

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

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**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 to chemical science that seeks to minimize the negative impact of chemical processes on the environment. One of the key principles of green chemistry is the utilization of renewable and environmentally friendly materials, such as clay. Clay is a highly useful material for adsorption, catalyst, and ion exchange purposes, owing to its large porosity. However, due to its tendency to swell, maintaining the shape of clay can be challenging. Clay can expand with hydration and contract when dehydrated or heated, which can cause damage to the clay structure. To prevent this from happening, the interlayer area of the clay needs to be supported with a stable pillar to create a large pore volume, ensuring the clay maintains its porosity despite hydration and dehydration. This process is known as pillarization.

Bentonite, a type of clay mineral, has been widely used in various industrial applications due to its unique properties, such as high surface area and cation exchange capacity.

To enhance the porosity, active sites, and adsorption capacity of bentonite, surface and structural modifications are recommended to improve its performance in areas such as adsorption and catalysis. Different modification techniques have been used to improve bentonite-clay properties, including acid modification [1], polymer modification [2], alcohol modification [3], surfactant modification [4], organic material modification [5], nanocomposite modification [6], and metal doping modification [7]. The modified bentonite exhibits improved properties, such as increased stability, improved reactivity, and enhanced adsorption capacity, making it a more effective material in its application.

This article aims to evaluate the utilization of pillared interlayered-bentonite/clays in the context of green chemistry, with a focus on adsorption and catalysis to reduce the waste. The main objective of this article is to provide valuable information to researchers about the pillarization of bentonite or clays and its performance tests as an adsorbent and a catalyst. For this purposes, after short introduction, some application of modified bentonite or clays as adsorbents and catalysts are illustrated.

## 2 Utilization of PILCs as Adsorbent

Adsorption is the ability of a particular solid to absorb 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. Therefore, more cost-effective alternatives, such as bentonite, have been developed.

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. There are two types of surface modification: impregnation and organo-functionalization or grafting. Impregnation involves replacing exchangeable inorganic cations with organic cations, which can change the surface properties of bentonite from hydrophilic to hydrophobic or organophilic [10]. On the other hand, organo-functionalization or grafting involves the grafting of organic groups on the bentonite mineral surface [11].

The adsorption ability of bentonite can also be improved by treatment with strong inorganic acid, which alters its structure, chemical composition, and physical properties. This process results in the so-called "organo-bentonite" [12].

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 [7].

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. 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 modified pillared clays

Material	SSA (m <sup>2</sup> /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		Cr(VI)	183.2-296	-	[20]
Al-Zr-PILC	162	Cu(II)	22.23	65-98	[7]
		Cd(II)	26	-	
		Co(II)	16	-	
Cr-PILC	184.3	Pb(II)	199.65	99.82	[21]
Al-Fe-PILC		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 to its use as an adsorbent, the utilization of pillared interlayered clays (PILCs) in the field of catalysis has also become a research focus. And similar challenges have arisen, particularly regarding the stability of its porosity. 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  $\text{TiO}_2$ , 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 ( $\text{H}_2\text{O}_2$ ) and solid catalysts through redox bonding to the decomposition of  $\text{H}_2\text{O}_2$  [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 modified pillared clays as catalyst

Material	Pollutans	Reaction process	% conversion	Ref.
Al-Cr PILC	phenol	Catalytic Wet Air Oxidation	-	[30]
$\text{TiO}_2\text{-ZnO/clay}$	acetaminophen	Photocatalytic degradation	90	[31]
Co/Al-PILCs	Azo dyes	oxidation	69	[32]
Fe/Al-PILC	$\text{NO}_x$	reduction	90	[33]
Fe/Ti-PILCs	$\text{NO}_x$ , propene	reduction	95	[34]
Fe,Zn,Al-PILCs	Orange II	catalytic wet peroxide oxidation	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]
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The catalytic process using modified 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 the catalytic process using modified clays can vary depending on the specific modification technique employed and the nature of the reaction. However, there are some common underlying principles and mechanisms involved.

One mechanism is the interaction between the reactant molecules and active sites on the surface of the modified clay catalyst. The modification of clay can introduce additional active sites, such as functional groups or metal species that enhance the catalytic activity. The reactant molecules adsorb onto these active sites, leading to the formation of intermediate species and subsequent chemical transformations.

Another mechanism is the enhancement of mass transfer and diffusion within the modified clay catalyst. The modified structure of the clay can provide a more favorable environment for reactant molecules to reach the active sites, improving the overall efficiency of the catalytic process [46],[47].

Furthermore, the modified clay catalyst can also exhibit selectivity towards specific reactions or products. This selectivity can be attributed to the unique properties introduced during the modification process, such as the presence of specific functional groups or metal ions. These properties can influence the adsorption and reaction pathways, leading to preferential formation of certain products [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, includ-

ing 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 ( $\bullet OH$ ) 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 ( $\bullet O_2^-$ ) 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 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:** Modified clays 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:** Modified clays 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:** Modified clays 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:** The modification of clays 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 modified clays 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 modified clays 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, modified clays 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 modified clays 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 modified clays as adsorbents and catalysts presents a promising approach in various fields, aligning with the principles of green chemistry. Modified clays offer several advantages, including enhanced adsorption capacities, selectivity control, and improved catalytic activity. These advancements contribute to the development of sustainable and efficient processes for pollutant removal and chemical transformations.

As adsorbents, modified clays demonstrate improved efficiency in the removal of heavy metal pollutants from wastewater. The introduction of modifications enhances their adsorption capacities and selectivity, allowing for the effective removal of specific contaminants. This targeted approach minimizes waste generation, reduces the need for large quantities of adsorbents, and promotes the concept of green chemistry by providing a more sustainable solution for pollution mitigation.

Furthermore, the application of modified clays as catalysts offers several benefits in the realm of green chemistry. Modified clays with tailored catalytic properties enable selective transformations, leading to desired product distributions and minimizing the formation of unwanted side products. The stability and reusability of modified clays contribute to waste reduction and cost-effectiveness, further supporting the principles of green chemistry.

The concept of green chemistry promotes the design and utilization of chemical processes that are environmentally friendly, economically viable, and socially responsible. The application of modified clays as adsorbents and catalysts aligns with these principles by offering efficient and sustainable solutions for pollutant removal and chemical transformations. The use of abundant and cost-effective clays, coupled with their enhanced performance through modification, demonstrates the potential for greener alternatives in various industries and applications.

However, it is important to continue research and development in this field to address the limitations associated with modified clays, such as limited catalytic sites and specific reaction requirements. By further exploring the modification techniques, optimizing catalyst design, and expanding the scope of applications, the potential of modified clays as adsorbents and catalysts in green chemistry can be fully realized, leading to more sustainable and environmentally conscious practices in the future.

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