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Clay and clay minerals: A brief review from fundamentals to applications

ABSTRACT

Clay and clay minerals are naturally occurring materials and available abundantly on the earth. They are inexpensive, and have a range of structures and properties with mechanical and heat stability. They are layered magnesium or aluminium silicates composed of tetrahedrally coordinated silicate sheets and octahedrally coordinated magnesium or aluminium hydroxide sheets. Because of natural abundance and environment friendly nature, clay and clay minerals have been used in different industrial sectors. In this review article, classification of clay minerals, structures, properties and their applications in different sectors have been discussed. Some of the important sectors, where clay and clay minerals are being used extensivelyare Agriculture and farming, Fertilizers and soil conditioners, Pesticides and Herbicides, Animal feeds, Food industry, Detergent industry, Cosmetic and pharmaceutical industry, Biomedical industry, Textile and paint industry, Oil and gas Exploration, Construction Industry, Environmental Protection, Carbon dioxide capture, Photocatalysis, etc. We tried to update the current knowledge with recent developments and progress in clay and clay minerals in this review.

Keyword: *Clay, Clay minerals, structure,property, applications, agriculture industry, pharmaceutical industry.*

1. INTRODUCTION

Clay has been recognized and utilized by humans since ancient times [1]. It is nearly indispensable in modern living and is used in the preparation of various materials for a wide range of applications. Clay is a naturally occurring material with a malleable texture when damp, but ithardens throughcalcination.Clay minerals belong to the category of hydrous layer aluminosilicates, comprising a significant portion of the phyllosilicate mineral family, with particle sizes ranging from at least 2 mm to 4 mm in at least one dimension. Due to their small size and high surface area-to-volume ratio, clay minerals exhibit distinctive properties. They are crucial components of soils, estuarine, delta, lake, and ocean sediments [2]. A variety of clay types and clay minerals exist, each with diverse industrial applications.

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A variety of clay types and clay minerals exist, each with diverse industrial applications. Clay minerals have also been used in traditional medicine for curative and therapeutic purposes throughout history. The physicochemical attributes of clay minerals, such as their substantial adsorption capacity, exchangeability, water dispersibility, and rheological behaviour, make them well-suited for a wide array of applications. Numerous clay minerals find their use in various industries, including cement, agriculture, paper, paint, food, ceramics, petroleum, pharmaceuticals, and biomedicine, owing to their abundance, cost-effectiveness, and multifaceted roles. The demand for clay-based products is consistently growing.In the construction sector, clay minerals play a pivotal role as reinforcing agents in tiles and bricks.

Moreover, they significantly contribute to enhancing soil properties within the agricultural domain. They also play a crucial role in environmental protection against contaminants and toxic elements. Extensive research has focused on the application of clay minerals for the removal of hazardous substances like heavy metals, pharmaceutical compounds, and dyes from polluted water. Additionally, some organic compounds can undergo polymerization reactions catalysed by clay minerals. The future anticipates a high demand for clay-based nanocomposites and pillared clays. Consequently, it is imperative to collate the latest knowledge and research within this field while outlining the necessary advancements.This review article strives to highlight the diverse applications of clay and clay minerals in significant industries.

2. CLAY AND CLAY MINERALS

There isa variety of clay, such asCeramic clays,Paper clays, Earthenware clays, Stoneware clays, Ball clays, Fire clays, kaolin clays, etc. Clay minerals are the main components of raw materials of clay and are formed in presence of water. They are of different types, such as montmorillonite, halloysite, vermiculite, kaolinite, illite, chlorite, sepiolite, and palygorskite [3,4]. According to structures, classification of clay minerals is shown in Fig. 1 [4].

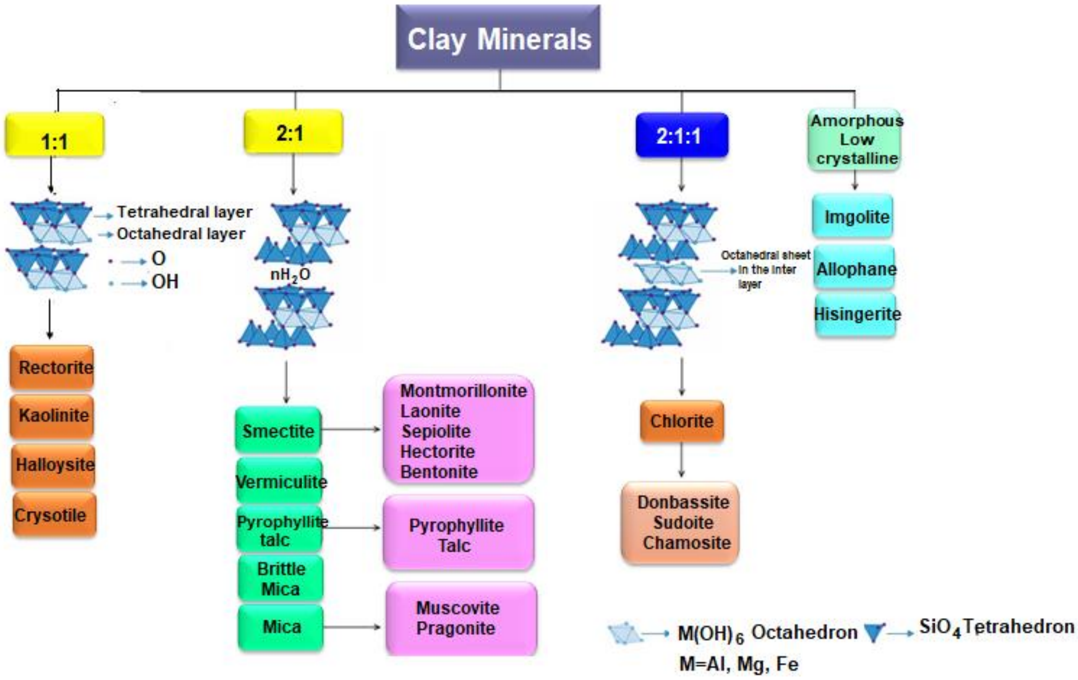

Figure 1. Clay classification [4]

In clay minerals, there are tetrahedral (T) and octahedral (O) sheets forming 1:1 (T-O) or 2:1 (T-O-T) sheets (Fig. 2) [5]. Kaolinite and serpentine are the examples of 1:1 clay mineral. Octahedral sheet is located between tetrahedral ones in 2:1 type of clay minerals. Depending on the nature of the atoms present in the layer structure, it can acquire a negative charge.In 2:1 family, the minerals present arepyrophyllite, vermiculites, talc, smectites, micas and chlorites [5]. The Octahedron is formed by linking six oxygen atoms to the cation such as Al^{3+}, Mg^{2+}, Fe^{3+} or Fe^{2+}. While the tetrahedron core is built with connecting four oxygen atoms with the cation such as Al^{3+}, Fe^{3+} or Si^{4+}.

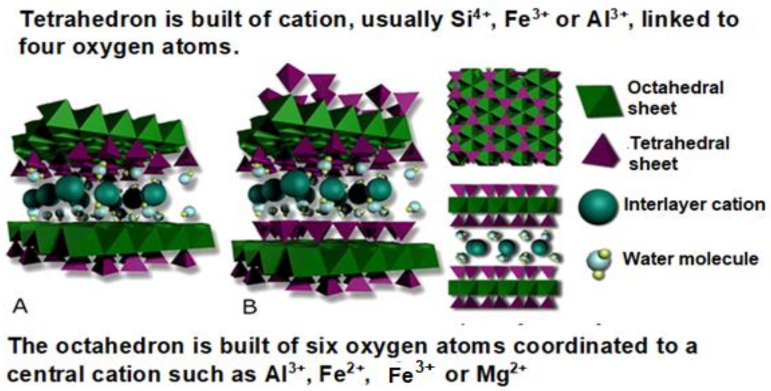

Figure 2. Representation of T-O (A) T-O-T (B) type clay minerals [5]

Kaolinite, with the chemical formula of “$Al_2[Si_2O_5](OH)_4$, is a naturally occurring inorganic silicate clay mineral with a layer structure”. It consists of siloxane and gibbsite-like layers and has lot of applications.Clays that are rich in Kaolinite mineral are known as kaolin. In general kaolinite is always present in clay.Crystal structures of some clay minerals are shown in Fig.3 [6].

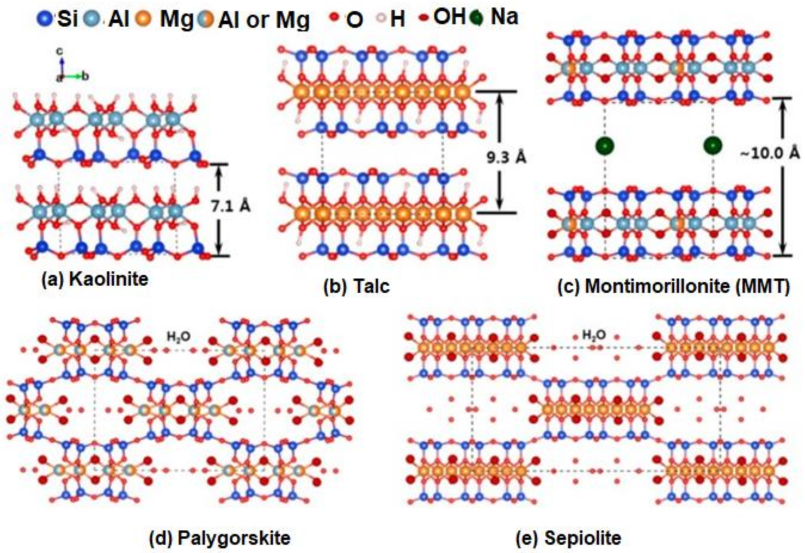

Figure 3. Crystal structures of some clay minerals [6]

3. CLASSIFICATION OF CLAY MINERALS

Clay minerals are classified as in Fig.4. [7,8].The atomic structure of the clay minerals consists of two basic units, an octahedral sheet, and a tetrahedral sheet. The silica tetrahedral sheet and the octahedral sheet are joined by sharing the apical oxygens or hydroxyls to form what is termed as the 1:1 clay mineral layer (e.g. kaolinite) or the 2:1 clay mineral layer (e.g. illite).

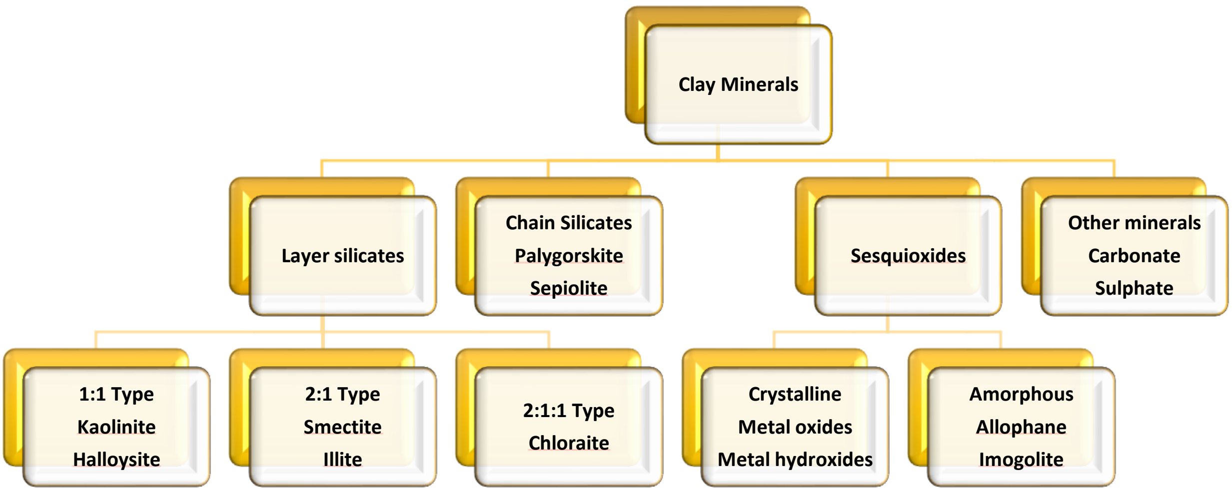

Figure 4.. Classification of the clay minerals

Kaolinite is an ideal di-octahedral clay mineral belonging to the phyllosilicate family and the kaolin/serpentine group, characterized by the chemical formula $Al_2Si_2O_5(OH)_4$. This mineral exhibits a layered structure, with several polymorphs sharing the same formulation, including dehydrated halloysite, dickite, and nacrite. The fundamental building blocks of kaolinite's structure are $Al(OH)_6$ octahedra, which combine through shared edges to form two-dimensional octahedral sheets. To maintain electro-neutrality within these sheets, approximately one-third of the octahedral positions remain vacant, akin to the arrangement found in gibbsite ($Al(OH)_3$). In the arrangement of kaolinite's atomic structure, a tetrahedral sheet is linked to an octahedral sheet via O_2−/OH− bonds (Fig. 5) [9]. This linkage is facilitated by the apical oxygens of the SiO_4 tetrahedra, which interact with one corner of the $Al(OH)_6$ octahedra. This unique connectivity results in a mineral structure of the 1:1 type, often referred to as TO. The interplay of these interconnected sheets contributes to kaolinite's characteristic properties and behaviour, making it a significant mineral in various geological and industrial contexts.

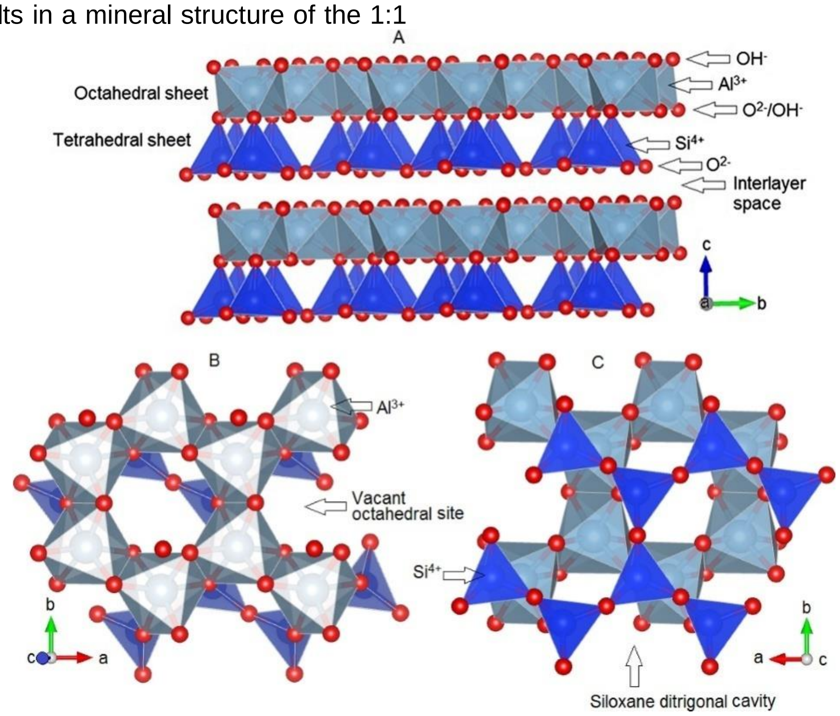

Figure 5. Polyhedral representation of the kaolinite structure, oriented along the indicated axis. Side view (A), top view (B), and bottom view (C) [9]

Illite minerals have a 2:1 layer structure with an interlayer structure and general formula ($K_{1-1.5}A1_4[Si_{7-6.5}A1_{1-1.5}O_{20}]$ (OH_4). Al^{3+} occupies a quarter of the tetrahedral sites creating a negative charge in the layer structure, balanced by monovalent cations, commonly K^+, occupying interlayer sites (Fig. 6). Illites combine the properties of swelling and dispersible clays because of their interlayered structure. These unique characteristics make it challenging to stabilize illite clays [10]. The morphology of illite is irregular with granules or elongated spines.

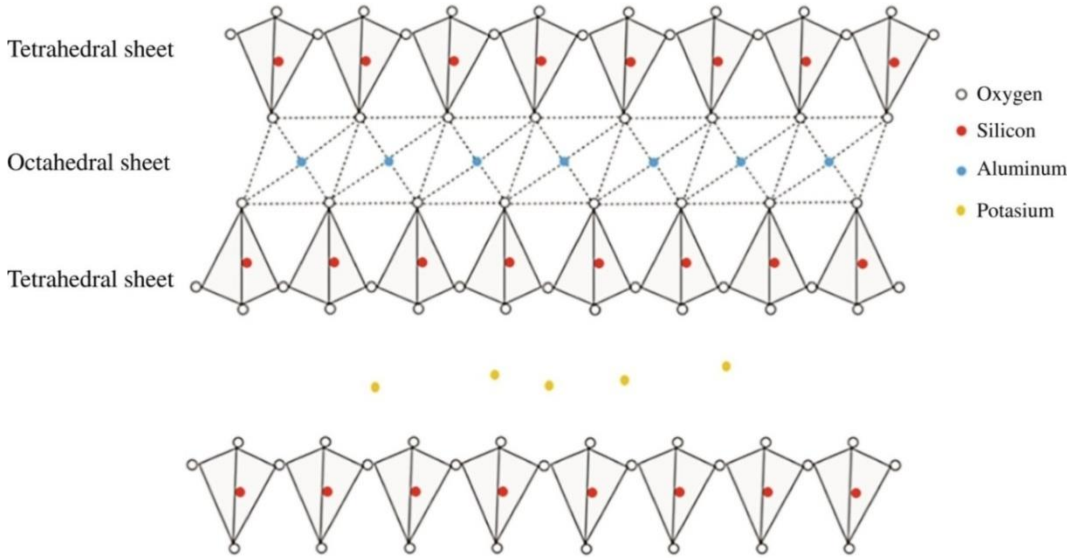

Figure 6. Illite structure [10]

4. PROPERTIES OF CLAY AND CLAY MINERALS

4.1. Ion exchange ability

Clay minerals can adsorb some cations and anions based on the charge balance requirement in the overall or local structural unit. A research work reported by Kim has shown the removal of five different metal ions through adsorption and ion exchange property of clay minerals [11]. These ions are in a position to get exchange easily with other external ions without altering the basic silicate structure of the mineral [8]. The reacting ions display quantitative relationship among them that makes ion exchange reactions more complex than the sorption. The exchange capacity depend on the size of the particles, quality of crystallinity and the nature of the adsorbed ion. Thus instead of having a unique value of exchange capacity, a number of values are obtained for a specific mineral. The exchange capacity of the minerals having hydroxyl groups in the structural unit e.g.imogoloite, allophane, kaolinite etc vary with change of pH. The change of acidity or basicity of the medium has pronounce effect on the dissociation of the hydroxyl group.

It has been observed that under a specific set of conditions, any two ions are not equally exchangeable. For example, replacing power of calcium is higher than sodium and thus sodium can be easily replaced by calcium but not the other way round. Hexagonal cavities of the silicate layer is occupied by potassium and ammonium ions because of their similar size. These cations are preferentially adsorbed between the layers of vermiculite or vermiculitic minerals. Various 1:1 layer minerals have negative surface charge due to the dissociation of the surface hydroxyl groups. These negative surface charge can strongly adsorb heavy metal ions such as zinc, copper, lead etc.

Table1. Specific surface area and cation exchange capacity of important clay minerals

Clay Mineral	Cation Exchange Capacity (CEC) at pH7 (milliequivalents/100 gm)	Specific Surface Area (SSA),(m^2/gm)
Illite	10-40	10-100
Kaolinite	3-15	5-40
Smectite	80-120	40-800
Chlorite	10-40	10-55
Palygorskite/ Sepiolite	3-20	40-180
Halloysite (Hydrated)	40-50	1100
Vermiculite	100-150	760
Allophane	30-135	2200
Imogolite	20-30	1540

The cation exchange method is used to improve the chemical and physical properties of smectite clay mineral which was further used for removal of ascorbic acid [12]. The ion exchange capacity of clay minerals has important role in determining the economical use of these minerals. Thecation exchange capacity (CEC) of some important clay minerals are listed in Table 1 [8].

4.2. Swelling behavior

The swelling of clay mineral happens when water is adsorbed by the interlayer space causing expansion between the layers. The reason behind the expansion or swelling is due to the force that the clay particles interact with each other or the interaction energy among them or more specifically due to the hydration energy. Swelling process is associated with huge volume change due to the change in water content in the clay mineral. The swelling capacity of clay minerals depend on many factors: (a) Charge density of the layers (b) Valency of the interlayer ions (c) Concentration of ions in solutions (d) Water content in the interlayer of the clay minerals (e) composition of the clay minerals [8]. Fig. 7 depicts the clay minerals with different swelling capacity and Table 2 displays the swelling potential of different clay minerals.

Swelling is possible when the clay minerals contain more than 50% mineral particles in size range of lesser than two micron. Understanding swelling capacity of clay minerals are of prime importance in designing light weight building. Although the key component in a swelled clay mineral is a dispersed silicate layer, the chemical composition depend on other elements also [13].

Table 2. Different clay minerals types and their swelling potential

Clay Mineral	Basal Spacing (Å)	Swelling Potential
Kaolinite	7.2	Hardly any
Vermiculite	10-15	High
Chlorite	14	None
Montmorillonite/Bentonite	9.8-20	H1gh
Mica	10	Low

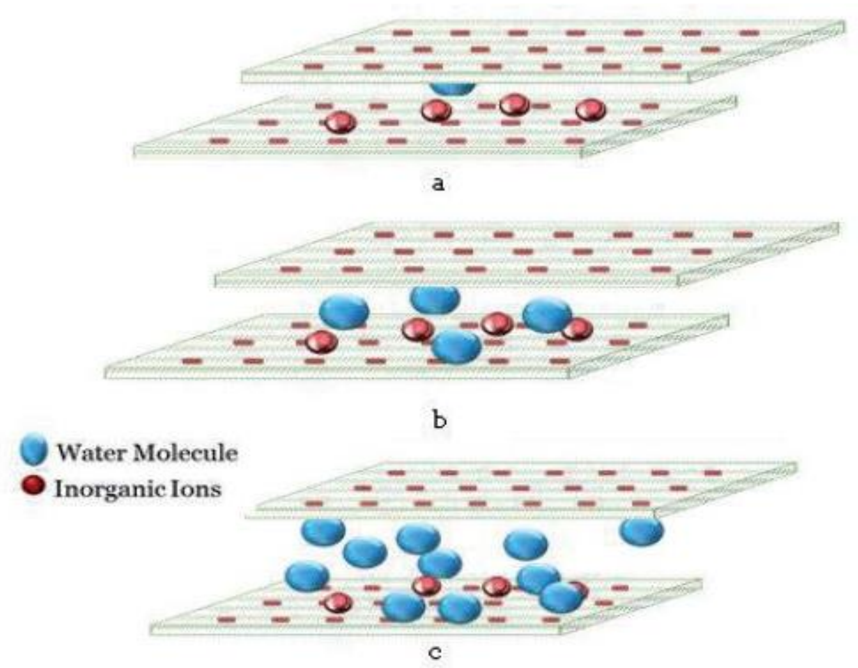

Figure 7. (a) Non-swelling clay minerals, (b) clay minerals with low swelling capacity and (c) clay minerals with highswelling capacity. [8]

4.3. Adsorption capacity

Clay and clay minerals have good adsorption power. The adsorption can happen by three different mechanism. Firstly, in physical adsorption, the material binds over the surface of finely divided clay particles through non-ionic interaction. The second way of adsorption is ion exchange adsorption through electrostatic interaction. The third method is through the addition of small molecules in pores or cavities to eliminate larger molecules partially or completely by adsorption.

The adsorption capacities of clay minerals is influenced by many factors. Large surface area, high cation exchange capacity, low permeability, high retention capacity are the reason behind high adsorption capability of clay and clay minerals. The adsorption capacity also depends on the structure and chemical composition of the clay minerals. Adsorption takes place via different active sites present in the cay mineral surface for example, exchangeable cations (Na^+, K^+), hydroxyl groups of acidic/basic sites (Al, Al-OH, Mg-OH, SiOH), unsaturated coordinating ions (Al^{3+}, Mg^{2+}), oxygen anions etc. These active sites take part in physical adsorption by van der Waal interaction or by hydrogen bonding through the hydroxyl group. Chemical adsorption can also happen by the formation of stronger chemical bond between the surface of clay minerals and the molecules. Recently lot of research work is going on adsorption of heavy metals and organic pollutants for water remediation and CO_2 capture for environmental protection that are discussed in the application of clay minerals section.

4.4. Surface charge property

The chemical properties of clay minerals are influenced by the surface charge present on them. The formation of organic complexes, swelling, shrinkage, migration of ions etc are markedly modified by the amount of the electrical surface charge present on the clay minerals. Based on the surface charge characteristics clay minerals are divided into two types [7,8]:

i) Clay minerals with negative surface charge: The clay minerals acquire permanent negative charge because of isomorphous substitution in octahedral and tetrahedral sheets. The ions present in the interlayer spaces are used for the balancing of negative charge. Thus the negative charges are also termed as structural charge. This charge is pH independent.

ii) Clay minerals with variable surface charge: The variable surface charge originated from the protonation of silanol group (Si-OH) present on surface edge. This type of charge can be either positive or negative depending on the extent of protonation or deprotonation of the silanol group. This type of charge vary based on the pH of the solution.

The aggregation behavior and adsorption of contaminants from electrolyte solution is affected by the surface charge property of the clay minerals. The exposed crystal faces of the clay particle charging properties are different than the internal faces, resulting significant anisotropic behaviour. To describe the surface activities of clay minerals, understanding surface charge density and surface potential is very important.

4.5. Specific surface area

Clay minerals have large specific surface area (SSA) (Table3) and display high reactivity. SSA can be defined as surface area per unit mass or per unit volume of the clay minerals. The reactivity differs from one clay mineral to the other one. For example the order of reactivity is Montmorillonite>Illite>Kaolinite.

The size and shape of the elements present in clay minerals can influence the SSA. It is observed that both internal and external SSA increases with the decrease of particle size. Some well known clay minerals such as smectite, vermiculite, sepiolite, palygorskite etc have large internal surface area. Montmorillonite and vermiculite belonging to expanding clay minerals have high SSA upto 810 m^2/g which is the total of internal and external sutrface area. On the other hand non-expanding clay minerals e.g. kaolinite has only external surface area leading to SSA upto 10-70 m^2/g. Acid activation of clay minerals using inorganic acid can enhance the SSA value to a significant amount.

Table 3. Different clay minerals types with their chemical formula and molecular composition

Name of Clay mineral	Chemical formula/Mol. Wt.	Molecular Composition				Type	Specific surface area (m^2g^{-1})
Kaolinite/Halloysite	$Al_2Si_2O_5(OH)_4$ **MW:258.16gm**	Al	20.90%	Al_2O_3	39.50%	1:1	5-20
		Si	21.76%	SiO_2	46.55%		
		H	1.56%	H_2O	13.96%		
		O	55.78%				
		Total	100%	Total	100%		
Sepiolite	$Mg_4Si_6O_{15}(OH)_2{\cdot}6H_2O$ **MW:613.82 gm**	Mg	15.84%	MgO	26.26%	2:1	150-900
		Si	27.45%	SiO_2	58.73%		
		H	1.97%	H_2O	17.61		
		O	54.74%				
		Total	100%	Total	102.61%		
Palygorskite	$(Mg,Al)_2Si_4O_{10}(OH){\cdot}4(H_2O)$ **MW:411.35 gm**	Mg	8.86%	MgO	14.70%	2:1	150-900
		Al	3.28%	Al_2O_3	6.20%		
		Si	27.31%	SiO_2	58.43%		
		H	2.21%	H_2O	19.71%		
		O	58.34%				
		Total	100%	Total	99.03%		
Mica	XY2-3Z4O10(OH,F)2 with X=K,Na, Ba, Ca, Cs, (H3O), (NH4); Y=Al, Mg, Fe2+, Li, Cr, Mn, V, Zn; Z=Si, Al, Fe3+, Be, Ti	Varied composition				2:1	50-200
Montmorillonite/Bentonite	$(Na,Ca)_{0.3}(Mg,Al)_2Si_4O_{10}(OH)_{2n}\ H_2O)$ **MW:549.07 gm**	Na	0.84%	Na_2O	1.13%	2:1	700-800
		Ca	0.73%	CaO	1.02%		
		Al	9.83%	Al_2O_3	18.57%		
		Si	20.46%	SiO_2	43.77%		
		H	4.04%	H_2O	36.07%		
		O	64.11%				
		Total	100%	Total	100.58%		
Chlorite	$(Mg,Fe,Al)_6\ (Si,Al)_4O_{10}(OH)_8$	Varied composition				2:1:1	-

Vermiculite	$(Mg,Fe^{2+},Fe^{3+})_3[(Al,Si)_4O_{10}](OH)_2.H_2O$ **MW:504.19 gm**	Mg	8.68%	MgO	14.39%	2:1	500-700
		Al	23.01%	Al_2O_3	43.48%		
		Fe	9.97%	FeO	12.82%		
		Si	5.57%	SiO_2	11.92%		
		H	2.00%	H_2O	17.87%		
		O	50.77%				
		Total	100%	Total	100.48%		
Talc	$Mg_3Si_4O_{10}(OH)_2$	Varied composition				2:1	-
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$ **MW:389.34 gm**	K	6.03%	K_2O	7.26%	2:1	10-100
		Mg	1.87%	MgO	3.11%		
		Al	9.01%	Al_2O_3	17.02%		
		Fe	1.43%	FeO	1.85%		
		Si	25.25%	SiO_2	54.01%		
		H	1.35%	H_2O	12.03%		
		O	55.06%				
		Total	100%	Total	95.27%		

4.6. Plasticity

Plasticity is another useful property of clay minerals for their diversified application. Plasticity is defined as the property of a material by which the shape of the material is deformed without rupture under the influence of a finite force and when the force is removed it comes back to its initial shape. This property is controlled by the composition of the clay minerals, presence of organic compounds, specific surface area, size distribution of the particles, dispersion characteristics of particles, viscosity and surface tension of water. Along with these applied pressure, temperature and additives also affects the plasticity property of clay minerals. The clay-water system with high plasticity requires strong force for deformation without rupture while a system with low plasticity can deform and break easily in presence of a weak force. Morphology of clay minerals is a deciding factor on the plasticity property. When water is added in clay minerals, platelet like structure can easily slide past each other and improves the plasticity. Plasticity increases with increase of water content and reaches a maximum and it varies from clay to clay.

The cohesion force is higher in moist clay compared to the dry clay as the air trapped inside the pores between dry clay particles are removed during wetting process. When the pores are occupied by water the body ruptures because of deformation and plastic clay is formed. The minimum amount of water that is needed to form plastic clay is called plastic limit. If further amount of water is added, the clay becomes a paste with reduced strength and sticky nature. At this point the water content in the clay mineral is termed as liquid limit. Beyond this further addition of water will make dispersed clay. The water content difference between these two limits is known as plasticity index. Clay minerals are sometimes classified according to the their liquid limit and plasticity index (Fig.8) [7].

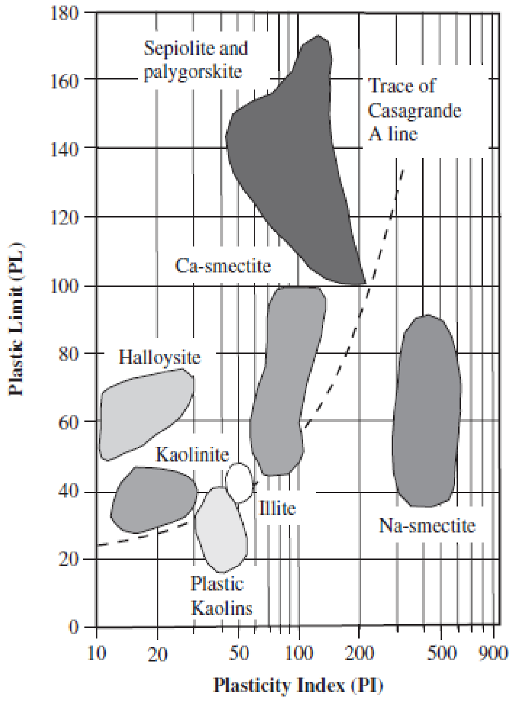

Figure 8. Classification of clay minerals according to plastic limit and plasticity index

4.7. Dispersion/flocculation

Addition of water in clay minerals leads to dispersion. At wet condition the solid particles are separated and dispersed into the liquid phase. The flocculation happens when the dispersed clay particles come closer and joined together to produce cluster of particles or flocks of bigger sizes. Dispersion in clay mineral is controlled by the attractive and repulsive forces present at the surface of a colloid in electrical double layer. The attractive and repulsive forces are balanced for dispersion. The variation in pH of the solution hampers the dispersion of clay minerals. At higher pH dispersion of kaolinite, smectite and arid-zone clays increases [7,8]. The electro kinetic properties of clay minerals are affected by the change of pH of the solution. The variable charge present on the external surface of clay particles play important role in influencing pH by varying the electrical potential.

4.8. Catalytic properties

Expansible clay minerals for example, smectite, vermiculite have the capacity to fill the inter layers with large inorganic ions [14]. The multivalent inorganic cations are partially fill the interlayer space similar to islands. Various hydroxy compounds of iron, zinc, chromium, titanium aluminium etc. are used as inter-layering inorganic compounds. These materials are thermally stable and form a porous interlayer space to act as pillared clays. These pillared clays with large surface area, balanced pore size and high porosity can perform the role of an efficient catalyst [15].A lot of research is currently going on modification of structural and morphological composition for enhancing the catalytic properties of clay minerals [16].

In a similar way some organic compounds can also exchange inorganic cations from the inter-layers of expansible clay minerals [17]. Water molecule present on the external surface or inter-layer spaces can be replaced by polar organic molecules. Polyhydric alcohol such as ethylene glycol or glycerol can form stable complex with smectite and vermiculites. The reaction of organic molecules with clay minerals change their properties from hydrophilic to hydrophobic. Thus affinity to bind with water decreases while tendency to bind with organic molecules increases. These clay minerals can act as surface catalysts for organic reactions. Moreover, these organic clay minerals have extensive applications in paints and plastic industry.

5. APPLICATIONS OF CLAY AND CLAY MINERALS

Clay and clay minerals are being used in various sectors as shown in Fig.9. In the following sections a detail discussion on each application areas has been elaborated.The summary of the application of clay and clay minerals in different industries are listed in Table 4 to make it handy for the readers.

Figure 9. Applications of Clay and clay minerals in different area

Table 4. Summary of application of clay minerals in different industries

Industries	Type of clay used	Properties of clay exploited	Modification of the clay	Task accomplished	References
Agriculture	Zeolites, bentonites	High sorption capacity, binding ability, cation exchange capasity	Nanoclay-polymer composite used for slow release of nutrient	Soil conditioner, soil fertility, carrier of bioactive molecules	[18], 19, 20]
Fertilizer	Palygorskite, Kaolinite and smectite, bentonite	High water retention capacity	Clay mineral coated fertilizer	Controlled release of fertilizers, enhanced crop production	[21,22, 23, 24]
Pesticide and herbicide	clinoptilolite and montmorillonite	Adsorption	surfactant modified clay mineral	Controlled release of Pesticides and herbicides	[27.28, 29], [30, 31]
Animal Feed	Kaolin, bentonite, smectite, montmorillonite	Adsorption, cation exchange capacity	Clay minerals mixed with feed	Adsorption of mycotoxin and heavy metals, binder, anticaking agent	[32, 33, 34], [35, 36, 37]

Food Industry	Bentonite, Clay based nano-composites	Adsorption, organoleptic property, Catalytic property	Clay minerals mixed with nanoparticles	Room temperature storage, clarification agent, bleaching agent	[38-48]
Detergent	Kaolin, bentonite	Adsorption, high foaming ability	Mixing of clay with surfactants	Removal of dirt, oil and pesky stain, softening of hard water	[49, 50, 51, 52]
Pharmaceutical Industry	Kaolinite, Smectites, mirabilite, palygorskite, sepiolite etc.	High specific area, sorption capacity, favorable rheological properties, chemical inertness, swelling capacity	Functionalized and organo modified clay mineral	Laxative, wound healing, anti-inflammatory, anti-bacterial, dermatological protector,	[53-58]
Cosmetics	Kaolinite, Smectites, bentonite, Illite, Palygorskite, naturel clay, etc.	Ion-exchange, adsorption, lubricant property	Formulation with surfactants and organic polymers	Cleansing, Anti-aging, anti-wrinkle, Sucscreens, hair care products,	[59, 60]
Biomedical	Kaolinit, montmorillonite, sepiolites,halloysite, Hydrotalcite, Smectite, etc.	high adsorption capacity, large surface area, ion exchange capacity, colloid and thixotropy, chemical inertness swelling property,low toxicity	Functionalization of clay surface with surfactant, composite with graphene, silicate organic molecules, polymer etc	excipients in some formulation; lubricants in manufacturing pills; disintegrants; anticaking and thickening agents; binders and diluents; emulsifiers; and carriers of biologically active molecules, slowing down drug release for prolonged administration of drug	[61-72]
Textile and Paint Industry	Kaolin	Water Dispersability, adsorption	Used as fillers	corrosion resistance, weather resistance, tanning agent	[73-80]
Construction Industry	smectite and kaolinites, bentonite	load-bearing strength, resistance to wear, resistance to chemical attack, attractive appearance, and an ability to take a decorative finish	alkali activated metakaolin to geopolymer, nanoclay mixed cement, flyash modified clay	durability, and mechanical strength, compressive strength, low carbon emission,	[87, 88]
Water Treatment	Hallosite, bentonite, Illite, palygorskite, montmorillonite, etc.	Adsorption	functionalized clays such as pillared clays and porous clay	dye , heavy metal removal	[89-95]
Environment protection	Kaolinite , smectites, sepiolite palygorskite, montmorillonite, bentonite, etc.	adsorption property and thermally stability, swelling capacity	Acid treatment and organic species insertion	Pollutant removal of soil and water, CO_2 Capture	[13, 90], 96, 104]
Photocatalyst	Kaolinite, Smectites, halloysite, sepiolite	Adsorption and degradation	Composite of clay mineral with semi-conductors e.g. TiO2, ZnO etc.	Removal of organic pollutants	[108-123]
Leather	Kaolinite, Smectites	Water dispersion property	Polymer composite of clay minerals	Used as filler and flame retardant	[128-130]

5.1. Agriculture and farming

Clay minerals can be regarded as staple in many products used in modern agriculture. There are some unique and beneficial properties of clay minerals that make it possible to attain the important objectives of agriculture industry [18]. The diverse properties of clay that are utilized in agriculture are: high sorptive capacity, binding ability, controlled release, environment friendly and modifiable features. Excellent sorptive capacity allows clay to serve both as adsorbent and absorbate. In arid region, there is high requirement of water retention [19]. Thus, clays are used for moisture management purpose. Among various clays, bentonites with good binding ability are used as effective binding agent in many agricultural products. Further clays can serve as carrier of agricultural products through controlled release of active ingredient [20]. The clay minerals are of low cost and are sustainable. In addition to these qualities, the properties of clays can be modified according to the needs of the producers to improve production and enhance specific features of agriculture products.

5.2. Fertilizers and soil conditioners

Clay minerals have found wide applications as fertilizers and conditioners in the form of carriers, binders, additives, and coatings [21,22]. It can be used as granular carrier or coating for controlled release of active ingredients [23,24]. The slow or gradual release of nutrient greatly reduce the nutrient runoff in fertilizer application. Moreover, the crop can get the nutrients periodically instead of one-time feed. This ensures proper growth without damaging crop with overdose of nutrients in case of single shot supply of nutrients.

Among different clays, bentonite is known for their excellent water retention capacity and thus attractive for use in fertilizer products. Successful crop production is completely dependent on soil health and its water content. In arid region moisture retention is a challenging task but the clay minerals help to solve the issue [25]. In agriculture, soil preparation is largely dependent on the quality and amount of clay present in the soil. The colloidal particles of clay enhance viscosity, elasticity and permeability to water. Dryness of soil increases when bentonite clay is added, where pH of soil is enhanced which in turn favours plant growth.

Bentonite and kaolin can reduce the concentration of nutrients and thus used as diluent in fertilizers and improve their flowability [26].Bentonite is used with superphosphate and mixed fertilizer with 0.25 to 0.5% proportion.

5.3. Pesticides and Herbicides

The beneficial qualities of clay that are important in fertilizers can be used in pesticides, insecticides and herbicides as well. These chemicals are generally obtained in liquid form or thick liquid paste form making their application tough. When these chemicals are used with granular clay material, they are easy to handle andmore efficient in their role as pesticides or herbicides. Moreover, the controlled release behaviour of these products limits the flow of the harmful chemicals used in pesticides, insecticides, and herbicides to the surface of earth or ground water [27,28]. Like the fertilizers, clay minerals can also be used as diluent in these harmful chemicals to reduce concentration so that the damage to crops or the person handling these can be managed [26]. The vapor pressure and photo-degradation of pesticides can be reduced when used with clay, which may lower the environmental risks of the application of pesticides, insecticides, and herbicides [29-31].

5.4. Animal feeds

Because of the super adsorption capacity clays are used as adsorbent of mycotoxins present in animal feed [32]. The productivity and health of animals are in danger due to the serious health issues caused by mycotoxins in animal feed. Moreover, when human consumed the animal derived food products, they also fall under potential health risk. The clay can adsorb these harmful components and leave them outside the living body [33]. Table 5 displays some research data on the effect of clay minerals on change of body weight gain and feed conversion ratio for broiler chickens. Clays can perform other beneficial activity such as slowing down the movement of food through the digestive system to improve digestion process. Several studies have reported that clay improves the food degradation and enhance the efficiency of feed. It can control the acidity in rumen of cows. Milk productivity from cows, egg production from chickens can be increased by adding clay in the animal feed as binders [26].

Clay minerals with very fine particles are the most suitable for application in veterinary science. Kaolins and smectites are most used in animal nutrition as growth promoters and supplements for the treatment of gastrointestinal disturbances, particularly diarrhoea [34]. Several clays are commonly used as technological additives in feed manufacturing as binder and anticaking agents, as well as mycotoxin binders, not only for improving feed quality, but also for enhancing the nutritive value of animal diets [35].Clay minerals are one of the most widely used approaches in the animal industry. Clay minerals have excellent adsorption performance that can affect the transference and transformation of mycotoxins in feed [36]. Dairy producers frequently add clay as a feed supplement to reduce the symptoms of aflatoxin and subacute ruminal acidosis in lactating cows [37].

Table 5. Effect of clay mineral on change of body weight gain (BWG) and feed conversion ratio (FCR) for broiler chickens. [33]

Clay used	No. of Days of Expt.	% of clay added	BWG	FCR
Kaolin	56	1.0	-3.3	-5.0
		2.0	-7.4	2.9
		3.0	-0.9	-5.4
Kaolin	42	1.5	5.4	-3.1
		3.0	6.0	-7.2
Bentonite	42	1.5	0.4	-12.9
		3.0	5.3	-1.1
Sepiolite	42	1.0	3.3	-4.9
		2.0	-1.4	-1.8
Sepiolite	42	0.5	2.1	-2.2
		1.0	2.6	-2.8
1:1 ratio of palygorskitewith zeolite	42	2.0 (exp 1) 2.0 (exp 2)	1.9 8.5	2.2 -1.1
Sodium bentonite	42	1.0	3.0	-7.6
		1.5	-0.8	1.5
calcium bentonite	42	1.0	2.0	-7.0
		1.5	-0.3	2.0

5.5. Food industry

Storage of foods specially fruits and vegetables are a serious issue for maintaining a clean environment. The freezing process requires a huge amount of electrical power and along with-it pollutants are thrown away in the environment. Thus, scientists are looking for environment friendly, lowcost storage technology. Bentonite clay pyramid has been investigated by Al-Arfaj et al. for storage of regular fruits and vegetables [38]. They estimated various properties to compare the efficiency of bentonite clay pyramid with room temperature storage and refrigeration as a control. Weight loss, heterotrophic microbial count, and organoleptic quality of the stored products in the clay pyramid was found to be more beneficial than the other two examined control. The result suggests clay pyramid as a cheap, eco-friendly and electricity less method of food storage.

Moreover, clay minerals are used in clarification of beverages due to its absorption properties. In case of alcoholic beverages, protein of red and white wines is bonded with the clay minerals e.g. bentonite [39-42]. This is also used as clarification agent for casein, gelatine and albumin. Clay minerals are also used for oil bleaching and catalyst in esterification reactions. Li et al. investigated on enhancing the clarification effect of clay minerals by using mixture of bentonite and chitosan in apple juice [43]. Bentonite can act as an adsorbent for soybean and cotton oil bleaching for the production of edible oil [44,45].Acid activated bentonite is investigated as catalyst in the esterification reaction of oleic acid obtained from palm oil [46]. In addition to these, a lot of research is performed on nanocomposite-based clay minerals for food packaging purpose [47]. Many clay minerals display the behavior of antioxidant and antimicrobial agent in food products and enhance flavour profiles [48].

5.6. Detergent industry

Washing mechanism is a complicated process controlled by many factors. The detergent with good emulsifying property can perform better as a detergent [49]. They are good in suspending the dirt and behave as a protective colloid. Detergents must possess large surface area and interfacial adsorption area for undergoing dispersion and de-flocculation process. Many research has proved that if alkaline earth metal ions or polyvalent cations are present then washing capability is reduced. These polyvalent cations are adsorbed on the surface of detergents and electrical potential on the surface get lowered. Because of this, removal of dirt or impurities become difficult and they return on the surface of the cloth. Under this situation, negatively charged clay minerals can bind the alkaline earth metal ions such as Ca^{2+}, Mg^{2+} etc. and due to this, negative potential increases. This facilitates the washing process to a great extent. Clay minerals reduces the attractive force between the dirt particles and restrict their agglomeration. The impurities or the dirt particles cannot come back to the substrate when clays are present. Clay minerals can be an effective replacement for the harmful polyphosphates used in laundry industries. Bentonite when mixed with biosurfactants have several beneficial properties e.g. large surface area, high foaming ability, facile dissolution of detergents, effective adsorption of impurity, softening of hard water etc [50,51]. Fite et al. have shown that washing of cotton cloths become more softer when cleaned with ecological surfactant [52]. It is also reported that detergents mixed with kaolin can adsorb oil and water very easily. The pesky stains that remain after washing with laundry detergent can be effectively managed by adding kaolin during detergent formulation. These characteristics clearly indicates the potential of clay minerals to rule the detergent industries to reach the goal of sustainable environment.

5.7. Cosmetic and pharmaceutical industry

Clay minerals are known for their use in traditional medicine for healing and protection. The economic viability and special properties of clay materials place them in demanding position in cosmetic and pharmaceutical industries. They have some interesting physicochemical characteristics e.g. high surface reactivity for adsorption and cation exchange capacity, ideal rheological property, highwater dispersibility, colloidal and swelling capacity making them suitable for various biomedical, pharmaceutical and cosmetic applications [53-60]. They are used as excipients for stabilizing emulsions and suspensions since ancient time. They can function as both absorbents and adsorbates depending on requirement and control the rheological property of a system. Many clay minerals are used in various skin care products. Use of clay minerals are getting increased indermo cosmetic field due to their easy availability and environment friendly nature. Each clay minerals are uniquely related to various personal care or health care products for topical application. Wound healing, moisturizing, skin lightening, antisepsis are some important cosmetic or therapeutic roles played by the clay minerals [54].

In modern dermo cosmetic products presence of clays are ubiquitous. From face cream to sunscreen, cleanser, shampoos, make up cosmetics etc uses a large variety of clay minerals. The chemical, physical, toxicological parameters of clay minerals are checked for their specific applications as cosmetics or pharmaceuticals. They fulfil various role such as abrasives, glidants, emulsion stabilizer, coating agent, anticaking agent, viscosity increasing agent, binders, absorbents, adsorbents, suspending agent, diluents, lubricants, etc in topically applied skin care products.

In pharmaceuticals, the clay minerals can play the role of either active ingredients or excipients.[55,56] The therapeutic behavior of the minerals are mostly dependent on their chemical composition and physical and physico-chemical properties. Minerals with therapeutic properties and behaving as active ingredients are supplied as oral administration or ingestion or by topical application. In some cases, they are also administered parenterally. Oral administered minerals can serve the role of antacids, anti-anemics, laxatives, anti-diarrhoeaics, gastrointestinal protector, direct emetics, homeostatic, mineral supplements etc. Minerals used for topical application i.e. applied on the body surface can function as antiseptics, disinfectants, anti-inflammatories, keratolytic reducers, local anaesthetics, decongestive eye drops, dermatological protectors etc.

Clay minerals have multifaceted applications in cosmetics for example as sunscreen lotion, toothpaste, deodorants, face cream, makeup products (lipstick, eye-shadow), facial masks, cream, powder, bathroom salts etc [59,60]. Moreover, use of clay minerals is also known in spas, geotherapy, pelotherapy paramuds and aesthetic medicine. Table 6 lists the use of various clay minerals in pharmaceutical preparation [54] and Table 7 lists their application in cosmetic field [59].

Table 6. Pharmaceutical application of clay minerals [54]

Clay minerals	Application	Mechanism of action
Kaolinite	Local anesthetic, Anti inflammatory	Heat retention capacity and high absorption
Smectites, Palygorskite-sepiolite	Gastric and duodenal ulcer	H^+ ion neutralization ability and controlling bowel pH
Smectites, Palygorskite-sepiolite, kaolinite	Gastrointestinal activity	High specific surface area and sorption ability
Smectite, sepiolite, hydrotalcite	Antacids	Reaction with HCl, Release of non-toxic ions
Smectite	Antibacterial	High specific surface area and cation exchange ability, colloidal property
Smectites, Palygorskite-sepiolite, kaolinite	Antidiarrhoeaics	Astringent action of Ca^{2+} ion
Montmorrillonite	Antibacterial	Bacteriostatic and bactericidal properties helps skin treatment and wound healing
Natural Clay	Antibacterial	Microbicidal activity of disoved metal ions, biotic and abiotic actions
Organo-modified bentonite, illite, rectorite	Topical application for skin infection	Special surface property, physical property and mechanical properties are helpful in treating dermatological problems

Table 7. Application of clay minerals in cosmetics [59]

Clay minerals	Application	Mechanism of action
Kaolinite-talc, smectites	Skin care products	Adheres and adsorbs in skin , antiseptic action, high sorption capacity
Smectites, Palygorskite-sepiolite, talc, kaolinite	Cosmeceuticals (cream, lotion, powder)	High sorption ability, opacity
Bentonite and hectorite	Sunscreen	High refraction index, shielding of UVA/UVB ray
Smectites	Dry shampoo	High absorbance of natural oil, High water solubility
Natural clay with aloe vera	Peel-off facial mask	Adhesion and adsorbtion in skin

5.8. Biomedical industry

In addition to pharmaceutical and cosmetic applications, clay minerals are used in biomedical field as biosensor, biomaterials, drug delivery and regenerative medicine. The formulation of pharmaceutical products is modified by hybridizing with clay minerals. This direct hybridization helps in improving controlled drug release, better solubility of drug in water, enhanced dispersibility, improved adsorption. The drug-clay hybrids are used in various form of drug delivery system such as tablets and suspensions for oral delivery, creams, gels and lotions for topical use, gene therapy, wound dressing and trans-dermal delivery systems [61, 62].

When indomethacin is intercalated with montmorillonite, increased drug permeability was observed due to enhanced solubility as well as stability of amorphous indomethacin [63]. Hybridization of 5-fluorouracil (drug for colon cancer) with montmorillonite showed reduced side effects of the drug. Anti-Alzheimer drug donepezil, is hybridized with different smectites for controlled release of drugs [64]. Similarly, ranitidine was observed to exhibit prolonged drug release when hybridized with clay. The bioavailability of poor water-soluble drug can be enhanced by inter calation with clays. Prolong therapeutic action of amphetamine sulphate can be achieved by combining it with montmorillonite [65].

High water adsorption ability and high swelling capacity enables them to act as hemorrhagic agents to stop bleeding. Zeolite, kaolin, and cationic clay minerals are used in wound dressing gauze [66]. Clay minerals also play important role in gene therapy. Treatment of life-threatening diseases and genetic irregularities of DNA is delivered to target cells. Cationic clay minerals for example montmorillonite has been very effective in protecting DNA with the help of enzyme nuclease [67]. Hydrophobic organoclays are prepared by combining hexadecyltrimethylammonium with montmorillonite for carrying DNA and other macromolecules to overcome the electrostatic repulsive force between DNA and clay minerals [68]. Table 8 summarized few important clay minerals used for drug delivery applications [54].

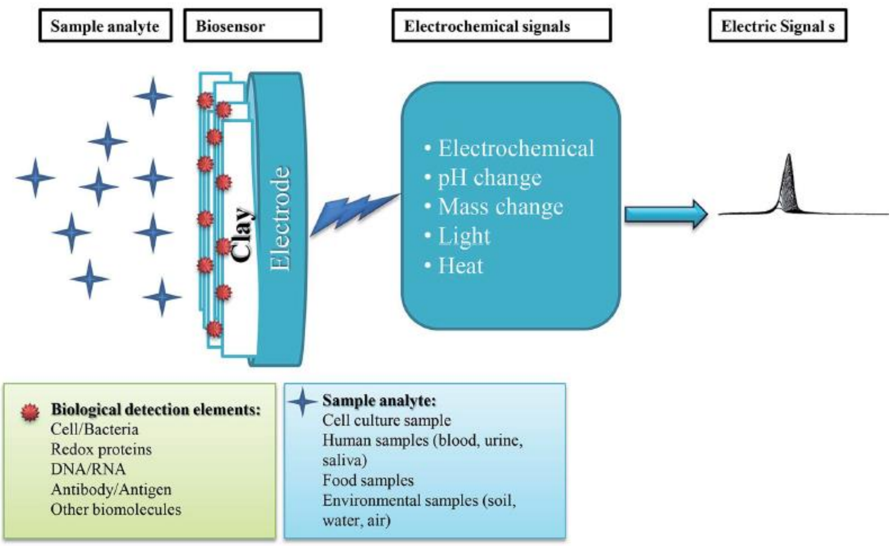

Figure 10. Application of clay minerals as biosensors [53]

Clay minerals are recently getting attention as biomaterials for use in tissue engineering and regenerative medicine. Primarily they perform four different roles in regenerative medicine: (1) Increase mechanical strength of biopolymers (2) Carrier of biomolecules (3) Enhancement in cell adhesion (4) Facilitation in proliferation and differentiation of stem cells. Various nanocomposites are formulated using clay minerals and biocompatible polymers as scaffolds, thin films, and hydrogels for use in wound dressing and medical device coatings [69].

Due to their special properties of cation exchange ability, chemical inertness and large surface area, clay minerals can perform as biosensors. Mostly smectites clay e.g. montmorillonite, nontronite, laponite etc. are used in clay based biosensors [70-72]. These biosensors known as clay-modified electrodes, are developed by deposition of thin films of clay over a conductive substance. Fig.10 diagrammatically represents some of the application of clay minerals as sensors [53].

Table 8. Applications of clay minerals in drug delivery [54]

Clay Mineral	Application systems	Mechanism of action
Smectite	Hydration activated delayed release system	Disintegrant agent due to Hydrophilic and swelling property
Hydrotalcite	Encapsulation of drugs inside LDHs	Charge balance mechanism between hydrotalcite layer and interlayer space
Smectite, montmorrillonite, hydrotalcite	Extended release system	High cation exchange ability
Montmorrillonite	Colon delivery system	Interaction between drug and natural mineral
Montmorrillonite	Gene delivery system	Multiwalled carbon nanotube and silver nanoparticle stabilized starch and Montmorrillonite is more effective
Nanocomposites, films, hydrogel composites of clay polymers.	Targeted delivery system	Reduce absorption by interacting with drugs
Hydrotalcite	Cellular uptake	Layered double hydroxides as nonviral vector
Sepiolite, Montmorillonite, halloysite, laponite	Cell adhesion, Cell proliferation and differentiation, Skin engineering, regenerative medicine	Composite scaffolds for tissue engineering

5.9. Textile and paint industry

There is always requirement of enhancing the dyeability of textile fibres. Scientists are finding new technologies and methods for improving dyeability of fabrics by nano-clay pre-treatment [73,74]. Various research results showed that nano-clay pre-treated cloths have higher dyeability than the non-treated samples. The clays can interact with the dyes through high ion exchange capacity, π-interaction, and hydrogen bonding [75]. The other beneficial effect of nanoclay on fiber is that it reduces wrinkability, flammability and thermal degradation of cloth [76-78].

Paints consist mainly of oil emulsions. The stability and self-life of emulsions are enhanced in the presence of clay minerals due to their large surface area and high adsorption capacity. As the clays can absorb water, the permeability of water is reduced when clays are present in paint emulsions. Because of this less moisture content paint, objects can be protected from corrosion [79,80]. Moreover, clay minerals are also used as tanning agents in paint formulations.

5.10. Oil and gas Exploration

The early decades of the last century were known as the oil and gas exploration age, as there had been an increased demand for petroleum with the boom in the automotive industry and the industrial revolution. In those days, clay minerals, e.g., kaolinite, smectite, illite, chlorite, etc., were targeted to predict the quality and possibility of oil reservoirs. Moreover, they were an essential tool for stratigraphic correlation, environmental determination, and identification of hydrocarbon-rich zone [81]. By the 1970s, the study of clay minerals by X-ray diffraction became a well-established procedure for diagenesis and reservoir quality prediction [82]. Later, clay minerals have been routinely used to study hydrocarbon emplacement time and petroleum system analysis [83]. The main uses of clay and clay minerals in oil and gas exploration can be summarized as follows:

(i) Indication of tectonics and sedimentation: During the formation of petroleum-containing sedimentary basins, the clay minerals inside the rock undergo several changes in composition and crystal structure due to changes in tectonics and sedimentations. Thus, clay minerals can be helpful to predict and understand the tectonic/structural regime, the chronology of various geological events, and overall basin evolution history. Even in tectonically complex areas, this method can be successfully used [84].

(ii) Indicator of hydrocarbon generation and expulsion: The first step for exploration of oil and gas is to identify a possible region as an oil and gas source. This can be used to study organic-rich source rocks, which can give information on whether they can generate hydrocarbon at a given depth in a specific geological time and whether the hydrocarbons have reached the expulsion stage. As clay rocks coexist with organic matter in sedimentary basins, any change in organic matter will also affect the clay minerals. In fact, it is strongly believed that clay minerals in shales act as a catalyst in petroleum genesis as they absorb and concentrate the organic matter [81]. The ordering of Illite/smectite (I/S) is a critical parameter. For example, detailed research on the gulf coast has shown that mixed-layer illite/smectite (I/S) can be used as a geo-thermometer and indicator of thermal maturity. On the other hand, the presence of illite-smectite-tobelite proves that the oil generation step has occurred, and the absence of tobelite indicates that rocks have not been heated adequately to produce large amounts of oil [85]. If the part of illite is about 25% in the mixed layer, then clay mineral loses lots of pore water, and less oil is generated. 25-50% illite in a mixed layer indicates a good amount of oil generation, while greater than 75% illite indicates that hydrocarbon has been cracked to generate dry gas [86].

Apart from the two above-mentioned uses, the study of clay minerals is also essential in (iii) reservoir quality prediction and (iv) Indices for hydrocarbon migration and accumulation [86]. Finally, although clay mineralogy is an essential aspect of oil exploration, their study has been a challenging task in the past. This is because clay minerals have a sheet structure and can be resolved at the sub-micron level. There is a very minute difference between clay minerals and other silicate minerals. However, modern analytical tools such as QEMSCAN (Automated Mineralogy and Petrography), FIB/SEM (Focused Ion Beam/ Scanning Electron Microscope), EDS (Energy-dispersiveX-ray spectroscopy), have facilitated the study of clay minerals.

5.11. Construction Industry

The construction industry is as old as modern civilization. In the construction industry, the following materials are required: (i) Cement and concrete, (ii)Limestone-calcined clay cement, (iii) Geopolymer and concrete (iv) bricks. In all these materials, clay-based minerals are used in one way or the other.

Nano-clay decreases setting time and workability of Portland cement and also in presence of optimum amount, increases hydration, durability, and mechanical properties. It has a nucleation effect, pozzolanic effect, filling effect, bridging effect and barrier effect. In presence of nano-clay, amounts of C-S-H and C-A-S-H are increased but the size of CH crystals is decreased. In general, in presence of nano clay, hydration properties are increased. It is reported that nano-metakaolin (NMK) is a better accelerator than nano-SiO_2 and nano-$CaCO_3$.

Supplementary cementitious materials (SCM) modify the properties of cement. As SCMs are not very limited, efforts have been made to use naturally occurring waste materials such as clay, which are abundant in silicate and aluminate and can initiate pozzolanic reactions. Clay-based SCMs include flash-calcined clay, calcined clay, mechanically activated kaolin, and metakaolin (MK). MK is most promising among all these minerals due to increased packing density and pozzolanic activities [87].

Limestone Calcine clay cement, prepared by blending clinker, calcined clay, limestone, and gypsum is an environmentally friendly, cost-effective alternative as compared to Portland cement as it can decrease CO_2 emission by 40% and requires lower calcination temperature for clay. Calcined clays such as kaoline can have more significant pozzolanic activity, and as a result, it can reduce the clinker content by as much as 50% and increase its strength. Moreover, in LC^3-50 blends, C_3S was increased due to the filler effect of calcined clay [87].

Clay-based geopolymer concrete are nowadays used in the construction industry. They have many benefits, including low carbon emission, reduced raw material use, cost-effectiveness, longer life, and recyclability. The most common clay used is MK which is produced when natural clay (kaolin) is calcined at a moderate temperature.

When treated with an alkali activator such as NaOH/ Na_2SiO_3 or KOH/K_2SiO_3 followed by the binder, MK generates geopolymer (Fig.11) [88].

Clay bricks have been used in construction since ancient times. They can withstand extreme cold, heat, rainfall, wind, and even deterioration caused by humans. Clay bricks are made by sun drying the moulded clay bricks and then by firing. The quality of the bricks depends on the moulding pressure, firing temperature, source of fire, and on other materials such as glass mixed with clay. On a micro level, brick quality depends on the properties of the clay, such as crystal structure, elemental composition, shrinkage behaviour, and plasticity (Fig.12).

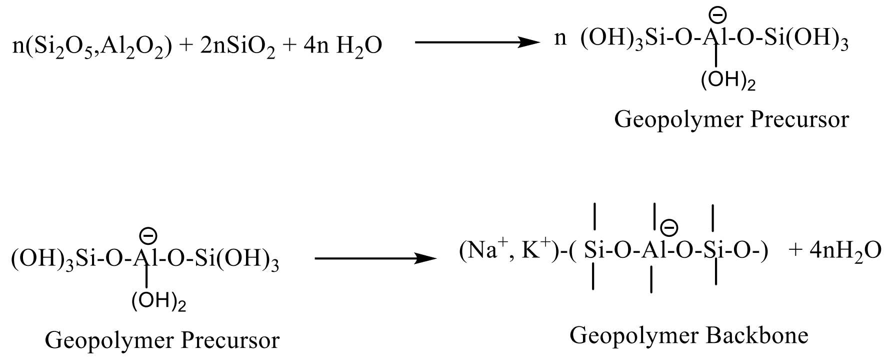

Figure 11. Geo-polymerization reaction

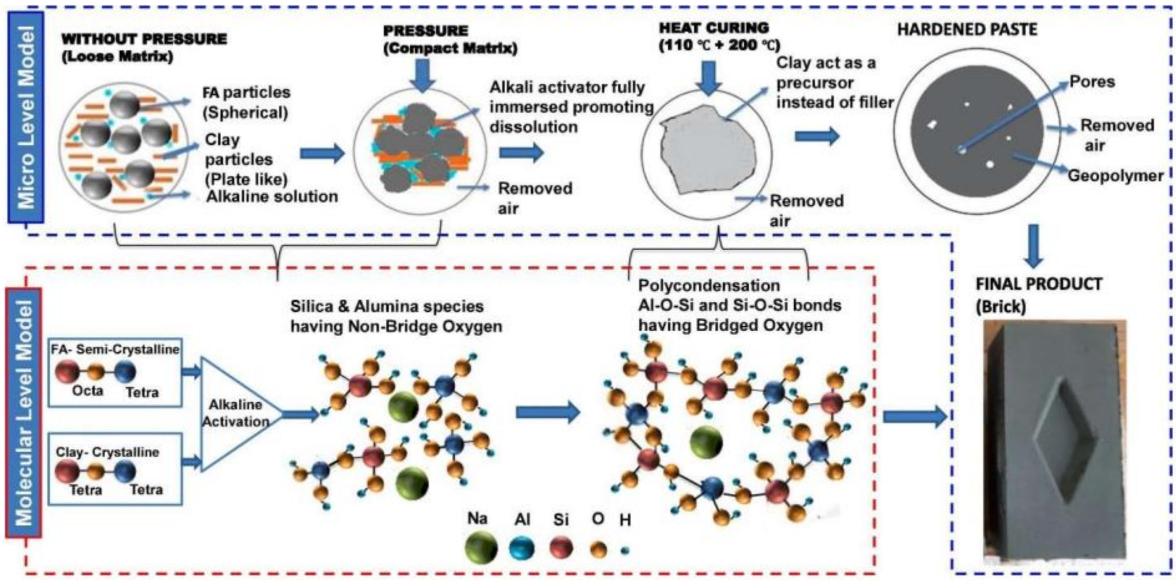

Figure 12. Strength gain mechanism at a micro and molecular level in clay bricks [88]

5.12. Environmental Protection

Clay and clay minerals have been used as barrier and containment materials since ancient times. They have been widely used in containment remediation as they are readily available in mine deposits and soils, cheap, and have high water absorbing capacity [89]. Due to their inherent properties, such as high surface area, charge density, swelling capacity, etc. , they can be used as a low-cost material for the remediation of pollutants from water and soil [13]. Clay minerals have a negative surface charge, high cation exchange capacity, and are hydrophilic in nature. Consequently, they are an excellent adsorbent for cationic and hydrophilic pollutants such as toxic metal ions, but they are not very efficient towards anionic or hydrophobic pollutants such as poly aromatic hydrocarbons (PAH). Thus, clay minerals are very effective in remediation of cationic contaminant via a cation exchange mechanism. For example, bentonite is used nowadays as an adsorbent and as a natural alternative to activated carbon, which is synthesized in the laboratory. Apart from that, kaolinite, palygorskite, sepiolite, and vermiculite have also been utilized for the adsorptive removal of pollutants. Selected examples of clay minerals used for the removal of cationic contaminant isgiven in Table 9 [90].

Adsorption of heavy metal ions by clay minerals follows a complex mechanism which can be summarized as (i) covalent bonding between the pollutant and the mineral, (ii) complexation of metal ions to the negatively charged surface, (iii) electrostatic attraction, and (iv) ion exchange [91]. Clay dosage, pH of the medium, temperature, and type of clay profoundly affect the absorption process efficiency. The adsorption capacity of the clay mineral can be significantly enhanced by modifying it, for instance, organic material, nano zero-valent iron and acid-modified clay, clay-metal oxide nanocomposite, clay-carbon nanocomposite, and heat-treated clay are all examples of modified clay [91-95].

Table 9. Natural clay minerals for pollutant removal [90].

Type of clay	Pollutant	Efficiency (amount adsorbed mg/g/Removal %)
Bentonite	Cd(II)	11.20
Kaolinite	Cd(II), Cu(II), Ni(II)	10.78, 6.80,140.84
Montmorillonite	Cu (II)	17.88
Natural clay	Hg (II)	9.70
Palygorskite	Cu (II)	2.35
Jordanian kaolinite	Pb (II)	13.32
Natural untreated clay	Basic yellow 2,	833.3
Bentonite	Malachite green	91%
Natural clay	Methomyl	32.9%
Bailen smectite (12% smectite)	Metalaxyl and fludioxonil	3300 and 304 µg/g
Kaolin	Crystal violet	47.27
Illitic-kaolinite natural clay	Methylene blue (MB) and crystal	violet 100 and 330 mg/g

5.13. Carbon dioxide capture

The incessant use of fossil fuels has led to an elevated atmospheric CO_2 level. As CO_2 is a greenhouse gas, its excess presence has caused global warming and acid rain. The devastating effects of climate change can be seen worldwide in animal and plant kingdoms. Thus, carbon dioxide removal is a vital topic requiring attention from the global scientific community. The most common technology for CO_2 removal is adsorption, membrane purification, and cryogenic distillation. While cryogenic distillation is expensive and unsuitable for large-scale applications, membrane purification has severe limitations when CO_2 is present in fewer quantities [96]. Adsorption methods using amine-based compounds are perfect for carbon dioxide capture. However, they also have drawbacks concerning the highly corrosive nature of the amine compound and the high energy requirement during regeneration. Several porous materials such as metal-organic frameworks, and graphene organic frameworks, are also suitable adsorbent for carbon dioxide. However, they have low thermal stability and high cost for synthesis [97,98]. Thus, clay and clay-based mineral are very good alternative as they have excellent adsorption properties, thermally stable, cheap and easily available.

Adsorption of CO_2 by raw clay minerals have been reported by several authors. Kaolinite and smectites are known to adsorb CO_2 although with poor adsorption capacity. A few examples of raw clay-based minerals for CO_2 adsorption are depicted in Table 10 [96].

Table 10. Clay based minerals in CO_2 adsorption

Type of clay mineral	Adsorption Efficiency (mg/g)	Adsorption condition
Montmorillonite	22	10 ◦C, 1 bar, 90 min
Montmorillonite	10	45 ◦C, 1 bar
Montmorillonite	7	25 ◦C, 1 bar
Sepiolite	65	25 ◦C, 1 bar
Sepiolite	41	45 ◦C, 1 bar
Saponite	15	45 ◦C, 1 bar
Sepiolite	137	25 ◦C, 120 bar
Bentonite	14	45 ◦C, 1 bar
Bentonite	5	25 ◦C, 1 bar
Bentonite	6	25 ◦C, 1 bar
Kaolinite	3	25 ◦C, 1 bar
Kaolinite	0	25 ◦C, 1 bar
Palygorskite	12	45 ◦C, 1 bar
Palygorskite	18	25 ◦C, 1 bar

It is proposed that CO_2 molecules are adsorbed on the external surface of the mineral where -OH groups react with CO_2 molecule leading to the formation of HCO_3^- species [96]. Many authors have also proposed that smectites can adsorb CO_2 in interlayer region which causes the layers to move apart (Fig.13). This change in interlayer distance depends on the adsorption pressure and the hydration of counter-cations present in the interlayer region [99]. Moreover, it has been observed that the inter-laminar cation plays an essential role in CO_2 adsorption as it is directly related to the hydration energy of the cation [100]. When a mixture of CH_4 and CO_2 is subjected to adsorption, the clay mineral selectively adsorbs CO_2 as there is a strong affinity between CO_2 and the solvated cation present between the layers [101]. CO_2 adsorption by mica is also well-studied. Like the previous case, CO_2 reacts with the hydroxyl group from the structure of mica to form HCO_3^- which in turn reacts with another CO_2 molecule and cations present between the layers of mica.Moreover, it was found that adsorption capacity can be enhanced by using a higher pressure [102]. Fibrous phyllosilicates such as sepiolite and palygorskite can form a molecular sieve to retain CO_2. This process is highly dependent on temperature. The adsorption capacity of 65mg/g and 18 mg/g for sepiolite and palygorskite at 25^{o}C and 1 bar pressure has been reported by Cecilia et al. [103]. However, when the temperature is raised to 45^{o}C at 1 bar pressure, adsorption capacity of 41mg/g and 12mg/g was observed for sepiolite and palygorskite, respectively [104].

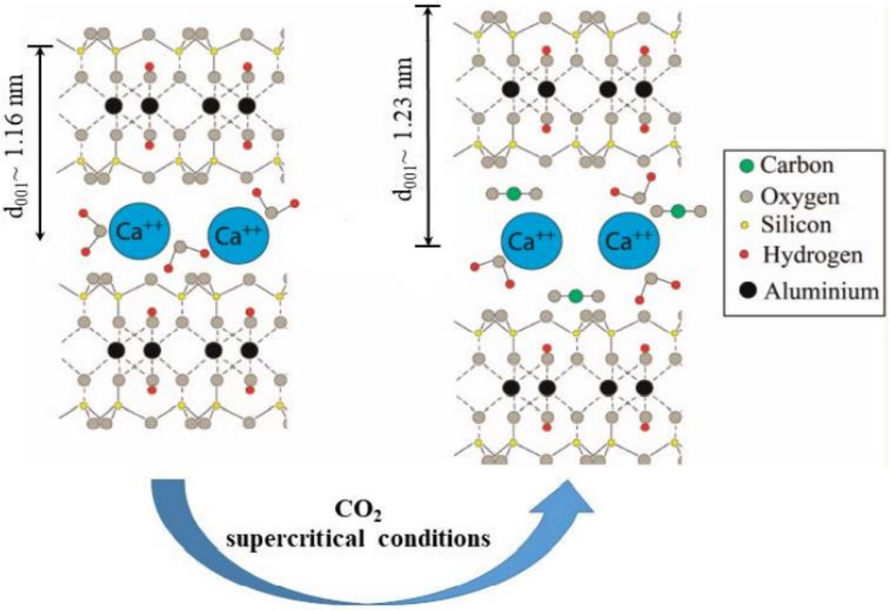

Figure 13. CO_2 adsorption on the interlayer spacing of smectite [96]

To improve the efficiency of clay minerals towards CO_2 adsorption, clay minerals can be modified by acid treatment. Acid treatment increases pore size and pore volume [105]. However, this may not always be beneficial, as studied by Cecilia et al. [103]. This decrease can be due to the loss of cation between the layers interacting with the adsorbed CO_2molecule [96]. Another way of increasing the adsorption efficiency is to insert an organic species, such as a cationic amine-rich dendrimer in laponite, as polyamidoamine (PAMAM), in the interlayer region [106] (Fig.14).

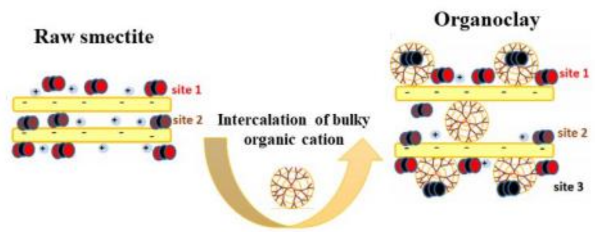

Figure 14. CO_2 adsorption in raw smectite and dendrimer- loaded smectite [106]

Poly (amido amine) dendrimers have also been intercalated between layers of mica and montmorillonite with enhanced adsorption capacity for the latter case only [107].As dendrimers interact with the CO_2 molecule very strongly, the adsorption capacity increases while the regeneration process becomes difficult.

5.14. Photocatalysis

Semiconductor supported materials used as photocatalysts for the degradation of various environmental pollutants is well studied in the literature. Different support materials include graphene, nanoparticles, activated carbon, and clay minerals. Clay mineral-semiconductor hybrids are remarkable because, clay often increases the efficiency of the semiconductor. For example, TiO_2 nanoparticle – clay mineral composite material has been widely used as a photocatalyst for the removal of organic pollutants. The presence of clay minerals as support matric reduces the chances of aggregation. Additionally, they increase the interaction between the catalyst and the contaminants and reactive species and the pollutants by pre-adsorption of the contaminant. Overall efficiency increases compared to the bare TiO_2 nanoparticles, as reported by Kibanovaetal. The authors noted that TiO_2 nanoparticles supported on hectorite and kaolinite clay minerals could efficiently degrade two volatile organic pollutants namely toluene and D-limonene [108]. TiO_2 nanoparticles deposited on smectitesor vermiculite have been used successfully for photocatalytic degradation of 2,4-dichlorophenol. The results indicated that the photocatalytic activity was similar tocommercial P25 [109]. Some other examples of TiO_2-clay mineral hybrid photocatalysts are the degradation of ionic and non-ionic herbicide by laponite-TiO_2 hybrid [110], halloysite-TiO_2 hybrid [111], and TiO_2-sepiolite nanocomposite [112]. Other than titania, other metal oxide nanoparticles have also been used by researchers. For example, α-Fe_2O_3 nanoparticles/vermiculite clay mineral photocatalysts have shown high activity for the photocatalytic reduction of CO_2 [113] Ag_3PO_4/rectoritenano-composite [114], ZnO/halloysite nanocomposites [115], and Co_3O_4/halloysite [116]have been successfully used as photocatalyst for the degradation of methylene blue. Some other examples include ZnO/smectite hybrid for the decomposition of ibuprofen [117], $BiVO_4$/palygorskite for the decomposition of tetracyclin [118], Pd-CuO/palygorskite for decomposition of methylene orange dye [119],Zr doped TiO_2/Cloisite for degradation of antipyrine [120],W doped TiO_2/Cloisite for degradation of atrazine [121] and Fe_3O_4/smectite for degradation of rhodamine-B [122]. Clay mineral-based photocatalyst are not only cheap, stable, and easily available, but they are also very versatile and has vast potential to be applied in extensive scale processes [123].

6. FUNCTIONALIZED CLAY AND THEIR APPLICATIONS

Clay minerals are made up of layered sheets. The in-plane bonding in these materials is strong covalent bonding but out of plane bonding is mostly weak van der Waal's force. Thus these materials can be exfoliated very easily into single layer or few layered nanosheets serving as high performance materials. Exfoliation dramatically improves specific surface area and thus enhances surface activity related properties. Mainly three different method of exfoliation is used e.g. direct delamination, intercation assisted and ion-exchange assisted exfoliation (Fig.15).

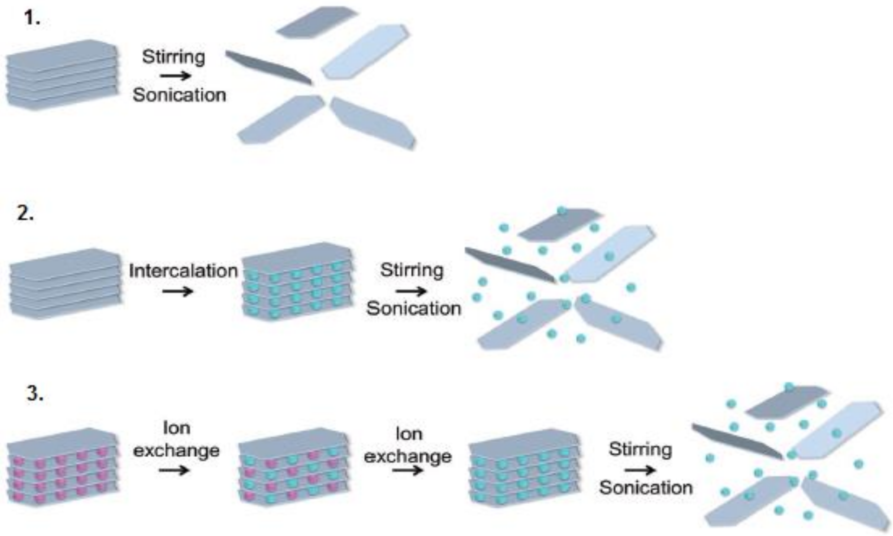

Figure 15. Different methods of exfoliation: 1. Direct delamination 2. Intercalation assisted exfoliation 3. Ion exchange assisted exfoliation. [131]

Direct delamination is efficiently performed by stirring or ultra-sonication. For example Na^+-MMT can be exfoliated completely from aqueous dispersion by vigorous stirring at pH 5.6 within a weak. The ultrasonication method can exfoliate Na^+-MMT within half an hour. The chosen solvent plays important role in deciding the efficiency of the exfoliation.

Intercalation is used to increase the interlayer distance in clay minerals to assist the exfoliation process. The process involves intercalating polar molecules into the layers. The layered structure undergoes swelling in the liquid environment and weakens the interlayer attractive force. This is followed by agitation through stirring thermal shock or ultra-sonication detach the layers to form nanosheets. Sometimes a combination of different exfoliation method is also used to convert the nanoclay into nanosheet form.

Ion exchange assisted exfoliation is used for charge balanced clays such as smectite clays. The surface sheet of smectites have permanent negative charge that remains unaffected by pH of the neighbouring environment. The excess negative charge is balanced by absorbing Na^+ or Ca^{2+} ions. These self ion exchanged clays are very stable and do not undergo exfoliation by agitation. They require special ion exchange treatment by bigger cations to increase the inter layer distance. Thus exfoliation process is facilitated by introducing additional species in the interlayer space.

After exfoliation, the nanosheets are assembled into a variety of nanostructures using suitable strategies such as casting, dip coating, spray coating, Vacuum filtration, Electrophoretic deposition, 3D printing etc. (Fig.16). Each of these methods have their own advantages and disadvantages.

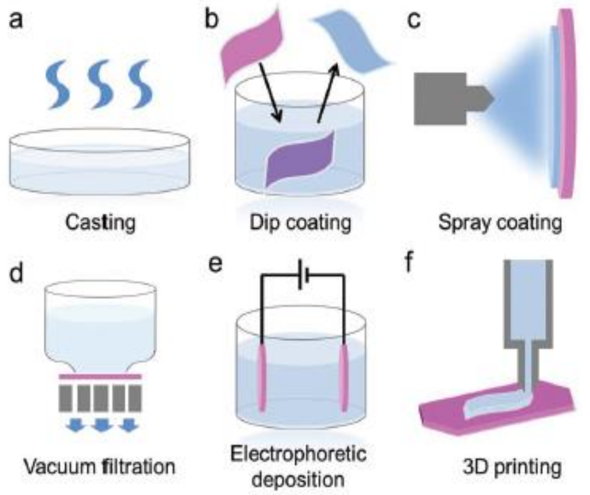

Figure 16. Types of assembly method of nanosheets. [131]

Casting is a simple and easy self assembly method for nanosheets. In this method the dispersion is put into some moulds such as petri-dishes followed by drying at ambient environment. Casting is used for preparing large nanosheets with highly ordered nanostructure. The dip coating method involves immersing the substrate into the dispersion of desired chemicals and then drying. This is a very common method of preparing large scale nanostructures. However it lacks formation of ordered structure and additional steps are required to achieve ordered nanosheets. In the spray coating technique the desired clay dispersions are made aerosol and sprayed onto the substrates. This process has the advantage of low dosage and fast drying. The sample deposition is uniform producing thermochromic nanostructured films. Another technique vacuum filtration is the most admired method to prepare cost effective nanosheets. In this processs the nanosheets are dispersed in water and then filtered at negative pressure. By this method nanosheets are reconstructed into a ordered and uniform structure in the presence of external pressure. The electrophoretic deposition method is performed in two steps. The dispersed clay particles are first moved towards an electrode using an external field. Next the particles form a coherent deposit over the electrode. This method is widely used for the preparation of nanostructure for various applications. The advantage of electrophoretic deposition method includes speed, uniformity and automation. 3D printing is a powerful and facile technique for fabricating various functional materials. Clay nanosheets react with several polymers to form highly viscous dispersion. These clay and polymer nano-composites are most demanding 3D printing inks. This method is highly promising for fabrication of multifunctional materials with unique properties and shape.

When clay minerals are Functionalized by incorporating organic moieties onto their surfaces, the properties are enhanced and can be used in a better way in different sectors. Functionalized clay minerals, such as organoclays, are widely used as nanofillers in polymer matrices to improve mechanical properties, barrier properties, flame retardancy, and thermal stability. Functionalized clay minerals can be employed as highly efficient adsorbents for separating oil-water mixtures and purification of water. Montmorillonite clay functionalized with thiol group enhances adsorption capacities for removal of heavy metal ions from water and the adsorption process is given in Fig. 17 [124].Functionalized clays are also used as carriers for controlled drug delivery and catalysts in various chemical reactions in cosmetics and personal care products and improve soil stability making the soil more resistant to erosion caused by water or wind. There are many other applications of Functionalized clay minerals. Natural clay minerals, with many benefits for human health, have been used in traditional medicine and different industrial applications. Use of clays and clay minerals for protection and disease treatment is as old as mankind. Laponite, a synthetic clay mineral with similar properties to natural healing clays, when functionalized with different amino acids for the purpose of wound dressing applications, becomes more effective [125].

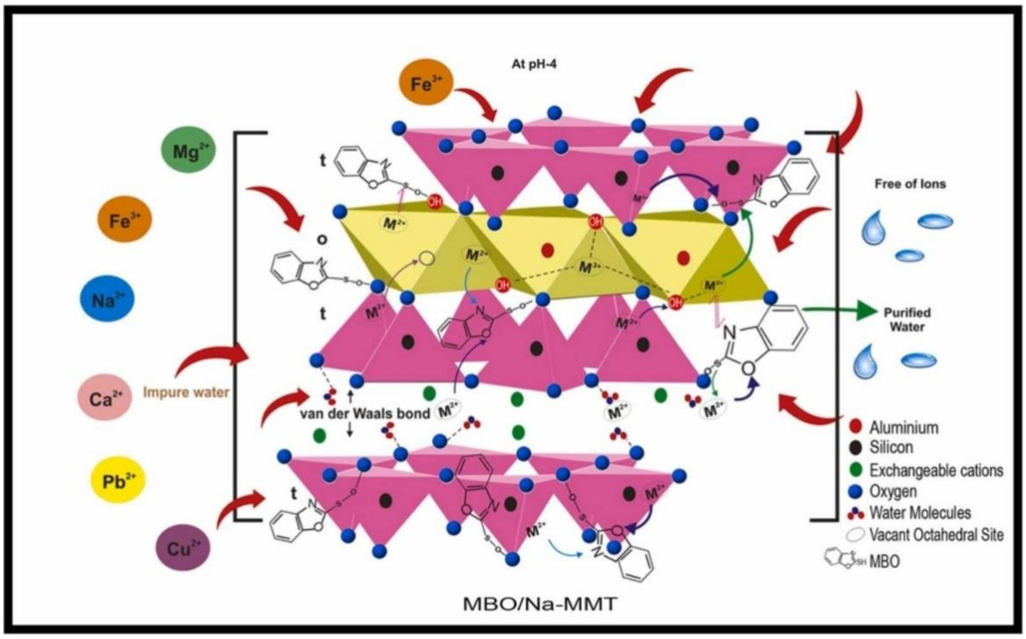

Figure 17. Adsorption of heavy metal ions on Sodium montmorillonite (Na-MMT) functionalized with 2-mercaptobenzoxazole (MBO) containing thiol group [124]

Water is polluted by different industries (Fig.18) [126]. Natural clay minerals can be used for wastewater treatment. Besides their availability and economic sustainability, they have limitation because of small surface area, poor affinity towards organic pollutants, etc. On the other hand, polymeric resins have adsorption capacity but suffers from pH dependency and higher cost. Clay-polymer nanocomposites (CPNs) are much better for removal of pollutants [126].

Figure 18. Different sources of water pollution

Co or Cu modified Kaolin can function as a catalyst for electrochemical oxidation of wastewater obtained from the pulp and paper-making industry. Photocatalytic efficiency of TiO_2 may be improved by supports of clay minerals [127]. Naocomosites of clays are extensively used in leather industries [128-130].

The application of clay minerals can be broadened by strategically designing them as multifunctional materials through exfoliation as per need [131]. A large number of clay minerals are exfoliated to convert them into 1-D nanosheets or layerd nanosheets having excellent physicochemical properties. These functional materials have application in electronics, nanostructured membranes, energy conversion, environment protection, waste water treatment, biomedical field and many other important areas.

7. OUTLOOK AND CONCLUSION

Use of clay and clay minerals are as old as the human civilization. This is because of its easy availability, low cost, stability, and other physicochemical properties such as charge density, surface area, ion exchange, and swelling capacity. With the industrial revolution and advancement of technology, new and sustainable materials are required to solve the challenges of modern society. Clay and clay-based minerals are one such material that has wide application in various industries like agriculture and food, textile, petroleum, construction, cosmetics, detergent, and biomedical, to name a few. This review article presents a systematic discussion on clay and clay-based minerals and their industrial applications.

Surface modification of clay minerals by useful target objects or by structural transformation of clay mineralscan produce functional materials that are useful in different sectors with emerging interest. These composite materials act as high performance functional materials for adsorption of pollutants, reinforcing materials, carrier of drug and pharmaceuticals, catalysts, energy materials and many other advanced technological applications. Importance should be given to design and fabricate these functional materials in a sustainable and eco-friendly manner.

As evident from the discussion throughout this review article, research on clay minerals and their application is age-old, albeit a lot is needed to be done in this ever-emerging area. The application of clay minerals depends on their size, chemical composition, layered structure and electrical charge.Specially their biocompatibility play an important role and make a difference in their application in biomedical field.Study of clay minerals need multidisciplinary knowledge from chemistry to geology and from mineralogy to materials science. A detailed understanding of this field can lead to development of synthetic clay minerals that mimic the properties of the natural clay, with improved sustainability. Moreover, it will also assist us in formulating materials that have desirable catalytic, electric, magnetic, and structural properties at micro and nano levels. Collaborative research, along with advancement in modern instrumentation methods, can contribute significantly to the fields of clay and clay mineral studies.

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Conflict of interest

The author declared no potential conflicts of interest with respect to the research, authorship, and publication of this article.

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IZVOD

GLINA I MINERALI GLINE: KRATAK PREGLED OD OSNOVA DO PRIMENE

Glina i glineni minerali su prirodni materijali i dostupni su u izobilju na zemlji. Oni su jeftini i imaju niz struktura i svojstava sa mehaničkom i toplotnom stabilnošću. Oni su slojeviti magnezijum ili aluminijum silikati koji se sastoje od tetraedarsko koordinisanih silikatnih listova i oktaedaralno koordinisanih listova magnezijuma ili aluminijum hidroksida. Zbog prirodnog bogatstva i ekološke prirode, glina i glineni minerali se koriste u različitim industrijskim sektorima.U ovom preglednom članku razmatrana je klasifikacija minerala gline, strukture, svojstva i njihova primena u različitim sektorima. Neki od važnih sektora u kojima se glina i minerali gline intenzivno koriste su poljoprivreda i poljoprivreda, đubriva i regeneratori zemljišta, pesticidi i herbicidi, stočna hrana, prehrambena industrija, industrija deterdženata, kozmetička i farmaceutska industrija, biomedicinska industrija, industrija tekstila i boja, industrija nafte i gasa, zaštita nafte i gasa. hvatanje dioksida, fotokataliza, itd. U ovom pregledu smo pokušali da ažuriramo sadašnja saznanja sa nedavnim razvojem i napretkom u glini i mineralima gline.
Ključna reči: *Glina, minerali gline, struktura, svojstva, primene, poljoprivredna industrija, farmaceutska industrija.*

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