

A SHORT REVIEW ON CLAY MATERIAL AND ITS APPLICATION FOR WATER TREATMENT

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Abstract: The clays are naturally occurred with large surface area and cation exchange capacity. Clays are frequently utilized for the adsorption of toxic dye and heavy metal contaminants in water because of their environmentally benign character. Numerous studies involve clay, modified clay, and the introduction of inorganic or organic elements into the interlayer space of the clays. As a result, process-wise selectivity changes may be possible. By treating the clay surface with acid and/or base or functionalizing it with specific additions, the surface can be encouraged for larger exchanges. In this review article, we have summarized recent works on the use of natural and modified clays as selective adsorbents for water treatment.

Keywords: Clay; Cation exchange capacity; Water treatment; Toxic dye; Heavy metal

1. Introduction:

1.1. Clay Minerals:

The term "clay minerals" has denoted to a family of phyllosilicates that often form near the surface of the earth to give clay with resistance, its malleability, and then become hard upon drying or burning. The clay minerals could be classified into seven groups according to the characteristics of layer type (1:1 or 2:1), the magnitude of net layer charge (x) per formula unit, the type of interlayer species was: kaolin-serpentine, pyrophyllite-talc, smectite, vermiculite, mica, chlorite, and interstratified clay minerals [1]. The term referred aluminosilicates with water group that produce majority of clay (2 nm) content of the soil. These natural resources were arranged similarly to the main minerals that are chemically or structurally derived from the crust of the Earth. However, weathering cause changed in the normal process of atoms and ions inside their structures. The majority of the natural resources were produced by metamorphic rocks under high pressure and temperature conditions. These minerals were rather stable inside the Earth, but once they are exposed to the surface environment, changes might take place. Quartz, mica, and feldspar are some of the main minerals that could persist in soils despite their high resistance, while other, less tough minerals were more susceptible to breakdown and weathering, leading to the formation of secondary minerals. The end product of further altering the main mineral structure (incongruent reaction) or neoformation, which involved for manufacture of more stable structure by recrystallization and precipitation (congruent reaction) to form secondary minerals. Because of their platy or flaky nature and the fact that one of its primary structural constituents was a stretched sheet of SiO_4 tetrahedra, these secondary minerals were frequently referred to as phyllosilicates [2]. Typical structure of Natural clay can be seen from Figure 1.

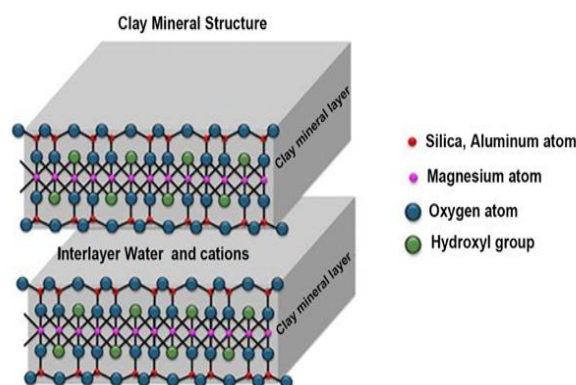


Figure 1. Typical structure of Natural clay. Image adapted from <https://www.jpl.nasa.gov/images/pia17598-clay-mineral-structure-similar-to-clays-observed-in-mudstone-on-mars> [3].

Clay minerals were commonly categorized into three types based on the quantity and arrangement of tetrahedral and octahedral slips in the fundamental assembly. Depending on how much variety was available, these were further classified into five classes. Tetrahedral and octahedral sheets were the basic building blocks of layer minerals and are present in a 1:1 ratio. The $Al_2Si_2O_5(OH)_4$; the general formula of kaolin group represented the two-sheet mineral type of clay. Kaolinite, which was dioctahedral and exhibits Al^{3+} octahedral and Si^{4+} tetrahedral coordination, was the most common mineral in this class. Van der Waals bonds, which bind the sheets together, were formed by the hydroxyls of the octahedral sheet and the basal oxygens of the tetrahedral sheet.

Layers of clay minerals were thought to be held tightly together by hydrogen bonds. The twisting group, whose general formula is $Mg_3Si_2O_5(OH)_4$, represented the trioctahedral variety of the 1:1-layer minerals. Two tetrahedral sheets were joined to an octahedral sheet to form a three-sheet mineral type known as 2:1, which included the mica, smectite, and vermiculite groups. Talc [$Mg_3Si_4O_{10}(OH)_2$] and pyrophyllite [$Al_2Si_4O_{10}(OH)_2$] were prominent examples of the electrically neutral 2:1 type mineral, in which adjacent layers were connected to one another by Van der Waal's connections. Despite the fact that these two minerals were rarely found in soils [2]. Table 1 provides information on the characteristics of clay minerals.

Table 1: Properties of clay mineral groups. Adapted the table as Open Access Article [2].

Group	Layer type	Net negative charge (cmolk ⁻¹)	Surface area (mV)	Basal spacing (nm)
Kaolinite	1:1	2-5	10-30	0.7
Fine-grained mica	2:1	15-40	70-100	1.0
Smectite	2:1	80-120	600-800	1.0-2.0
Vermiculite	2:1	100-180	550-700	1.0-1.5
Chlorite	2:1:1	15-40	70-100	1.4

The basic layer structure of the group of minerals known as chlorites is 2:1, similar to that of talc or pyrophyllite, with an interlayer brucite- or gibbsite-like sheet forming a 2:1:1 structural arrangement. The 2:1 negative charge of the layer is balanced by the net positive charge produced by the isomorphic replacements in the interlayer hydroxide sheet. However, a variety of cation types might exist in these gibbsite- or brucite-like islands, which lead to numerous diverse mineral species in this group. Due to the absence of water adsorption in the interlayer gap, chlorites were regarded as non-expansive materials.

Clay minerals were infrequently discovered in the soil environment as homogeneous mixes of several mineral kinds, groups, or phases. Rather, they were intricate blends of main minerals and intermediates with a range of structural and compositional traits. A single mineral grain could also be composed of more than one type of clay or have particles that fall halfway between two well-known minerals. Interstratified or mixed-layer minerals were the names given to these types of minerals. These mixed-layer mineral sequences include kaolinite-smectite, chlorite-vermiculite, mica-vermiculite, and mica smectite. The soil clay fraction might also contain trace amounts of other substances, such as some of the oxides, hydroxides, and hydroxy-oxides (sesquioxides) of Si, Al, and Fe as well as some problematic crystalline aluminosilicates, in addition to the phyllosilicates already discussed. Quartz and opal were typical examples of Si-oxide minerals that were typically found in the clay fraction due to their remarkable resistance to weathering. Opal was a quartz polymorph that is weakly crystalline and forms as a precipitate in Si-supersaturated fluids, in volcanic ash, or as a result of biological activity. Goethite (FeOOH) was the most common clay fraction. Gibbsite $Al(OH)_3$ was the main Al-hydroxide representative in clay segments of severely worn soils, and it is a Fe-mineral. The weakly crystalline aluminosilicate clay minerals allophane and imogolite were typically found in clay fractions of soils formed of volcanic rocks [2]. The correct clays must then be chosen in order to serve as an efficient adsorbent, which required a convertor. The amount of surface acid sites, the specific surface area, and the pore volume were all increased by clay mineral alteration [4]. Table 2 provides a detailed explanation of clay minerals.

Table 2: The properties of clay minerals. Adapted the table as Open Access Article [5].

Interlayer material	Group	Octahedral Character	Species
1:1 Clay minerals			

None or H ₂ O Only $\epsilon_c = 0$	Serpentine- Kaolin	Tri	Amesite, berthierine, Brindleyite, cronstedtite, Fraipontite, kellyite, Lizardite, nepouite
		Di	Dickite, halloysite (planar) Kaolinite, nacrite
		Di-Tri	odinite
2:1 Clay minerals			
None $\epsilon_c = 0$	Talc - pyrophyllite	Tri	Kerolite , pimelite, talc, willemite
		Di	Ferripyrophyllite, pyrophyllite
Hydrated exchangeable cations $\epsilon_c = 0.2 - 0.6$	smectite	Tri	Hectorite, seponite, Sauconite, stevensite, swinefordite
		Di	Beidellite, Montmorillonite, volkonskoite
Hydrated exchangeable cations $\epsilon_c = 0.6 - 0.9$	Vermiculite	Tri	Trioctahedral vermiculite
		Di	Diocahedral vermiculite
Non hydrated monovalent cations $\epsilon_c = 0.6 - 1.0$	True (flexible) mica	Tri	Biotite, lepidolite, Phlogopite, etc.
		Di	Celadonite, illite, Glauconite, muscovite, Paragonite, etc.
Non hydrated Divalent cations $\epsilon_c = 1.8 - 2.0$	Brittle mica	Tri	Anandite, bitytite, Clintonite, kinoshitalite
		Di	Margarite
Hydroxide sheet, ϵ_c variable	Chlorite	Tri	Baileychlore, chemosite, Clinochlore, nimite, pennantite

1.2. Modified clay minerals:

To get rid of organic molecules, surfactants could convert the clay mineral's hydrophilic qualities into hydrophobic ones. Techniques for altering clay, such as thermal treatment and acid activation, were efficient. Clay impregnation, clay composites modified with hybrid silicates, clay composites supported by nanoscale zero-valent iron, clay-supported manganese iron oxide-bentonite clay composite, clay composites with activated carbon, magnetic/polymer-clay composites, and clay composites with biochar were some of the unconventional techniques for altering clay minerals. The porosity of the clay material could be increased through chemical and physical procedures since clay minerals have suitable adsorption capacities. Clay minerals have been altered using inorganic acids, bases, salts, heat treatment, pillaring by various polyhydroxy cations, clay modified with polymers, and surfactants [4]. Physical grinding, heat and acid treatments, ion exchange and pillaring events, organic and polymer loading reactions, micro- and nanocomposites generation, and organic and polymer loading reactions could all lead to the strategic structures helpful for fascinating environmental contaminants. The various modified clay minerals showed different process of production, characteristics, and applications relevant to environmental effects [6]. A wide range of modifications to montmorillonite's characteristics and properties had been described in the literature. These included pillaring, intercalation, heat treatment, and acid activation. Using hybrid chitosan-montmorillonite materials as a kind of eco system as an alternative to metallic salts in the treatment of water, particularly for the formation of drinking water, which was a novel problem, had been extensively explored [7].

1.2.1. Pillard clay material:

The common pillaring method can be used to increase the porosity, specific surface area, mechanical and thermal stability, and catalytic activity of clay minerals. This procedure helped the clay to become an excellent adsorbent for preserving the environment. The main objective of pillared clay (PILC) preparation was to eliminate persistent

porosity in untreated clay minerals. Its porosity was maintained when hydrating or dehydrating PILC. Previously, organic cations and organometallic pillars were mostly utilized. Most PILCs were used in catalytic processes, but they also had the characteristics needed to be an adsorbent in molecular sieves and for environmental protection. The clay must be refined, acid-activated, or biologically altered before being intercalated by the pillaring agents. PILCs were materials with an extremely porous structure that are made by separating clay layers with pillaring agents [4]. The purification and Na-activation of clay was the first step in the total synthesis of PILC. The formation of the pillaring solution was the following step, which is followed by the reaction of exchange between the interlayer space and the pillaring solution's polyoxycation and the formation of a stable PILC during the calcinations process. In recent years, attempts have been made to increase the clay mineral's ability to absorb contaminants from wastewater. There has been published research on the use of PILCs in wastewater treatment. The enhancement of the structural and textural qualities of bentonite clays was another benefit of PILCs. As a result, it is now possible to create green technologies for PILC synthesis, modification, and application at lower synthesis costs. Microwaves and ultrasonic waves were applied during the ageing, precipitation, and intercalation processes with the powdered clay in order to create mixed metal PILC with Al₁₃-Fe and Al₁₃-Fe-Ce in the solid state. This artificial technique was described by Olaya et al. (2009) [8]. The pillarization might increase the surface acidity regions of the clay minerals. Lewis' acidity sites are more prevalent in PILCs than Bronsted's acidity sites. Lewis' acidity sites were produced when the pillars undergo a transformation into metal oxide clusters during the calcination process. The Bronsted acidity sites in clay minerals originate from their structural hydroxyl groups and eventually disappear after heat treatment as a result of protons entering the clay's lattice sites. The PILCs' surface area, surface acidity, porosity, thermal and mechanical stability, and other qualities could all be enhanced by the addition of several pillaring agents.

In contrast to the traditional way of the pillaring process, this method used a straightforward operation method to reduce the amount of water. In this study, the pillaring agent and the powdered raw montmorillonite in the dialyzed form. In this investigation, a little amount of de-ionized (DI) water was used in an operation method to reduce amount of water. Sarabadan et al. (2019) [9] developed the Zeolite-Montmorillonite (Zeolite-Mt) nano adsorbent. In order to remove the contaminated and cationic dye Crystal Violet (CV) from water, a produced nano adsorbent was used.

1.2.2. Organic component containing clay:

Clay's crystalline structure was altered to incorporate organic molecules, most typically quaternary ammonium cations, to create organoclays [6]. Many classes also discussed the use of organoclays synthesised from other environmentally beneficial organic compounds, like vitamins (thiamine) and amino acids (e.g., arginine, lysine), for the impurity-elimination process [10]. Because they were cationic, organic molecules interacted with hydrated cations in the clay mineral's interlayer area. Another result of the quaternary cationic N atom in the compound is a lengthy alkyl chain, which gives the substance its hydrophobic properties. The complexity and hydrophobicity of alkyl chains, which can be single, double, or triple branched and have a range of lengths, were increased. The interlayer region of the natural clay material contained hydrated cations, which gave it a hydrophilic characteristic. Due to interactions between quaternary ammonium compounds and clay minerals, which result in hydrophobic organoclays, these hydrated cations were replaced with hydrophobic organic cations [6]. Clay nanocomposite was originally created by treating clay minerals with organoclays. Hydrophilic polymers worked well with natural clay. Therefore, following the intercalation of polymers, the clay's naturally hydrophilic surface can be converted to an organophilic one. The most common cationic surfactants for the polymer intercalation process were typically alkylammonium and alkyl phosphonium cations in their primary, secondary, tertiary, and quaternary forms. Due to their adaptable molecular structure and two projected single-tail surfactants whose head groups were covalently bonded by a hydrophobic insert of variable length, dimeric surfactants have recently attracted a lot of attention [4].

A clay mineral should be able to hold more organic molecules if it has a higher Cation Exchange Capacity (CEC) value. Smectite or montmorillonite (MMT) was a better option for tolerating an organic alteration than kaolinite or palygorskite. The expanding properties of the clay mineral were a vital factor to take into account while choosing a clay mineral for organoclay manufacture. Unlike kaolinite and palygorskite, which would only adsorb the organic molecules as an outer surface coating, clay minerals like MMT would be able to introduce the organic molecules in its interlayer structure. Organoclays were commonly used in environmental applications where electrostatic attraction, ion exchange, and hydrophobic partitioning were the primary contaminant removal techniques [6]. Kryuchkova et al., 2021 [11] evaluated the adsorption properties of pure montmorillonite (MMT) and montmorillonite treated with stearyl trimethyl ammonium using drugs such as carbamazepine, ibuprofen, and paracetamol as a test (hydrophobic MMT-STA). The efficiency of adsorption was assessed under various backgrounds for solution pH, temperature, contact time, initial medicinal concentration, and adsorbate/adsorbent

mass ratio. MMT-STA surpassed clean MMT in the elimination of all the drugs tested. The ability of hydrophobic montmorillonite to bind to medications was greatest for carbamazepine (97%) followed by ibuprofen (95%) and paracetamol (63-67%).

1.2.2. Hybrid organic-inorganic clay material:

The inorgano-organo-clay materials were made by substituting inorganic polycations for the exchangeable cations in montmorillonite and then functionalizing the polycations with the necessary organic molecules. The research had utilized benzothiazole, coupled modified montmorillonite with hydroxyl iron pillared and cationic panthenol intercalation (Fe-CPMMt), in an effort to reduce the effects of the increasing pollution. The results of the batch adsorption experiments showed that the maximum adsorption capacity of Fe-CPMMt for benzothiazole was 69.72 mg/g, compared to the original acidified sodium montmorillonite, alone hydroxyl iron pillared montmorillonite (Fe-AMt), and alone cationic panthenol intercalated montmorillonite, were 11.39 mg/g, 43.68 mg/g, and 38.18 mg. The Langmuir isotherm adsorption model and the pseudo-second-order kinetic model were both well-fit by the endothermic and sluggish benzothiazole adsorption process on Fe-CPMMt-1.0 [12].

1.2.3. Acid activated clay mineral:

Clay minerals could be subjected to an acid treatment to alter their surface and enhance their adsorption properties [13]. First, in acid-activated clay, protons had been intercalated between clay interlayer gaps. The presence of dissolving cations, such as cations from the partial dissolution of the octahedral layer, as well as minor damage to the silicate layer might also be noticed. The dissolution of some Fe(II), Fe(III), Al(III), and Mg(II) of the octahedral layer demonstrated the significance of cracked edge Al/Mg-O-bonds after acid treatment. Numerous studies had been conducted on the impact of temperature, contact time, and acid content on the structural alteration of clays. These limits should be managed at levels below what is ideal for the clay structure. Because of the more complex interaction between specific surface area, porosity, and acid concentration, proton saturated clay showed a high CEC level [5]. Concentrated inorganic acids harm the environment by increasing the production of acidic wastewater, rusting equipment, and operational dangers. In contrast, clay minerals with just marginally negative properties could be modified further using organic acids (such as carboxylic and sulfonic acids). In recent times, collective alteration employing various functional groups was a promising way to minimize the critical elements of acid activation and to improve interface properties for a wide variety of pollutant elimination. Acid activated clays presented significant barriers to sewage treatment that must be overcome [4].

1.2.4. Thermally modified clay:

Thermal modification based on altering the micro and macro characteristics of clay structures has been used to change the physico-chemical and structural features of clay minerals and to boost their adsorption capacity. The size, form, porosity, crystallization, and amorphization of clay could be changed by heating. The temperature ranges at which dihydroxylation and dehydration take place were available for thermal stimulation in three different ranges. Dehydration reduced adsorbate waters while dihydroxylation reduced structural waters, which also impacts the macro- and micro-porosity of clay minerals. Clay minerals, including the kaolinite group, commonly transition to an amorphous shape while retaining some structural frameworks at this temperature. An advancement in temperature took place when crystal phases can form. In this situation, clay minerals lose their native crystallographic orientation [4]. The weakly adsorbed water and volatile compounds were removed by heating the bentonite to 100 °C, which increased the clay's surface area. Again, clay minerals can be treated at temperatures higher than 500 °C, which causes dihydroxylation of their surfaces and edges, so decreasing their surface area. However, this development only happens up to a certain temperature, over which the reverse reaction occurs. The heat treatment could speed up the heavy metal adsorption by altered clay minerals [6]. Researchers looked at how the mechanical, thermo-mechanical, and thermal properties of phenolic composites reinforced with carbon fibre were altered by OMMT, an organo-modified kind of montmorillonite nanoclay (CFRP). CFRP using various O-MMT concentrations (ranging from 0 to 2.5 wt%) was made. With the addition of 1.5 wt % O-MMT, it was found that the heat resistant polymer composite had the best properties.

1.2.5. Use of other chemically active component for modified clay:

Recent years have seen a steady increase in research on clay polymer nanocomposites, particularly in the fields of automotive, food packaging, paper coating, sensors, and water remediation. Combining clay and polymer yields

a nanocomposite material with at least one phase that is in the nanoscale range (100 nm). There were three basic methods for creating clay polymer nanocomposites: melt intercalation, in-situ polymerization, and solvent extraction. In melt intercalation, a mixture of clay material and polymer was melted in a melting chamber under controlled stirring rates, residence periods, and temperatures in a nearly solvent-free environment. To clean up contaminated water, clay polymer composites produced from both synthetic and natural polymers were used. For enhancement of adsorption capacity, prevent monomer agglomeration, and increase mechanical and thermal strength, clay particles were added to polymer matrixes [6]. Montmorillonite was a soft phyllosilicate mineral that was a member of the smectite family and has a 2:1 expanding crystal structure. Nonmetallic clays with the typical chemical formula $(Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)_4O_{10}(OH)_2 \cdot nH_2O$ make up the majority of its composition. These minerals belonged to the monoclinic clay-like mineral subclass. Chemically hydrated sodium calcium aluminium magnesium silicate hydroxide was $Na_xCa_y(Al, Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ with K, Fe, and other common alternatives to cations were available; the precise ratio of cations changes depending on the source [14].

2. Adsorption of water pollutants by clay from water:

2.1 Adsorption of several hazardous dyes:

During an adsorption process, a species (adsorbate) was transferred from the solution to the solid surface (adsorbent), held together by physical and/or chemical forces. Very few recent reports have been available for dye adsorption by clays. Sarabadan et al., 2019 [9] employed Response Surface Methodology (RSM) with Zeolite-Montmorillonite to explore how variables including pH, temperature, adsorbent dosage, and starting dye concentration affected the effectiveness of dye removal (RSM). To maximize the efficiency of dye removal, RSM changed the experimental setting. The optimal conditions for maximum dye removal were reached at pH 9, 25 °C, 2 g/L of adsorbent, with a starting dye concentration of 40 mg/L. Under these conditions, the greatest removal efficiency was 99.9%. Pormazar and Dalvand, 2020 [15] employed modified montmorillonite nano clay in 2020 as a super adsorbent to remove Direct Red 23 dye from aqueous solution. It had been investigated how the ideal parameters, such as contact time, initial dye concentration, adsorbent dose, pH, and ionic strength, affected the effectiveness of adsorption. The adsorption studies' findings indicated that pH 2 had the best percentage of DR23 dye elimination. According to zeta potential studies, the anionic dye's sulfonic groups and the adsorbent's positive surface charge interacted electrostatically to form the adsorption process. The pseudo-second-order kinetic model and the Langmuir isotherm were determined to be the best descriptions of the DR23 adsorption, and the maximum monolayer adsorption capacity at pH 2 and the adsorbent dosage of 0.05 g/L was found to be 2,500 mg/g.

2.2 Adsorption of heavy metals by clay minerals:

Due to their toxicity and widespread use, heavy metals pose a serious threat to the environment. Heavy metals that were common in aquatic environments had been linked to a variety of health issues in both people and animals. Since they were present in sludge, fertilisers, pesticides, municipal waste, mine waste, and smelting industries, heavy metals were the primary class of inorganic pollutants that pollute a significant portion of the earth. Due to their persistent, non-degradable, and accumulative qualities, the bulk of heavy metals were recognised to be cancer-causing substances and may pose a serious hazard to the living population. Several intricate adsorption processes, including surface complexation, ion exchange, and direct bonding between metal cations and clay mineral surfaces, were involved in the uptake of heavy metals by clay minerals [7]. A novel titanium pillared clay (Ti-PILC) impregnated with potassium iodine (KI) was created in the current investigation to extract elemental mercury (Hg⁰). The enhanced KI-impregnated Ti-PILC demonstrated good Hg⁰ removal capabilities due to its greater BET surface area compared to the original clay or the KI-impregnated clay. It was shown that a rise in temperature increased Hg removal's effectiveness. In order to study the red dye's adsorptive capabilities after being modified by hexadecyltrimethylammonium bromide, Cr (VI) removal was carried out in batch tests (HDTMA). The optimal pH range for the greatest Cr (VI) adsorption on red clay was found to be 4-6.5. In terms of cation exchange capacity, specific surface area, and adsorption capacity, smectites perform better than other types of clay. Clay/polymer nanocomposites frequently use organo-modified montmorillonites (OMMT). Depending on the pH, stirring time, common ion effects, eluent type, concentration, and volume of the solution, organically modified montmorillonite clay (OMHP-MMT) was employed to extract copper (II). After stirring for 10 minutes, it demonstrated good Cu (II) selectivity and removal efficiency over the pH range of 3.0-8.0. At pH 6.0, the maximum elimination efficiency (99.2%) was attained. Montmorillonite with carbon-improved aluminium pillars has been used to demonstrate efficient Cd (II) uptake from an aqueous solution.

Second-order kinetics was used to control the Cd (II) adsorption. At a pH of 6.0, Cd (II) adsorption was minimal; however, at a pH of > 6.0, it significantly increased [7]. The removal of Pb (II) and Cd (II) from contaminated water samples was studied using clays (Kaolinite and Montmorillonite). In contrast to Cd (II), which

was adsorbed endothermally, Pb (II) was adsorbed exothermally. The removal of copper and cesium from aqueous solutions demonstrated the sorbent capability of aluminum-pillared-layered montmorillonites (PILMs). Using modified kaolinite and montmorillonite that had been treated with tetrabutylammonium (TBA) bromide, the adsorption of Fe (III), Co (II), and Ni (II) ions from aqueous solution was carried out. However, under the same testing conditions, the calcined TBA clay minerals in this work exhibit a decreased adsorption capability compared to the parent clay minerals. The adsorption of Fe (II), Co (II), and Ni (II) was reduced by 55%, 47%, and 44%, respectively, by the reaction of kaolinite with TBA. Only 44, 41, and 42% of the parent montmorillonite's Fe (III), Co (II), and Ni (II) adsorption capabilities, respectively, were present in calcined TBA-montmorillonite. The large TBA groups that block several negatively charged sites and maybe also the pores are to blame for these unfavourable outcomes. It was possible to remove Co^{2+} , Sr^{2+} , and Cs^+ from an aqueous solution by using phosphate-modified montmorillonite (PMM). Co^{2+} and Sr^{2+} sorptions were endothermic and highly reliant on the pH of the starting solution, whereas Cs^+ sorptions were exothermic. Researchers believed that surface complexation was the primary mechanism of Co^{2+} sorption onto PMM because of the considerable pH dependency of Co^{2+} sorption (Uddin 2017). A potential adsorbent for removing As(III) and As(V) from arsenic-contaminated water was Ti-pillared montmorillonite. A TiO_2 -pillared montmorillonite (TiO_2/MMT) adsorbent was employed in another investigation to remove. An aqueous solution could be cleaned of As (III) and As (V). In the first 20 minutes, the adsorption capacity grew significantly, and in less than an hour, the adsorption equilibrium was reached. These findings showed that TiO_2 was a MMT adsorbent with enhanced arsenic adsorption capability.

Recently, Fe (II)-montmorillonite, an environmentally friendly clay substance, was used to decrease Cr (VI) in an aqueous solution. At an acidic pH and temperatures as high as 50 °C, the Cr (VI) reduction accelerated quickly. At a pH range of 3-5, a complete reduction occurred in about 5 minutes. The manufacture of nano@lignocellulose (nano@LC) and a nano@LC/MT nanocomposite, as well as the ability of the nano@LC/MT to adsorb manganese ions from aqueous solution, were both studied by An et al. in 2018. By varying the starting Mn(II) concentration, pH, adsorption temperature, and time, the parameters for Mn(II) adsorption on the nano@LC/MT nanocomposite were thoroughly investigated. The outcomes showed that at a Mn(II) starting concentration of 900 mg/L, a solution pH of 5.8, an adsorption temperature of 55 °C, and an adsorption period of 160 minutes, the adsorption capacity of the nano@LC/MT nanocomposite for Mn(II) achieved 628.0503 mg/g. Following the adsorption of manganese metal, the nanocomposite underwent significant morphological changes, which are depicted in Figure 3. [16, 17].

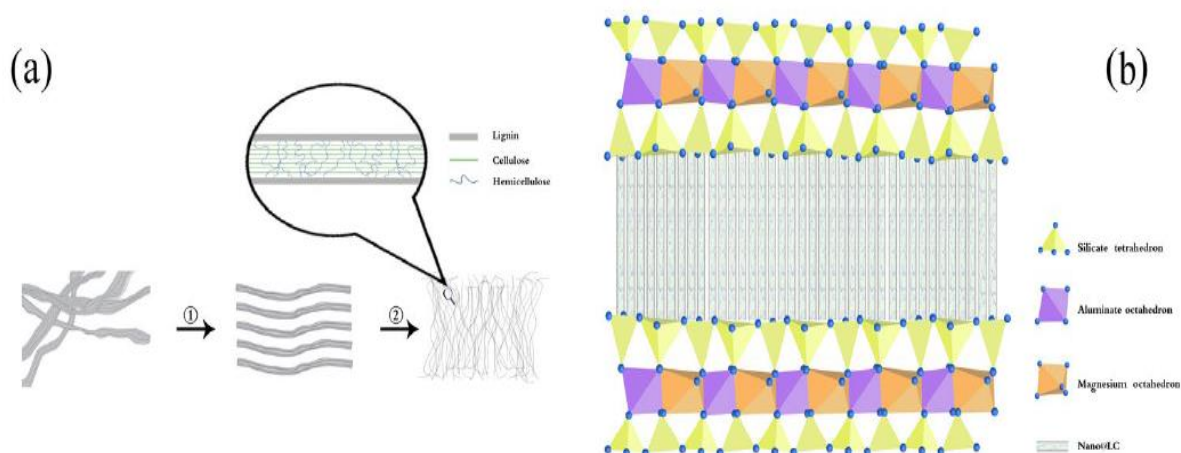


Fig. 3. Figure showing (a) Preparation of nano@LC: ① the intertwined lignocellulosic clusters are unwound and ② the LC beams are destroyed to afford nano@LC; (b) Schematic representation of the nano@LC/MT nanocomposite. Adapted from open access article [16].

3. Conclusions:

An effort has been made in this study to concentrate on recent advancements concerning clays and clay alteration. The removal of harmful metals and colours from water and wastewater was done using dyes. The clay's usage for waste water treatment proved successful. In addition, a variety of adsorbents could be covered with montmorillonites that have been intercalated or pillared, organically modified, inorgano-organically modified, thermally and/or acid activated. Despite the fact that there are still many information gaps that need to be

addressed, the current study demonstrates that the work has been created as a result of the use of clay and its modified varieties over the previous few recent years. Several of the urgent issues that demand action are: The effectiveness of these adsorbents in multi-component systems needs to be investigated for the adsorbents' practical use, as the majority of studies are restricted to single adsorbate systems. Researchers have not been very fond of column studies; thus, it is important to assess the costs of chemically altering clays with various chemicals and other methods.

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