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Charge Properties, Characteristics and Applications of Bentonite: A Concise Review

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ABSTRACT

Bentonite belongs to the smectite group of clay with montmorillonite as the primary subunit. Calcium and sodium bentonite are the two common types of bentonite which are used in various fields. As a filler material, surface modification is usually necessary to make bentonite more compatible with matrix materials. During the modification process, elemental additives can intercalate between the clay layers, promoting layer exfoliation. This results in a filler material with very high specific surface area-to-weight ratio. Consequently, even at low filler loading the resulting composites can exhibit significant improvements in mechanical and thermal properties. In aqueous environments, sodium bentonite swells more than its calcium counterpart due to the weaker interlayer bonding by monovalent Na^+ ions as compared to the stronger divalent Ca^{2+} ions. High water uptake could be advantageous in agriculture is but generally regarded as disadvantageous in separation processes such as wastewater treatment and oil & gas drilling exploration. Based on its wide availability, abundance and cost effectiveness, bentonite and other smectite clays are expected to attract more interest in the future. In addition, with various sustainability goals outlined by the United Nations, the use of natural materials like bentonite is projected to expand particularly in countries with substantial natural reserves.

1. Introduction

Clay minerals have been widely used in various industries such as agriculture, construction, material reinforcements, mining, petroleum derivatives recovery and wastewater treatment due to their unique properties. Apart from small particle size and porous which result in high surface area, clay minerals have negatively charged surface with hydrophilic nature. Due to these properties, clay

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minerals like bentonite can serve as effective additives in composite materials to improve material's strength even at minimal loading dosages. However, as an additive material in bio-composites, bentonite properties are modified to increase its compatibility with the matrix polymer such as modification using alkylammonium, amines and gelatin. This modification is possible due to bentonite's amphoteric characteristic. Bentonite belongs to smectite group of clay that consists of aluminosilicate layers and upon hydration and adsorption, clay layer intercalation and exfoliation can be achieved. This is a critical property of a reinforcement material that results in filler materials with a large aspect ratio in matrix polymers. On its original form, bentonite can be used for wastewater treatment but it is further enhanced in composite forms where increased surface area and negativity often result in better contaminant capture.

To appreciate its potential, this paper starts with the definition of clay minerals, followed by the common misconceptions around bentonite and montmorillonite. Based on the characteristics, a wide range of bentonite applications is discussed followed by the challenges and future directions of bentonite research and applications.

This article illustrates the immense potential applications of a common clay mineral such as bentonite. When limited resources and cost are often the limiting factors in developing a new material, one should go back to what nature has in abundance that is clay. This work can provide guideline for scientists working in clay research for various applications ranging from the basic applications in agriculture, to its advanced use in catalysis and contaminant management.

1.1 Clay, Clay Mineral and Bentonite

According to the International Association for the Study of Clays (AIPEA), clays are naturally occurring materials composed mainly of fine-grained phyllosilicate minerals that harden upon drying or firing. Clays usually consist of hydrous layered aluminosilicates with varying amounts of metal oxides and organic matter, example includes smectites, kaolinite and micas. They form through natural weathering and hydrothermal processes and constitute a major component of the soil fraction [1].

Among many types of clay minerals, smectites are widely studied and used in the industries due to their exceptional swelling ability. Smectites contain readily exchangeable cations such as Ca^{2+}, Na^{+} and Mg^{2+} while other transition metal cations such as iron, nickel, zinc, manganese, chromium and titanium are present in the octahedral layers. The general formula for smectites is reported as $Na_{0.7}Al_{3.3}Mg_{0.7}Si_8O_{20}(OH)_4.\ nH_2O$ [2]. There are several sub-types of smectite clays exist such as montmorillonite which was found in the Montmorillon, France and bentonite that originates from Fort Benton, Wyoming. Bentonite is widely cited in the literature as "a rock composed of crystalline clay-like minerals formed through devitrification process and chemical alteration of a glassy igneous materials such as tuff or volcanic ash". The two most common types of bentonite are sodium and calcium bentonite, whereas montmorillonite is a specific mineral without a subtype. Although their mineral compositions are identical, bentonite contains primarily montmorillonite with small amounts of iron, potassium, feldspar and quartz. Due to their high degree of similarity, the terms bentonite and montmorillonite are often used interchangeably in various contexts [1, 3, 4]. Unlike bentonite, montmorillonite is formed through the weathering of volcanic ash and other aluminium-rich minerals. It is widely available worldwide except in Antarctica [5].

2. Bentonite Charge System

2.1 Isomorphous Substitution

Montmorillonite is a 2:1 phyllosilicate clay consisting 70ft he tetrahedral sheets of silicon-oxygen (Si-O) separated by one octahedral sheet of aluminum-oxygen-hydroxyl (Al–O–OH) (Figure 1). Within this structure, the tetravalent Si^{4+} in the tetrahedral sheet and trivalent Al^{3+} in the octahedral sheet could sometimes be replaced by available trivalent Al^{3+} and divalent Fe^{2+} or Mg^{2+} from the environment. This process termed as isomorphous substitution occurs when ions of comparable size replace each other, however, substitutions with higher-valency cations are more common. Figure 2 illustrates the charge and size comparison of common cations with the selectivity of cation exchange is reported 70ft h in the order of Ca^{2+}>Mg^{2+}>K^{+}>Na^{+}. This selectivity is also influenced by the nature 70ft he adsorbing surface. For example, cation exchange (e.g. Al^{3+} replacing Ca^{2+}) renders part 70ft he oxygen coordination incomplete, giving the clay surface a net overall negative charge that can attract positively charged ions such as K^{+} and Na^{+} to adsorb onto the basal plane of montmorillonite layers [3, 5, 6].

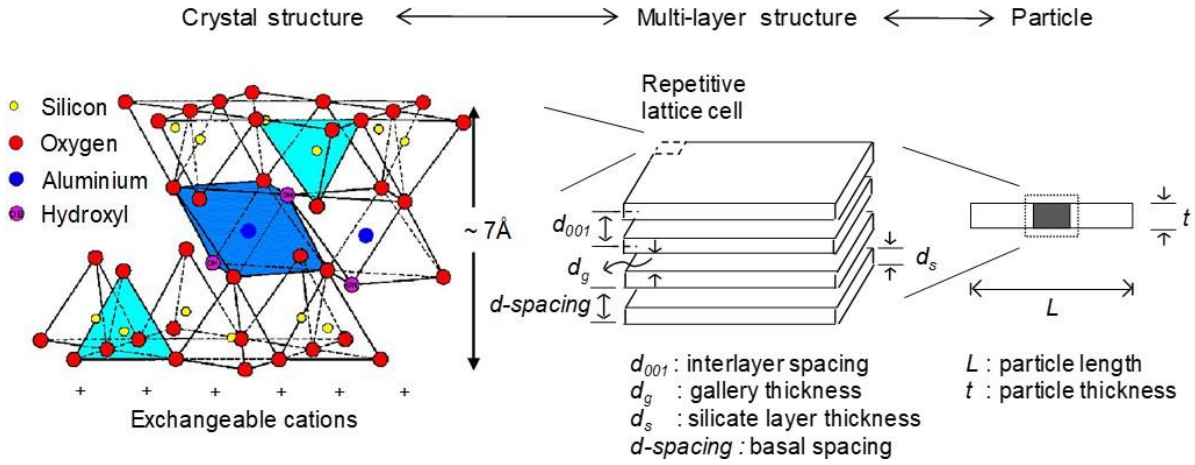


Fig. 1. Structure of montmorillonite. Modified from Sheng et. al [7]

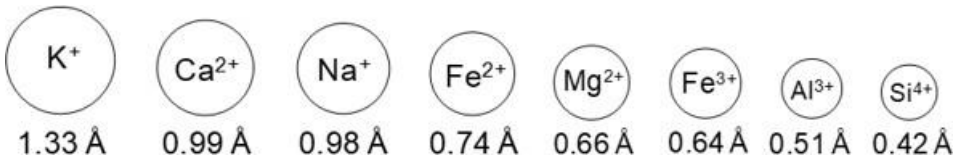


Fig. 2. Relative dimensions and charges of ions commonly found in soils [8]

Bentonite charges are a combination of charges on both the platelet surface and edges. Isomorphous substitutions such as Al^{3+} with Mg^{2+}, results in a permanent net negative charge on the surface. While at the platelet edge, the terminal mineral elements do not bind to any structural framework, a phenomenon known as “broken bonds”. The charge at the platelet edge is pH-dependent where the exposed terminal elements readily interact with electrolyte solutions. In clays with weakly charged surfaces such as kaolinites and talc, the edge charge can dominate the overall particle charge for clays. Whereas, for clays with highly charged surfaces like smectites and mica, the variable edge charges contribute insignificantly to the overall charge due to the dominant surface

charges [1, 9]. Exchangeable cations such as monovalent Na^+ and divalent Ca^{2+} are often found intercalated within the clay gallery layers.

2.2 Protonation and Deprotonation in Solution

In aqueous solution, the overall surface charge of bentonite is influenced by the dissociation of alumina (Al_2O_3), silica (SiO_2) and hydroxyl (OH) groups at the platelet edges. Alumina, an oxide of aluminium has a neutral charge at approximately pH 7 whereas silica is neutral at pH 4, a condition known as point of zero charge (PZC). At pH below than the PZC, these species carry a net positive charge whereas they become negatively charged at pH above than PZC. In a highly acidic solution (e.g., pH 1), these species protonate into $AlOH_2^+$, $SiOH_2^+$ and *clay*-OH_2^+ giving bentonite an overall positive charge. In a highly alkaline environment (e.g., pH 14), alumina and silica deprotonate as AlO^- and SiO^- while *clay*-OH becomes *clay*-O^-, resulting in an overall negative particle charge [10]. The protonation and deprotonation can be illustrated by Eq. (1) and (2) below, respectively:

Protonation (in an acidic medium)	:	Positively charged	(1)
Aluminol group	:	$-Al-OH\ +H^+\ \leftrightarrow\ -Al-(OH_2)^+$	
Silanol group	:	$-Si-OH\ +H^+\ \leftrightarrow\ -Si-(OH_2)^+$	
Deprotonation (in an alkaline medium)		Negatively charged	(2)
Aluminol group	:	$-Al-OH\ \leftrightarrow\ -Al-O^-+H^+$	
Silanol group	:	$-Si-OH\ \leftrightarrow\ -Si-O^-+H^+$	

However, some regions of the clay remain permanently negatively charged due to isomorphous substitution in the clay lattice as previously mentioned. This contributes to a pH-dependent amphoteric character of bentonite [3, 10]. This behaviour governs bentonite's interaction with ions in solution. In an adsorption system, solutes can be classified as either charged species (ions) or uncharged species (molecules). Charged ions interact with bentonite surfaces via electrostatic forces such as ion exchange. Uncharged molecules may adsorb on the surface via van der Waals forces or other non-electrostatic interactions which are less influenced by the surface charge.

Charged ions can further be categorized as potential determining ions or specifically adsorbing ions. Potential determining ions, such as H_3O^+ and OH^- in oxide system directly participate in surface reactions, dictating the net surface charge. Specifically adsorbing ions, like Ca^{2+} and K^+ in aqueous solution do not involve in the acid-base equilibria but bind to specific sites on bentonite structure, influencing the surface potential. Both types of charged ions contribute to the overall charge behaviour of bentonite. From Eq. (5) and (6) above, H^+ and OH^- ions are vital in determining surface charge due to their direct protonation and deprotonation processes, thereby classifying them as potential determining ions [4, 11].

2.3 Surface Potential

Bentonite charges arise from isomorphous substitution and protonation / deprotonation of clay species. In adsorption systems, the solution pH determines the overall charge of the clay particles thereby dictating the ionic interaction between cations (ions in the solution) and the solid-phase adsorbent. The interaction between oppositely charged ions at the solid / solvent interface generates an electrical potential known as surface potential (ψ). Simply, surface potential refers to the electrical charge present on the surface of clay particles.

As depicted in Figure 3, cation concentrations at the interface decreases with increasing distance from the solid surface, creating a condition called potential gradient. The region where cations interact with solid surface is termed as electric double layer that consists of the Stern layer (closest to the solid phase) and the diffuse layer (within the liquid phase). The Stern layer contains active sites on the clay surface that attract cations from the solution while, the diffuse layer contains cations in the liquid phase that are drawn towards the Stern layer. The electric double layer system reaches equilibrium during the adsorption process. This behaviour influences how bentonite interacts with solution particularly with water, affecting its application for soil amendment, wastewater treatment and construction [8, 12].

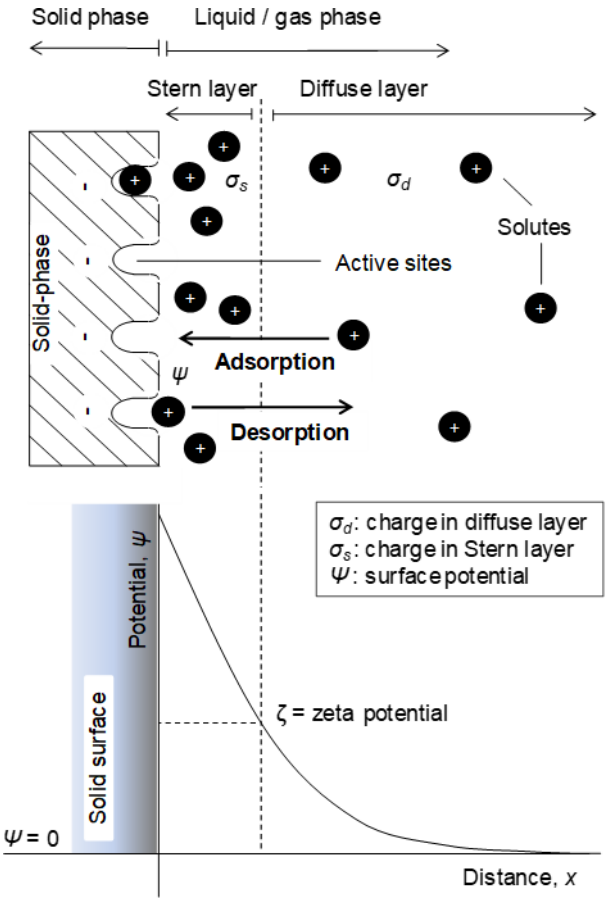


Fig. 3. Relative dimensions and charges of ions commonly found in soils [8]

The magnitude of surface potential is influenced by the activity of potential determining ions in the solution and can be quantified using the Nernst equation as follows [4]:

$$\psi = \frac{RT}{nF} \ln \left(\frac{[H^+]}{[H_{P+C}]} \right) \tag{3}$$

where ψ is the magnitude of surface potential (volt), R is the universal gas constant (8.314 volt.coulomb/mol.K), T is the absolute temperature (K), n is number of moles of exchanged electrons during electrochemical reaction (moles), F is the Faraday's constant (96'485 coulomb/mol), $[H^+]$ and

$[H^+]_{PZC}$ are molar concentrations of hydrogen ions in solution and on the surface at point of zero charge (PZC).

For a pH-dependent charge behaviour such as in bentonite clay, the charge system during an adsorption process is influenced by the hydrogen ions, hence the Nernst equation can be simplified to:

$$\psi = -\frac{2.303\,RT}{F}(pH - PZC) \tag{4}$$

At room temperature 25°C (298 K), the term 2.303 RT/F equals to 0.059 V, resulting in a simplified Nernst equation:

$$\psi = 0.059(PZC - pH) \tag{5}$$

Despite its widespread use in electrochemistry, the Nernst equation has several limitations in practical applications. These include its assumption of ideal conditions such as uniform charge distribution in the electric double layer region, constant temperature, the system is in equilibrium state and mono-sorption (single-species adsorption). In reality, surface potential varies with ion activity that is higher near the solid surface and decreasing with distance. Besides, the actual system temperature fluctuates which affects the ion activity significantly. Because the equation assumes equilibrium state, it neglects the reaction kinetics and activation energy of adsorption processes [4, 6].

The Nernst equation works well for dilute aqueous solutions with a single electrolyte. For non-aqueous solutions or high ionic strength solutions, corrective measures are needed to quantify the activity coefficients such as using the Debye-Hückel or Pitzer equations [13]. Lastly, the equation ignores specific adsorption, ion exchange and surface complexation effects. In the case of specific adsorption, the ions can adsorb at any pH of the solution such as metal ions (Cd^{2+}, Cu^{2+} and Pb^{2+}) binding to bentonite's hydroxyl groups. Similarly, amphoteric surfaces can interaction with solution species at any pH conditions.

There are several theories to describe the surface potential at the solid-liquid interfaces. Helmholtz's Model (1879) proposed a rigid plate-like capacitor layer where a fixed layer of counterions is adsorbed on the surface. Later, Guoy-Chapman's model (1910) introduced the diffuse layer concept that suggests the counterions are not a fixed and rigid layer but rather spreading out in solution. The Stern model (1924) combined the initial two models making it the most widely used in literature to describe surface potential. Stern layer adsorption is often described by the Langmuir isotherm which assumes monolayer adsorption. In later period, Yates (1974) proposed a model that incorporated ion-specific adsorption. Each of the models has unique features and limitations [12-14].

2.4 Point of Zero Charge (PZC) and Isoelectric Point (IEP)

The point of zero charge (PZC) and isoelectric point (IEP) describe charge behavior in solution that is dependent on the material type and the solution conditions. According to the International Union of Pure and Applied Chemistry (IUPAC), PZC is the pH at which the net surface charge of a material is zero due to the equal number of positive and negative surface charges [4]. This term is widely used for solid surfaces such as clays, minerals and oxides. For example, alumina (Al_2O_3) has a PZC of pH 7

while Silica (SiO_2) has a PZC of pH 4. When pH < PZC, the surface is positively charged (favourable for anion adsorption) while at pH > PZC, the surface is negatively charged (favourable for cation adsorption) [15]. This concept is important for adsorption processes as it dictates the affinity of anions and cations towards solid surfaces. From Figure 3, the diffuse layer charge (σ_d) is zero at PZC where adsorbed potential determining ions and specific adsorbing ions become part of the solid phase, neutralizing the potential gradient at the interface.

Isoelectric point (IEP) is the pH condition at which the electrokinetic potential or also known as zeta potential equals to zero. Is it usually applied for proteins, biomolecules and colloids to indicate their stability in suspension. For example, hematite (Fe_2O_3) has an IEP between pH 7-9 where at pH = IEP, particles have high tendency to aggregate [16]. Moving away from the IEP, the electrostatic repulsion increases, enhancing colloidal stability. The IEP is crucial for determining the electrokinetic stability of biomolecular systems. In a hybrid system such as clay in gelatin solution (a protein-based medium), the summation of surface charges and electrokinetic potential is zero at both the PZC and IEP [8]. In such cases, both terms can be used interchangeably, though under certain circumstances they are different concepts.

Theng (1980) proposed that when PZC and IEP coincide, the condition is known as pristine point of zero charge (PPZC) [17]. This concept is more relevant to amphoteric solid phases such as bentonite because adsorption is not entirely dictated by the solution electrolyte. For uniformity, the definitions of PZC and IEP as according to IUPAC are adopted in this review paper. The most common method for determining PZC and IEP is acid/base titration where the pH corresponding to zero surface charge is taken as PZC while pH at which zeta potential is zero is taken as IEP.

3. Other Characteristics

Apart from the charge system discussed, other key characteristics of bentonite include morphology, surface area, cation exchange capacity (CEC), basal spacing and thermal degradation. Understanding these properties are important as they influence the behavior of bentonite in various applications such as adsorption, material development, agriculture, soil amendment and more.

Morphology analysis reveals the particle shape, structure and porosity of bentonite particles which influence adsorption efficiency and mechanical stability. It is measured using microscopic techniques such as scanning electron microscope (SEM), transmission electron microscope (TEM) and atomic force microscopy (AFM). For elemental analysis, SEM can be equipped with an Energy Dispersive Spectroscopy (EDS) function to determine what elements are present in a sample. Surface area reflects availability of active sites on the solid surface for adsorbate binding, crucial for wastewater treatment and catalysis. Surface area is related to morphology as smaller, irregular shaped and porous particles have a higher surface area. It is commonly determined using particle size analyzers such as Brunauer-Emmett-Teller (BET) and laser particle sizing [18].

Cation Exchange Capacity (CEC) reflects the strength of solid surface to exchange cations which is a useful indicator for heavy metal adsorption. To measure CEC, bentonite is suspended in exchangeable cation solutions such as ammonium acetate (NH_4OAc), sodium acetate (NaOAc) and barium chloride ($BaCl_2$) to displace the clay's cations. The displaced cations in the solution can be quantified using the elemental analysis techniques such as Inductively Coupled Plasma - Optical Emission Spectroscopy (ICP-OES) and Atomic Absorption Spectroscopy (AAS) [9, 13, 14].

Basal spacing refers to the interlayer distance between bentonite sheets where larger spacing indicates higher potential for adsorbate intercalation, critical for nanocomposites and drug delivery systems. Basal spacing of powdered bentonite is analyzed using X-ray diffraction (XRD) machine. Stability of bentonite at high temperature is assessed through its thermal degradation behavior,

which indicates its suitability for insulation materials and refractory applications. Thermal degradation is analyzed using thermogravimetric analysis (TGA) with modern TGA instruments are usually integrated with differential scanning calorimetry (DSC) or differential thermal analysis (DTA), collectively termed as TGA-DSC or TGA-DTA [3, 19].

Table 1 summarizes the common characterization methods of bentonite, functions and reported values from the literatures for the two common types of bentonite which are calcium and sodium bentonite. This information is valuable for researchers to predict bentonite's behavior in various environments and to modify its properties for specific purposes.

4. Applications of Bentonite

The diversity of bentonite use is due to its abundance, low-cost, well-understood characteristics and the wide possibilities of modification in terms of physical, rheological and sorption properties. Today, bentonite has found various applications as outlined in Table 2. The following paragraphs discuss selected applications with respect to the properties.

Bentonite has a high degree of swelling in water, enabling it to retain a large amount of water compared to other types of clays. For that reason, bentonite is used in adhesives, construction materials, drilling slurry, agricultural soil improvers, and wet-mash type animal feeds [26-30].

Due to its surface negativity and non-toxicity, bentonite is utilized as a neutralizing agent for radioactive disposal, bedding for animal litter, pelletizing aid for animal feed pellets, pharmaceutical drug carriers and detoxing aid in human and ruminant diets. The characteristics above coupled with small particle size make it a good dispersing agent in adhesives, greases, inks and cosmetic products [30, 31]. Bentonite is used in the food industry to stabilize emulsions by acting as an intermediate between oil and water [1]. Bentonite can be used in municipal and industrial wastewater treatment processes to adsorb contaminants and in some applications, it can form flocs after adsorption and settle to the bottom of a tank [32, 33]. This makes the recovery of spent adsorbent less complicated. In the wine industry, bentonite is used to clarify wine by adsorbing dissolved protein that causes a hazy appearance. Bentonite is the preferred adsorbent because it is low-cost and inert, resulting in minimal impact on the flavour of the wine and can be easily removed by sedimentation [34, 35]. Another well-established application for bentonite in the food industry is in edible oil bleaching prior to deodorization [36-39].

Clays were long used in building construction and pottery due to its swelling property, enabling high degree of workability [40-42]. Modern industries use bentonite as additives and filler materials in composites due to its various unique characteristics. The use of bentonite has been shown to improve the mechanical properties of composites at a very low dosage. In nanocomposites, bentonite is used because the clay particles can disperse well at the nanoscale and interact with various organics to form bio-nanocomposites. It is non-toxic and is suitable for bio-based applications such as reinforcement materials in bioplastic. However, as bio-composite filler, bentonite must be modified with organics to increase its compatibility with the matrix. This step however, can be straightforward due to its amphoteric characteristic that allows for ionic and non-ionic adsorption to occur. Often during the modification step, layer intercalation and exfoliation can be achieved resulting in filler material with very high specific surface area to weight ratio. It was shown that significant improvements in the mechanical and thermal properties of bloodmeal-based composites were demonstrated with a very low dosage (0.5 wt%) of protein-modified bentonite in blood-meal based bioplastics [43, 44].

Table 1
Clay characterization techniques and literature values [1, 3, 4, 8, 20-25]

Properties	Technique	Description	Literature values	
			Calcium bentonite	Sodium Bentonite
Morphology	SEM	Detailed 2D images at resolution from 1 nm. Elemental analysis can be conducted with EDS integration.	SEM particle size (μm)	
			2*	40, 75*
	TEM	Shadowy 2D images with greater resolution than SEM. High resolution TEM (HRTEM) has a resolution from 0.05 nm.	* *Reported values vary significantly as the size can be manipulated manually.*	
	AFM	Atomic-level 3D topographic maps of a surface.		
Surface area	BET	Specific surface area of porous solid materials based on the adsorbed amount of inert gas such as N_2 onto powder samples.	N_2-BET surface area (m^2/g)	
			30-50	500
			80-94	750-860
	Gas Permeability	Surface area of membrane materials based on the amount of gas such as N_2 and air diffuse through.		
Cation exchange capacity (CEC)	ICP-OES and AAS	Replacement of cations such as with NH_4^+, Na^+ and Ba^{2+} ions from solution.	CEC (mEq./100g)	
			73-78	90-95
			88-105	115-130
Basal spacing	XRD	Basal spacing, crystallinity and phase identification, mineral presence and structural analysis of clay materials.	XRD basal spacing (Å)	
			12.8	9.6
			15-15.3	12-12.5
Thermal analysis	TGA	Mass loss as a function of temperature.	Mass loss (wt%)	
			T (°C)	Calcium	Sodium
			0-200	10.87	11.53
	DSC	Heat flow at phase transitions.	201-400	1.44	1.10
	DTA	Temperature difference between sample and a reference.	401-600	3.80	4.74
			601-800	0.52	0.84
	TGA- DSC/DTA	Simultaneous TGA-DSC or TGA-DTA.	>800 (ash)	83.26	81.80

The high mechanical and chemical stability of bentonite make it suitable for industrial separation processes like wastewater treatment and CO_2 capturing, nevertheless its micropore size distribution limits its application in catalytic and separation process. These properties can be improved by clay layers' intercalation with cations and clay activation via mechanical, thermal and chemical methods. As reported by Chen et al. [45], natural bentonite adsorbed minimal amounts of CO_2 but upon modification with Polyethyleneimine (PEI) using physical impregnation, the CO_2 adsorption increased significantly with greater selectivity towards CO_2 over N_2. Bustam et al. reported the modification of bentonite using mono-, di- and triethanolamine using intercalation process with the former demonstrated the highest CO_2 adsorption capacity at about 5 mmol/g as compared to just 0.9 mmol/g by the unmodified bentonite [46].

Application of bentonite-based composites for contaminant removal has increased significantly over the years. Recently, Vinodh et al. prepared a composite of bentonite and 3-aminopropyl triethoxy silane (APTES) using simple extrudation procedures to improve CO_2 adsorption. A 16 wt%

CO_2 sorption was achieved by 5% bentonite/APTES in comparison to 13 wt% and 3 wt% CO_2 sorption using pristine APTES and bentonite, respectively. In addition, the composite was able to maintain the sorption performance of up to 88.75% until 15 adsorption cycles [47].

Bentonite composite has also found application in advance oxidation process for wastewater treatment. Sonawane et al. reported Bi_2O_3-ZnO/bentonite composite preparation for photocatalytic oxidation of Congo red (CR). The produced catalyst demonstrated excellent photocatalytic oxidation under UV-light and degraded almost all CR in just about 1 hour with 0.029 min^{-1} pseudo-first order rate constant was achieved [48].

Table 2
Applications of bentonite

Applications	Function	Ref.
Adhesives	Gelling and binding chemicals and organic liquids.	[49]
Agriculture	Bentonite increases water and fertilizer retention capacity in soil and contains traces of elements for plants. Bentonite enhances biodegradation of petroleum-agricultural waste by promoting bacterial activity.	[27, 50]
Animal bedding	Absorbing and deodorizing animal waste.	[51]
Antimicrobial agent	Interlayer modification with amoxicillin for antibacterial hybrid material. Proven anti-bacterial property of bentonite clay–gemini (surfactant) hybrid material.	[52, 53]
Catalyst	Stable solid support for polymer catalysts.	[54, 55]
Cement, mortar and aggregates	Reducing aggregate segregation, improving workability and impermeability.	[56]
CO_2 capture	Removal of carbon dioxide (CO_2), sulfur dioxide (SO_2), and volatile organic compounds (VOCs) from automobile and industrial emission.	[45, 47, 57]
Construction	Stabilizing the structures. Bentonite-based geosynthetic clay liners for solid waste leachates control.	[40-42]
Drilling fluid	Thickening and thixotrophic agent for colloidal dispersions.	[26, 58]
Edible oil clarification	Removing suspended particles, free fatty acids, phosphorus and peroxide from crude edible oil such as palm and rapeseed oil.	[36-38]
Food packaging film	Providing exceptional swelling and CEC for safe and functional packaging materials.	[59, 60]
Foundry and casting	Optimizing the foundry consistency due to its binding capacity, high fusion temperature and high dry strength.	[61]
Gene and cell therapy	Biomateria interacts well with proteins and nucleic acids.	[62]
Ink	Controlling consistency and penetration during printing.	[63]
Ionic liquids	Synergistic interactions between bentonite and ionic liquid functionalized composites and increased dispersion stability.	[64]
Medicines, pharmaceuticals and cosmetics	Stabilizing antibiotics into bentonite pastes, medicinal use due to its antidotal effect; improving barium sulphate suspensions for radiological tests, purifying and concentrating vitamins and targeted drug delivery for cancer treatment.	[65-67]
Paint	Suspending and thickening agent in water-based paints; emulsifying agent in water and oil-based paints; improving pigment suspensions, viscosity, thixotropy control, brushability and spraying.	[30]
Paper	Preventing the agglomeration of fine particles of pitch, tar, waxes and resinous material which cause defects; increasing the pigments; improving the pigment distribution; dispersing and adsorbing pigment particles.	[30, 68]
Pesticides	Thickeners, carriers and diluents in pesticide.	[69]
Petroleum derivatives	Recovering chemical derivatives.	[70]

Photocatalysis	Degrading dye for water treatment. Reduction of hexavalent chromium by bentonite-based photocatalyst.	[48, 71]
Radioactive disposal	Absorbing the isotopes and fixing them against leaching. Study of self-sealing behavior of bentonite material for radioactive waste disposal.	[72, 73]
Filler material, hybrid and biomaterials and composites	Forming complexes and hybrid materials by various reactions with organics and polymers. Improving mechanical and thermal properties of composites.	[44, 74-76]
Soaps, cleaning and polishing compounds	Partial replacement for fatty acid due to its emulsifying action, affinity for carbon particles, detergent effect, dispersing agent and water softening action.	[77]
Waste water treatment	Dispersing, absorbing and adsorbing pollutants from wastewater. The use of alum to flocculate the clay-colloidal materials. Removal of phenols, heavy metals and drug residues.	[78-81]
Wine clarification	Removing protein and iron content and reducing hazy appearance.	[34, 35]

5. Challenges and Future Potentials

Bentonite has many industrial applications due to its advantageous physicochemical properties. The two predominant forms, calcium bentonite and sodium bentonite are abundant and cost-effective. Its large surface area, high cation exchange capacity (CEC) and amphoteric nature make it a highly effective adsorbent, particularly advantageous for wastewater treatment process. Sodium bentonite with smaller particle size, generally exhibits superior adsorption performance compared to calcium bentonite. However, its high swelling capacity poses challenges for particle settling and subsequent recovery after treatment. In contrast, calcium bentonite facilitates natural settling, enabling a more straightforward separation process post-adsorption. To increase the settling ability, the addition of multivalent ions can be used to suppress the electrical double layer between clay particles and liquid, reducing the interparticle repulsion and increase the tendency for particles to aggregate. In the case of sodium bentonite, addition of divalent cations such as Ca^{2+} can replace the Na^{+} ions within the interlayer and result in better particle settling such as that displayed by calcium bentonite [82]. Hence, the selection of bentonite adsorbent should be guided by the required adsorption efficiency and the practical considerations related to adsorbent recovery after the treatment process.

Following the adsorption process, spent bentonite adsorbent can be managed through direct disposal for unharmful adsorbate (organic materials from vegetable oil [38]) or requiring specialized treatment (phenols, heavy metals and pharmaceuticals from wastewater [81]), regeneration (microbiological regeneration of bentonite adsorbed organic micropollutants [83]) or reuse as a filler material in composite applications (gelatin adsorbed bentonite for biopolymer reinforcement [44]). Regeneration of spent bentonite poses environmental and economic challenges as conventional regeneration methods are typically expensive, non-sustainable and may lead to the formation of secondary pollutants. Therefore, there is a need to develop sustainable, environmentally friendly and cost-effective regeneration techniques. Further research is also needed to address the recovery of adsorbates and to explore strategies for their permanent immobilization or neutralization, thereby minimizing the risk of secondary pollution [37, 84, 85].

The use of bentonite as a filler material has been shown to enhance the mechanical properties of composites as reported in recent studies involving geopolymer [74], crumb rubber-concrete [86], paper [68], starch biofilm [87], food packaging [59], and basalt-epoxy polymer [88]. In some applications, specific properties of bentonite may need to be modified to improve its compatibility with the composite matrix. Various novel bentonite composites are continually being produced

owing to its tuneable properties. Bentonite continues to be an important component in the development of novel composite materials.

In medical field, bentonite has been used in drug delivery systems [66], cancer treatment [67] and as an antibacterial agent [89]. However, adverse effects have also been reported, such as a case involving a 3-year-old girl treated with bentonite intake resulted in severe hypokalaemia, possibly due to excessive gastrointestinal binding caused by an overdose. Consequently, comprehensive research is needed to establish safe and effective dosage guidelines for bentonite use as well as its potential side effects [65].

The demand for bentonite continues to rise due to its rapidly expanding applications, wide availability, and cost effectiveness. From its traditional use as a construction material, scientists have demonstrated its potential in advanced fields such as in medicine, radioactive waste remediation, catalysis and more. This upward trend is expected to grow steadily in the future. Countries with substantial natural bentonite deposits are exploiting this mineral as a national mining commodity. In 2022, the United States, India and China are the world's top three producers, collectively accounting for approximately 10 million metric tonnes or 54% of the world's bentonite production [90].

Conflict of Interest Statement

The authors declare no competing interests. No financial support, grants, or other forms of compensation were received that could have influenced the outcomes of this work. The research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Author Contributions Statement

All authors have contributed to this review paper. Drafting, writing and editing the manuscript, compiling authors' contributions and critical review: Rashid Shamsuddin and Hamad AlMohamadi; Literature compilation and review support: Ahmer Ali Siyal; Preparation of figures and discussion: Ali Shaan Manzoor Ghumman and Dzulkarnain Zaini; Conceptualization, supervision, and manuscript review: Mark Lay and Johan Verbeek.

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No datasets were generated for this review.

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No ethical approval is required for the review study.

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