfactant-Modified Clay for Adsorption of Mixtures of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous Solutions. *ACS Applied Engineering Materials* 1(1), 394-407 (2023).
5. Elnady, M., Saad, G., Eid, A., Aboelkhair, M.: Modification of Egyptian clay by different organic cations. *Egyptian Journal of Chemistry* 62(10), 1761-1769 (2019).
6. Cavalcante, A. L. G., Chaves, A. V., Fechine, P. B. A., Holanda Alexandre, J. Y.

- N., Freire, T. M., Davi, D. M. B., Neto, F. S., de Sousa, I. G., da Silva Moreira, K., de Oliveira, A. L. B., de Mattos, M. C., Oliveira, M. C. F., de Brito, M. V., Ballereau, S., Bernardes-Génisson, V., da Fonseca, A. M., dos Santos, J. C. S.: Chemical modification of clay nanocomposites for the improvement of the catalytic properties of Lipase A from *Candida antarctica*. *Process Biochemistry* 120 1-14 (2022).
7. Mnasri-Ghnimi, S., Frini-Srasra, N.: Removal of heavy metals from aqueous solutions by adsorption using single and mixed pillared clays. *Applied Clay Science* 179 105151 (2019).
 8. Nizam, N. U. M., Hanafiah, M. M., Mahmoudi, E., Halim, A. A., Mohammad, A. W.: The removal of anionic and cationic dyes from an aqueous solution using biomass-based activated carbon. *Scientific Reports* 11(1), 8623 (2021).
 9. Huang, R., Zhang, Q., Yao, H., Lu, X., Zhou, Q., Yan, D.: Ion-Exchange Resins for Efficient Removal of Colorants in Bis(hydroxyethyl) Terephthalate. *ACS Omega* 6(18), 12351-12360 (2021).
 10. Ouellet-Plamondon, C., Lynch, R. J., Al-Tabbaa, A.: Comparison between granular pillared, organo- and inorgano-organobentonites for hydrocarbon and metal ion adsorption. *Applied Clay Science* 67-68 91-98 (2012).
 11. Ma, L., Zhu, J., He, H., Tao, Q., Zhu, R., Shen, W., Theng, B. K. G.: Al13-pillared montmorillonite modified by cationic and zwitterionic surfactants: A comparative study. *Applied Clay Science* 101 327-334 (2014).
 12. Bensid, N., Zerdoum, R., Hattab, Z., Boutaleb, Y., Bououdina, M.: Intercalated organo-bentonite as efficient biosorbent for aromatic carboxylic acids from wastewater. *Journal of Molecular Liquids* 337 116443 (2021).
 13. Ilic, I., Jovic-Jovicic, N., Bankovic, P., Mojović, Z., Loncarevic, D., Gržetić, I., Milutinovic-Nikolic, A.: Adsorption of nicotine from aqueous solutions on montmorillonite and acid-modified montmorillonite. *Science of Sintering* 51 93-100 (2019).
 14. Najafi, H., Farajfaed, S., Zolgharnian, S., Mosavi Mirak, S. H., Asasian-Kolur, N., Sharifian, S.: A comprehensive study on modified-pillared clays as an adsorbent in wastewater treatment processes. *Process Safety and Environmental Protection* 147 8-36 (2021).
 15. Uddin, M. K.: A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. *Chemical Engineering Journal* 308 438-462 (2017).
 16. Ajduković, M. J., Jović, J. N. P., Milutinović, N. A. D., Banković, P. T., Mojović, Z. D.: The influence of clay modification on electrochemical behavior of

- quinhydrone. *Tehnika* 77 9-14 (2022).
17. Yu, R., Wang, S., Wang, D., Ke, J., Xing, X., Kumada, N., Kinomura, N.: Removal of Cd²⁺ from aqueous solution with carbon modified aluminum-pillared montmorillonite. *Catalysis Today* 139(1), 135-139 (2008).
 18. Eloussaief, M., Hamza, W., Kallel, N., Benzina, M.: Wastewaters decontamination: Mechanisms of PB(II), ZN(II), and CD(II) competitive adsorption on tunisian smectite in single and multi-solute systems. *32(2)*, 229-238 (2013).
 19. Kumararaja, P., Manjaiah, K. M., Datta, S. C., Sarkar, B.: Remediation of metal contaminated soil by aluminium pillared bentonite: Synthesis, characterisation, equilibrium study and plant growth experiment. *Applied Clay Science* 137 115-122 (2017).
 20. Mao, H., Zhu, K., Li, B., Yao, C., Kong, Y.: Synthesis of titania modified silica-pillared clay (SPC) with highly ordered interlayered mesoporous structure for removing toxic metal ion Cr(VI) from aqueous state. *Applied Surface Science* 292 1009-1019 (2014).
 21. Georgescu, A.-M., Nardou, F., Zichil, V., Nistor, I. D.: Adsorption of lead(II) ions from aqueous solutions onto Cr-pillared clays. *Applied Clay Science* 152 44-50 (2018).
 22. Budhyantoro, A., Widi, R. K.: Effect of the Surfactant Molecule as Intercalating Agent toward Natural Bentonite Structure. *International Journal of Materials Sciences* 8(2), 91-96 (2013).
 23. Fransiscus, Y., Widi, R. K., Aprilasti, G. O., Yuharma M. D.: Adsorption of phosphate in aqueous solutions using manganese dioxide. *International Journal on Advanced Science Engineering Information Technology* 8(3), 818-824 (2018).
 24. Ma, L., Zhu, J., Xi, Y., Zhu, R., He, H., Liang, X., Ayoko, G. A.: Simultaneous adsorption of Cd(ii) and phosphate on Al13 pillared montmorillonite. *RSC Advances* 5(94), 77227-77234 (2015).
 25. Miklos, D. B., Remy, C., Jekel, M., Linden, K. G., Drewes, J. E., Hübner, U.: Evaluation of advanced oxidation processes for water and wastewater treatment – A critical review. *Water Research* 139 118-131 (2018).
 26. Macías-Quiroga, I. F., Rojas-Méndez, E. F., Giraldo-Gómez, G. I., Sanabria-González, N. R.: Experimental data of a catalytic decolorization of Ponceau 4R dye using the cobalt (II)/NaHCO₃/H₂O₂ system in aqueous solution. *Data in Brief* 30 105463 (2020).
 27. Macías-Quiroga, I. F., Henao-Aguirre, P. A., Marín-Flórez, A., Arredondo-

- López, S. M., Sanabria-González, N. R.: Bibliometric analysis of advanced oxidation processes (AOPs) in wastewater treatment: global and Ibero-American research trends. *Environmental Science and Pollution Research* 28(19), 23791-23811 (2021).
28. Ribeiro, R. S., Silva, A. M. T., Figueiredo, J. L., Faria, J. L., Gomes, H. T.: Catalytic wet peroxide oxidation: a route towards the application of hybrid magnetic carbon nanocomposites for the degradation of organic pollutants. A review. *Applied Catalysis B: Environmental* 187 428-460 (2016).
 29. Quintanilla, A., Munoz, M.: Editorial Catalysts: Special Issue on Trends in Catalytic Wet Peroxide Oxidation Processes. *Catalysts* 9(11), 918 (2019).
 30. Baloyi, J., Ntho, T., Moma, J.: A Novel Synthesis Method of Al/Cr Pillared Clay and its Application in the Catalytic Wet Air Oxidation of Phenol. *Catalysis Letters* 148(12), 3655-3668 (2018).
 31. Tobajas, M., Belver, C., Rodriguez, J. J.: Degradation of emerging pollutants in water under solar irradiation using novel TiO₂-ZnO/clay nanoarchitectures. *Chemical Engineering Journal* 309 596-606 (2017).
 32. Macías-Quiroga, I. F., Pérez-Flórez, A., Arcila, J. S., Giraldo-Goméz, G. I., Sanabria-Gonzalez, N. R.: Synthesis and Characterization of Co/Al-PILCs for the Oxidation of an Azo Dye Using the Bicarbonate-Activated Hydrogen Peroxide System. *Catalysis Letters* 152(7), 1905-1916 (2022).
 33. Qian, W.-y., Su, Y.-x., Yang, X., Yuan, M.-h., Deng, W.-y., Zhao, B.-t.: Experimental study on selective catalytic reduction of NO with propene over iron based catalysts supported on aluminum pillared clays. *Journal of Fuel Chemistry and Technology* 45(12), 1499-1507 (2017).
 34. Wen, N., Dong, S., Su, Y., Deng, W., Zhao, B.: Effect of synthesis parameters on catalytic performance of Fe/Ti-PILC catalysts for SCR-C₃H₆ and in situ DRIFTS study. *Journal of Environmental Chemical Engineering* 8(6), 104555 (2020).
 35. Ye, W., Zhao, B., Gao, H., Huang, J., Zhang, X.: Preparation of highly efficient and stable Fe,Zn,Al-pillared montmorillonite as heterogeneous catalyst for catalytic wet peroxide oxidation of Orange II. *Journal of Porous Materials* 23(2), 301-310 (2016).
 36. Liang, X., Qi, F., Liu, P., Wei, G., Su, X., Ma, L., He, H., Lin, X., Xi, Y., Zhu, J., Zhu, R.: Performance of Ti-pillared montmorillonite supported Fe catalysts for toluene oxidation: The effect of Fe on catalytic activity. *Applied Clay Science* 132-133 96-104 (2016).
 37. Marković, M., Marinović, S., Mudrinić, T., Ajduković, M., Jović-Jovičić, N., Mojović, Z., Orlić, J., Milutinović-Nikolić, A., Banković, P.: Co(II) impregnated

- Al(III)-pillared montmorillonite–Synthesis, characterization and catalytic properties in Oxone® activation for dye degradation. *Applied Clay Science* 182 105276 (2019).
38. Widi, R. K., Budhyantoro, A., Riadi, L.: Esterification of palmitic acid over acid catalyst from modified bentonite. *International Journal of Applied Chemistry* 6(1), 11-18 (2010).
 39. Widi, R. K., Budhyantoro, A., Savitri, E.: Use of TiO₂-Fe₃O₄ pillared bentonite as photocatalyst in photodegradation of basic blue. *Journal of Chemical and Pharmaceutical Research* 7 183-188 (2015).
 40. Widi, R. K., Suciani, I., Savitri, E., Reynaldi, R., Budhyantoro, A.: Photocatalytic decolorization of Basic Blue 41 using TiO₂-Fe₃O₄-bentonite coating applied to ceramic in continuous system. *Chemical Engineering Communications* 207(2), 203-212 (2020).
 41. Savitri, E., Widi, R. K., Budhyantoro, A.: The effect of the calcinations temperature during synthesis of TiO₂-Fe₃O₄-bentonite as photocatalyst material. *Journal of Chemical and Pharmaceutical Research* 7 70-75 (2015).
 42. Widi, R. K., Savitri, E., Angelina, O., J, S., Budhyantoro, A.: Antibacterial Inactivation of *Escherichia coli* after TiO₂-Fe₃O₄-Bentonite Photocatalytic Treatment. *International Journal on Advanced Science, Engineering and Information Technology* 8 2367 (2018).
 43. Widi, R. K., Savitri, E., Budhyantoro, A., Yasaputera, R., Gunardi, J.: Application of Photocatalyst Material Bentonite Ti Based as Antimicrobial Paint. *International Journal on Advanced Science, Engineering and Information Technology* 10 2498 (2020).
 44. Widi, R. K., Budhyantoro, A., Savitri, E.: Catalytic performance of Al-HDTMA bentonite impregnated Fe on phenol hydroxylation. *International Journal of Applied Engineering Research* 9(20), 7521-7529 (2014).
 45. Widi, R. K., Budhyantoro, A., Christianto, A.: Phenol hydroxylation on Al-Fe modified-bentonite: Effect of Fe loading, temperature and reaction time. *IOP Conference Series: Materials Science and Engineering* 273(1), 012007 (2017).
 46. Fatimah, I., Fadillah, G., Yanti, I., Doong, R.-a.: Clay-Supported Metal Oxide Nanoparticles in Catalytic Advanced Oxidation Processes: A Review. *Nanomaterials* 12(5), 825 (2022).
 47. Baloyi, J., Ntho, T., Moma, J.: Synthesis and application of pillared clay heterogeneous catalysts for wastewater treatment: a review. *RSC Advances* 8(10), 5197-5211 (2018).

48. Kalmakhanova, M. S., Diaz de Tuesta, J. L., Massalimova, B. K., Gomes, H. T.: Pillared clays from natural resources as catalysts for catalytic wet peroxide oxidation: Characterization and kinetic insights. *Environmental Engineering Research* 25(2), 186-196 (2020).
49. Cardona, Y., Węgrzyn, A., Miśkowiec, P., Korili, S. A., Gil, A.: Catalytic photodegradation of organic compounds using TiO₂/pillared clays synthesized using a nonconventional aluminum source. *Chemical Engineering Journal* 446 136908 (2022).
50. Saeed, M., Muneer, M., Haq, A. u., Akram, N.: Photocatalysis: an effective tool for photodegradation of dyes—a review. *Environmental Science and Pollution Research* 29(1), 293-311 (2022).
51. Freitas, W., Trigueiro, P., Marinho, T., Honorio, L. M., Silva-Filho, E. C., Furtini, M. B., Cecília, J. A., Fonseca, M. G., Osajima, J.: The Role of Clay Mineral-Derived Photocatalysts in Insights of Remediation. *Ceramics* 5(4), 862-882 (2022).
52. Bel Hadjltaief, H., Galvez, M. E., Ben Zina, M., Da Costa, P.: TiO₂/clay as a heterogeneous catalyst in photocatalytic/photochemical oxidation of anionic reactive blue 19. *Arabian Journal of Chemistry* 12(7), 1454-1462 (2019).
53. Macías-Quiroga, I. F., Rengifo-Herrera, J. A., Arredondo-López, S. M., Marín-Flórez, A., Sanabria-González, N. R.: Research Trends on Pillared Interlayered Clays (PILCs) Used as Catalysts in Environmental and Chemical Processes: Bibliometric Analysis. *The Scientific World Journal* 2022 5728678 (2022).

Open Access This chapter is licensed under the terms of the Creative Commons Attribution-NonCommercial 4.0 International License (<http://creativecommons.org/licenses/by-nc/4.0/>), which permits any noncommercial use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license and indicate if changes were made.

The images or other third party material in this chapter are included in the chapter's Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the chapter's Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

