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PREPARATION OF CLAY MINERALS – NATURAL SURFACTANT COMPOSITES TO REMOVE ORGANIC DYES AND HEAVY METALS

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ABSTRACT

The rapid development of industry is considered to be the main cause of various environmental problems, which are mainly caused by the discharge of wastewater which contains many hazardous compounds. Dyes and heavy metals are type of hazardous substances that are often found in industrial wastewater and cause ecosystem damage. Dyes and heavy metals are more difficult to remove due to their inability to be broken down, so they can build up and reach dangerous levels. Adsorption is a straighforward and efficient method for dealing with hazardous substance contamination in water. Clay minerals, known for their efficient adsorption properties, were chosen for this procedure. Clay minerals are porous materials so they are suitable for use as adsorbents. The intercalation technique is a robust strategy to further increase the adsorption capacity of clay minerals, which is done by treating clay minerals with surfactants. Clay minerals modified with natural surfactants are considered as a potential choice for removal procedures. The use of this natural surfactant was chosen because of its excellent adsorption capacity and environmentally friendly properties. Polar lipids, natural surfactants, are commonly present in the lipid layers of plants and animals. This review focuses on the synthesis of modified clay minerals using different natural surfactants such as soybeans, saponins, lipopeptides, and rhamnolipids, as well as the use of alternative clay mineral/natural surfactant composites. This review describe various types of natural surfactants that can be used to modify clay minerals and their application in the adsorption process.

ABSTRAK

Pesatnya perkembangan industri dinilai menjadi penyebab utama berbagai permasalahan lingkungan, yang terutama disebabkan oleh buangan air limbah yang banyak mengandung senyawa berbahaya. Pewarna dan logam berat merupakan salah satu jenis zat berbahaya yang sering ditemukan pada air limbah industri dan menyebabkan kerusakan ekosistem. Pewarna dan logam berat lebih sulit dihilangkan karena ketidakmampuannya terurai, sehingga dapat menumpuk dan mencapai tingkat yang berbahaya. Adsorpsi adalah metode yang mudah dan efisien untuk menangani kontaminasi zat berbahaya dalam air. Mineral lempung, yang dikenal karena sifat adsorpsinya yang efisien, dipilih untuk prosedur ini. Mineral lempung merupakan bahan yang berpori sehingga cocok digunakan sebagai adsorben. Teknik interkalasi merupakan strategi jitu untuk lebih meningkatkan kapasitas adsorpsi mineral lempung, yang dilakukan dengan mengolah mineral lempung dengan surfaktan. Mineral lempung yang dimodifikasi dengan surfaktan alami dianggap sebagai pilihan potensial untuk prosedur penghilangan. Penggunaan surfaktan alami ini dipilih karena kapasitas adsorpsinya yang sangat baik dan sifatnya yang ramah lingkungan. Lipid polar, surfaktan alami, umumnya terdapat pada lapisan lipid tumbuhan dan hewan. Tinjauan ini berfokus pada sintesis mineral tanah liat yang dimodifikasi menggunakan surfaktan alami yang berbeda seperti kedelai, saponin, lipopeptida, dan rhamnolipid, serta penggunaan komposit mineral tanah liat/surfaktan alami alternatif. Ulasan ini menjelaskan berbagai jenis surfaktan alami yang dapat digunakan untuk memodifikasi mineral lempung dan penerapannya dalam proses adsorpsi.

Keywords: *Natural surfactant; Clay mineral; Modification; Adsorption; Application*

I. Introduction

In recent years, awareness of water-based organic dye contamination has grown significantly. Industrial waste from manufacturers, including textiles, paper, printing, carpet, plastic, food, and cosmetics [1], is the primary cause of this pollution. Organic dyes can have negative impacts on the environment. For example, when dyes accumulate as a layer on the surface of a body of water, their vibrant hues might reduce the penetration of light into the marine ecology. This will ultimately disturb the environment, as sunshine is a crucial energy source. Furthermore, dyes harm marine species because they are carcinogenic and toxic [2].

Heavy metals in water, soil, and air contribute to environmental contamination. Addressing rivers contaminated with heavy metals has become a top priority due to the direct correlation between the volume of trash discharged and the continuous expansion of industrial activities [3, 4]. Heavy metal pollution is a more enduring and chronic environmental issue than organic toxins due to their resistance to degradation or destruction. They build up in living creatures because the organisms consume the water. The presence of Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Fe^{2+}, Ni^{2+}, and other metals can harm organisms. Excessive levels of heavy metals in bodily fluids can potentially harm humans' psychological or other biological systems [5].

Multiple methods are available to purify water contaminated by heavy metals and chemical dyes. The treatment methods consist of precipitation, oxidation, reduction, and adsorption. Adsorption is the most commonly used method because of its economic advantage. This method uses either clay minerals or altered clay. The primary clay minerals in this process include montmorillonite, illite, muscovite, sepiolite, and palygorskite [6,7]. Clay minerals are composed of two layers: tetrahedral and octahedral. The layers are stacked in a 2:1 ratio. The negative surface charge of bentonite is linked to the substitution of Al^{3+} for Si^{4+} in the tetrahedral sites and Mg^{2+} for Al^{3+} in the octahedral sites. Cations, predominantly Ca^{2+} and Na^{+}, balance the negative charge in the interlayer gaps [8].

Using mineral clay as an adsorbent to eliminate pollutants relies on its innate properties, such as strong chemical and mechanical resistance, negative charge on its layers, surface functional groups, and cation exchange capability facilitated by its crystalline structure. Nevertheless, the material exhibits restricted adsorption capability and strong selectivity when exposed to high concentrations of organic dye [9]. It is recommended to make alterations to the mineral clay by adding appropriate organic molecules to improve its adsorption capacity and selectivity. The properties and composition of clay minerals allow for the insertion of organic compounds into the interlayer gaps by cation exchange using long- or short-chain organic cation surfactants.

"Natural surfactant" denotes surface-active molecules that have an affinity for adsorbing onto surfaces. They function by altering the chemical interactions of liquids at the surface boundaries. It is produced from natural chemicals from plants or the cell membranes of yeast, bacteria, fungi, or marine microorganisms. Natural surfactants can be obtained from plants by undergoing several separation processes, including extraction, precipitation, and distillation [10]. Bacterium-derived natural surfactants are typically generated through the fermentation process. Natural surfactants can be categorized into many classes, including glycolipids, lipopeptides, lipopolysaccharides, phospholipids, fatty acids, and neutral lipids [11-13].

Clay minerals altered by an artificial surfactant are the most commonly used surfactants. The most commonly used surfactant is alkyl quaternary ammonium cationic surfactant, including dodecyl trimethyl ammonium, benzyl dimethyl tetradecyl ammonium, and cetyl trimethyl ammonium, among others [14–17]. Synthetic surfactants are environmentally unfavorable because they use non-degradable ingredients. Another type of surfactant is natural surfactant, but there is less information on the production of organically modified clay. The increased expense and time required to produce natural surfactants compared to chemical derivative surfactants is the reason for this.

Moreover, these expensive procedures provide tiny quantities of functional natural surfactants [10]. Natural surfactants are more beneficial than synthetic surfactants for controlling heavy metals contamination. The advantages of natural surfactants stem from their origins in renewable resources, low or absent toxicity, strong surface activity, effectiveness in harsh temperature and pH environments, potential for reuse, and biodegradability. [10, 18–20]. Clay materials altered with natural surfactants have a greater adsorption capacity and reaction rate than unaltered and artificially changed clay materials. This review article provides an overview of using clay minerals and natural surfactants as a biodegradable and renewable composite to remove organic dyes and heavy metals. It covers preparation methods, mechanisms, factors influencing adsorption, and potential applications in cosmetics and pharmaceuticals.

II. Modified clay minerals with various natural surfactants for the adsorption process

II.1. Bentonite/Lecithin from Soybeans

Lecithin is a substance consisting of several phospholipids. It is a composite of different components found in organisms. Lecithin is primarily utilized in the pharmaceutical and culinary sectors because of its cost-effectiveness. Lecithin is used as an emulsifier in making chocolate and food coatings [21]. Egg yolks are the primary source of lecithin, but their expensive nature hinders their industrial application. To address this issue, the raw material for producing lecithin can be sourced from plant seed oil, particularly soybean oil. Soybean seeds, rapeseeds, and sunflower seeds are all found to contain high levels of lecithin based on multiple research [22].

Soybeans, scientifically known as Glycine max merilli, have minimal saturated fat and no cholesterol and are the sole plant-based food source of eight important amino acids. Soybeans also contain fiber, iron, calcium, zinc, and vitamins. Soy is a valuable source of protein and oil, containing around 40% protein and 20% oil. It is a valuable source of three natural surfactant materials: soy lecithin, soy protein, and soy saponin [23,24].

Employing both extraction and purification techniques will improve the lecithin content of soybeans. Soy lecithin molecules typically comprise 65-75% phospholipids (PLs), 34% triglycerides, and minor quantities of carbohydrates, pigments, and glycoside sterols. Phosphatidylcholine (PC) is the most prevalent phospholipid in lecithin, ranging from 23% to 46%. Phosphatidylethanolamine (PE) makes up 20% to 25%, and phosphatidylinositol (PI) accounts for 9% to 21%. The structure is illustrated in Figure 1 [25–28].

Soy lecithin is considered a natural surfactant due to being a neutral compound of zwitterionic phospholipids with amphiphilic properties. Moreover, organisms can tolerate it since it is a component of the cell membrane and can be digested. Soy lecithin is non-toxic. Merino et al. [24] examined the creation and properties of bentonite modified with soy lecithin, analyzing the impact of the mass ratio between soy lecithin and bentonite and the influence of different reaction durations. These experiments are carried out in a controlled environment with a constant temperature.

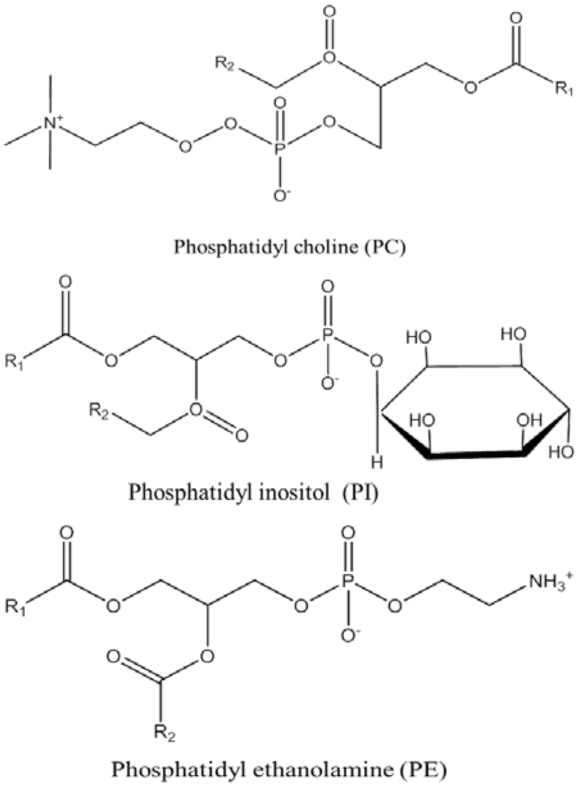

Figure 1. Chemical structures of phospholipids (adapted from reference [28])

The authors determined that the ratio of bentonite to lecithin directly influenced the ultimate characteristics of the composite. An optimal modification in the structure of bentonite was achieved with a ratio of 1.0:1.2 g of bentonite to lecithin. An increase in interlayer space is demonstrated by measuring the DTG curve and FTIR spectra. The authors determined that reaction time did not substantially impact the composite's final parameters, as equilibrium was achieved within 30 minutes of the beginning of the reaction.

The FTIR study indicates the potential occurrence of SL interactions at the surface of bentonite. Two additional bands have emerged at 2922 cm-1 and 2852 cm^{-1}, corresponding to the asymmetric and symmetric stretching vibrations of CH2, respectively. A strong absorption peak related to the C=O group in lecithin was detected around 1730 – 1737 cm^{-1}. Refer to reference [22] for a research publication with comparable findings.

Ouellet-Plamondon et al. [29] examined various methods for creating bentonite/surfactant composites. Three surfactant variations were utilized: HDTMA, lecithin, and topinin. The researchers assessed the surfactants' capacity to be inserted between the montmorillonite layers. The surfactant obtained from lecithin was discovered to offer increased thermal conformation stability for the composite. The surfactant chosen for modifying bentonite should be based on the intended usage of the bentonite-surfactant composite.

Wicklein et al. [30] and Luduena [31] determined that cationic ion exchange occurs on the surface of bentonite during the synthesis of organo-bentonite. This enables contact through Van der Waals' forces with other parts of soy lecithin because of the hydrophobic chains present. Below the isoelectric point, the organo-bentonite carries a positive charge [32]. Soy lecithin's property as a natural surfactant makes it environmentally safe and suitable for creating organo-bentonite.

II.2. Soils/saponin from *Quillaja saponaria* tree

Saponins are glycosidal triterpenoids that exhibit surfactant properties, including the capacity to generate foams through agitation. A mixture of nonpolar sapogenins and water-soluble side chains causes it. This configuration resembles manufactured surfactants when lipophilic and hydrophilic molecules are present [33]. Saponins can be categorized according to the active chemicals present on their surface. They are derived from secondary metabolites that plants and particularly lower marine creatures synthesize. They are mainly in angiosperms, with some found in ferns like Polypodium and Cyclamen species. They are also present in specific underwater creatures and potentially in algae. It is in different plant components, including roots, buds, flowers, and seeds [34,35].

A researched variant is raw saponin extracted from the *Quillaja saponaria* tree (Molina) by ultrasonic extraction in an aqueous phase technique [36]. *Quillaja saponaria* is a native plant extensively cultivated in Chilean woodlands. *Quillaja saponaria* bark extract is mainly used in the pharmaceutical, food, and chemical sectors. The sample contains 60 types of saponins and lower quantities of polyphenols, tannins, salts, and sugars [37, 38]. Despite the inexpensive nature of *Quillaja saponaria* wood, the extraction method for its saponins is expensive, leading to a decrease in its economic worth. New, cost-effective processing processes are being developed to extract saponins from *Quillaja saponaria* wood to enhance its economic potential.

Reverse-phase HPLC is the dominant analytical method for saponin analysis in Quillaja saponaria. Nord and Kenne analyzed the structure of each type of saponin in *Quillaja saponaria* bark extract and identified six major types of saponins using a reversed-phase HPLC separation process [39]. The saponin content in *Quillaja saponaria* bark ranges from 9% to 10%. Table 1 displays more plants that contain saponins along with their saponin levels [24].

Vinatoru explains an extraction process that involves two distinct physical events [40]. The first phenomenon is diffusion through the cell wall, and the second is rinsing the cells' contents when the plant cell wall is completely ruptured. Both of these events heavily involved ultrasonic radiation. Ultrasound extraction technology has an advantage over conventional extraction methods as it operates at a lower temperature, making it ideal for extracting substances that are sensitive to heat. Additionally, Soxhlet extraction, a technique within ultrasound-assisted extraction, can utilize a range of solvents selected based on the specific extract [41].

Gaete-Garretón et al. [42] studied technologies that enhance extraction efficiency by decreasing extraction time, temperature, and solvent quantity needed while maintaining sample quality. The examination utilized a specialized ultrasonic unit equipped with a stepped-horn stainless steel ultrasonic transducer in the alignment system. The study indicates that key factors affecting the process efficiency are granulometry, raw matter/solvent ratio, and extraction time. Cares et al. [36] have conducted comparable operations with comparable outcomes using different solvents. Ultrasonic extraction techniques are generally acknowledged for their exceptional benefits.

Table 1. Types of plants from different regions containing saponins

Plant materials		**Saponin content (%)**
Common name	**Latin name**	
Horse-chestnut (seeds)	*Aesculis hipocastanum*	3 – 6
Oat	*Avena sativa*	0.1 – 0.13
Sugar beet (leaves)	*Beta vulgaris*	5.8
Quinoa	*Chenopodium quinoa*	0.14 – 2.3
Chickpea	*Cicer arietinum*	0.23
Saffron crocus	*Crocus savitus*	1.2 – 3.4
Soybean (Sprouts and seeds)	*Glycine max*	0.22 – 0.47
Licorice (root)	*Glycyrrhiza glabra*	22.2 – 32.3
Ivy	*Hedera helix*	5
Alfalfa	*Medicago sativa*	0.14 – 1.71
Chinese ginseng	*Panax ginseng*	2 – 3
American ginseng	*Panax quinquefolius*	
Young leaves		1.42 – 2.64
Mature leaves		4.14 – 5.58
Roots (4 years old)		2.44 – 3.88
Green pea	*Pisum sativum*	0.18 – 4.2
Milkwort	*Polygala spp.*	8 – 10
Primula	*Primula spp.*	5 – 10
Quillaja bark	*Quillaja saponaria*	9 – 10
Soapwort	*Saponaria officinalis*	2 – 5
Sarsaparilla (Rhizomes and roots)	*Smilax officinalis*	1.8 – 2.4
Fenugreek	*Trigonellafoenum-graecum*	4 – 6
Yucca (Stalk and roots)	*Yucca schidigera*	10

Several recent publications focus on employing clay minerals treated with natural surfactants to remove heavy metal pollution. Gusiatin and Klimiuk [43] studied the efficacy of heavy metal removal by three soil types: loamy sand, loam, and silty clay, with clay contents of 20%, 40%, and 61%, respectively. The best metal removal efficiency was achieved in loamy sand (82–90%) and loam (67–88%) soils with a saponin concentration of 3%, while the lowest efficiency was seen in silty clay soil (39–62%) with a saponin concentration of 6%.

Hong et al. demonstrated that saponins extracted from Quillaja bark effectively remove heavy metals like Cd and Zn from polluted soil, achieving 90-100% removal rates for Cd and 85-98% for Zn [44]. The ideal pH range for this process was between 5.0 and 5.5. Zhan et al. [45] studied the mechanism and effectiveness of removing Cu, Cd, Pb, and Zn metals from irrigation waste using Quillaja bark saponin. The study found that altering the saponin concentration significantly impacted the removal efficiency of Cu, Cd, Pb, and Zn. The highest results were achieved with a 3.0% saponin solution, resulting in removal efficiencies of 43.87% for Cu, 95.11% for Cd, 83.54% for Pb, and 20.34% for Zn. The desorption ability of heavy metals followed the order: Cd > Pb > Cu > Zn.

II.3. Ca-bentonite/rarasaponin from Sapindus rarak DC

Sapindus rarak de Candole, commonly known as S. mukorossi, is a renowned plant with seeds used as a traditional detergent for biopesticides and health applications. Saponin is a bioactive compound from Southeast Asia, currently prevalent in regions across Asia and Africa. In India, this natural surfactant has historically been used for washing clothes, baths, and folk remedies because it creates foam in water. In Indonesia, it is used to produce traditional soap for laundering textiles, particularly batik. Unlike regular detergents, this fruit's traditional soap does not promote color fading.

Kurniawan et al. [46] utilized bentonite as an adsorbent and rarasaponin as a natural surfactant to create an organo-bentonite composite to eliminate methylene blue. Figure 2 displays the intricate composition and the suggested process of Ca-bentonite/rarasaponin. The diagram illustrates multiple phases of cation exchange, facilitating the incorporation of rarasaponin into the bentonite interlayer and beginning with the deacylation reaction of the rarasaponin structure, including two acyl groups ($C_2H_3O^{+)}$ attached to the carbonyl structure when diluted in a polar solvent. The incident activates the negative charge of oxygen atoms in the carbonyl group, making it a reactive binding site for raw bentonite. Excess H^+ ions protonate the surface of the silanol group on bentonite. Each protonation step results in a positively charged water molecule that neutralizes the oxygen atom adjacent to the deacylated carbonyl group while also protonating the silanol ($Si\text{-}OH_2^+$) group on the tetrahedral sheet of bentonite.

Rarasaponin was extracted before preparing the organo-bentonite composite. Chandra et al. [47] conducted rarasaponin extraction processes, whereas Schmitt et al. [48] explored microwave-assisted extraction of saponins from unrefined Sapindus mukorossi soap nuts. The method optimized the extraction of rarasaponin from fruits by disrupting internal cell structures to release intracellular products, aiding in the mass transfer of raw materials into a solvent to meet sustainable chemical parameters. This accomplishment is achieved by selectively exposing the process to microwave radiation to accelerate the heating mode. The saponin that was extracted undergoes rapid heating treatment using microwave irradiation. Zhou et al. [49] have discussed an alternative method for extracting Sapindus mukorossi. The fruit was subjected to two extractions using 75% ethanol for 30 minutes with a solid/liquid ratio of 1:6 (w/v).

Chandra et al. [47] illustrated the process of combining Ca-bentonite with rarasaponin in a 10:1 ratio by dissolving rarasaponin in 25 mL of distilled water and subsequently adding bentonite to the solution. This process includes physical interactions involving heating and stirring and chemical reactions involving bonding between acyl groups ($C_2H_3O^+$) from rarasaponin and a carbonyl group of bentonite.

Rarasaponin has been identified as a nonionic surfactant in multiple investigations. However, pH and ionic strength variations can likely lead to electrostatic effects due to the carboxyl groups on the side chain [48]. The research findings indicate that electrostatic interactions occur between the deprotonated silanol group (negatively charged) on the bentonite surface and the cationic dye at high pH (optimal at pH 8). FTIR analysis confirmed the successful intercalation of rarasaponin into the bentonite interlayer by ion exchange processes. The presence of the C=O stretch (ester carbonyl group) was verified at 1712 cm^{-1} [49]. This figure roughly corresponds to the results of Candra et al. [47], who found a value of 1729 cm^{-1}.

II.4. Na-Montmorillonite/lipopeptides (Na-MMT/LPSSF) from solid-state fermentation by Bacillus amyloliquefaciens

Lipopeptides are surface-active molecules produced by bacteria, fungi, and yeast. They are amphiphilic and exhibit potent antibacterial action and emulsifying and foaming capabilities. Scaling up is challenging because of the high production expenses [50]. Surfactin, iturin, and fengisin are the most widely recognized lipopeptides produced by Bacillus subtilis [51]. Tsuji et al. have provided a comprehensive summary of the classification, generating strain, biological activity, functional features, and applications of lipopeptides [52]. Lipopeptides have diverse industrial applications, including food and cosmetics for emulsification, demulsification, dispersion, foaming, moisturizing, and dispersing qualities.

Research has been conducted on the generation of lipopeptides by Bacillus amyloliquefaciens XZ-173 by solid-state fermentation with soybean flour and rice straw as the substrate [53]. Further research has been conducted on synthesizing modified Na-MMT/LPSSF from solid-state fermentation by Bacillus amyloliquefaciens to remove heavy metals in water [54]. The most effective adsorption ratio for heavy metals was determined to be 50:1 in Na-MMT/LPSSF variants, with the optimal pH set at 5.

X-ray diffraction examination confirmed the successful insertion of LPSSF into the interlayered space of Na-MMT, which is aligned parallel to the aluminosilicate layer. The adsorption capacity of heavy metal ions rises as the pH of the solution increases because the adsorbent surface undergoes deprotonation, leading to an increase in negative charge. The highest adsorption capabilities of Na-MMT/LPSSF composites were 68.66 mg/g for Cu^{2+}, 68.39 mg/g for Zn^{2+}, 62.15 mg/g for Cd^{2+}, 77.80 mg/g for Pb^{2+}, and 49.08 mg/g for Hg^{2+}. The Langmuir model provided the most accurate description of the isotherm data. The specific mechanisms of removing Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, or Hg^{2+} using Na-MMT/LPSSF composites have not been determined. The study's findings demonstrate that under certain composition variations, the Na-MMT/LPSSF (50:1) composite is a more effective adsorbent for removing metal ions from wastewater than employing Na-MMT alone.

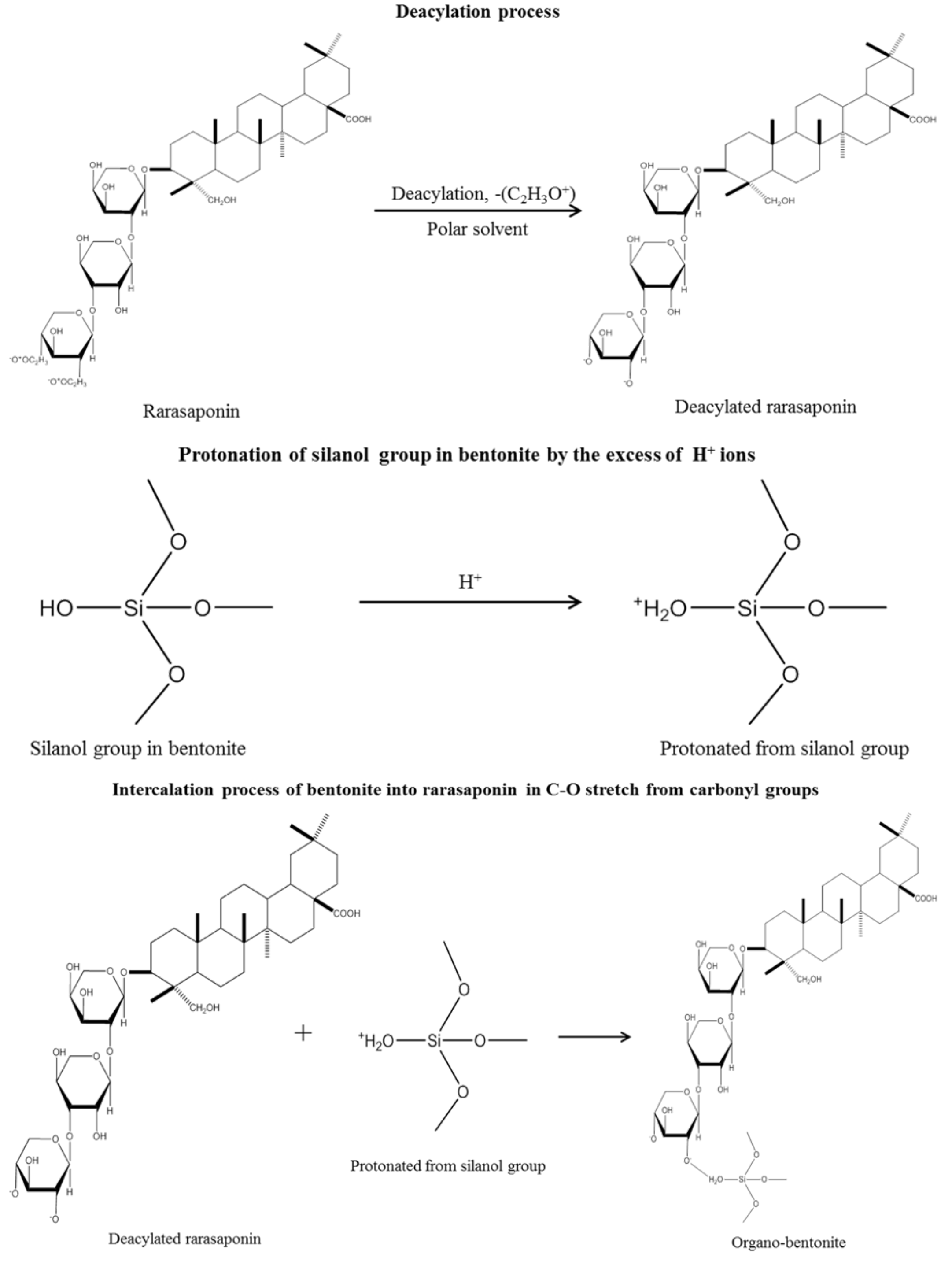

Figure 2. The mechanism of Ca-bentonite/rarasaponin [46]

A different method was examined for synthesizing clay/phospholipid and studying the adsorption process with organic methanol and ethanol solvents [30]. This study illustrates the bonding mechanism between the lipid molecule and the external surface of sepiolite, as well as the internal surface of Na-montmorillonite. The adsorption process was governed by phospholipid molecules on Na-montmorillonite and sepiolite in organic solvents. This process exhibited a sodium cation exchange mechanism, where intracrystalline water enhanced the lipid's attraction to clay.

II.5. Na-Montmorillonite/Rhamnolipids

Rhamnolipids generated by *Pseudomonas aeruginosa* are among the most thoroughly researched biosurfactants [55]. Rhamnolipid is a biosurfactant produced through the fermentation of isolated microorganisms. When used in soil flushing, it efficiently eliminates heavy metals from excavated soil. Rhamnolipids as biosurfactants can be recycled using precipitation procedures at low pH or by introducing air into the metal-rhamnolipid complex, leading to foaming because of rhamnolipids' inherent foaming characteristics [56].

Various rhamnolipids exist, including Type R1 (C26H48O9) and Type R2 (C32H58O13), with molecular masses of 504 Da and 650 Da, respectively [57]. Two further variations of rhamnolipid consist of two rhamnoses linked to β-hydroxydecanoic acid or one rhamnose associated with the same fatty acid. Rhamnolipid type I and type II are appropriate for dirt washing and heavy metal removal among these types [57]. The critical micelle concentration (CMC) was 10^{-4} mol/L at pH 6.8 and 4×10^{-5} at pH 5. The surface tension at the critical micelle concentration (CMC) is 30.0 mN/m for R1 and 31.2 mN/m for R^2.

Several studies have suggested using natural surfactants to eliminate heavy metals [58]. The study findings demonstrate that Cd (II) and Zn (II) ions in quartz can be removed by introducing rhamnolipids to soil components using the batch sorption method. The X-ray fluorescence (XRF) spectrophotometer examination revealed that SiO_2 compounds were the most prevalent, with the following detailed results: SiO_2 95.4%, Al_2O_3 2.97%, Fe_2O_3 0.13%, CaO 0.136%, TiO_2 0.159%, Na_2O 1.19%.

The pH and starting concentration have a distinct impact on the sorption process. Multiple investigations have verified that the ideal pH level is a significant factor in controlling the adsorption of heavy metal ions [59]. The surface charge is determined by the existence of H+ and OH- ions as potential electrolytes, influencing the net negative, positive, or neutral charge on the surface. At pH 3, they found that the entire net charge value was determined to be zero, known as the pH of zero charge (pzc). The sorption efficiency of Cd (II) and Zn (II) ions is influenced by pH, with the highest sorption capacity occurring at pH 6.4 within the pH range of 5.0 - 7.2. This indicates that the soil pH is higher than the point of zero charge (PZC), confirming that the soil surface has a net negative charge and can exchange cations.

III. Clay minerals modified with natural surfactant: Related Applications

Plants with Saponins, now recognized as natural surfactants, have a history of being utilized as traditional medicines, particularly in Asia. Natural surfactants have been increasingly utilized in the pharmaceutical sector for various purposes, such as drug release systems, anticancer medications, and drug delivery systems, and as adjuvant material in producing antitumor and antiviral vaccines [60]. Furthermore, natural surfactants and their use in environmental wastewater treatment can enhance certain clay materials. This alternative modification is a safe and effective option for usage in the biomedical area, as confirmed by sources [61].

Calabrese et al. [62] proposed utilizing biosurfactant-modified clay as a medication delivery method for orally administering cinnamic acid. The procedure includes incorporating a biocompatible nonionic polyoxyethylene sorbitan monolaurate surfactant into montmorillonite to evaluate its performance using the adsorption isotherm and the cinnamic acid release process. Montmorillonite is chosen for its characteristic structure, which comprises two layers of tetrahedral silica and one layer of Al^{3+} octahedral. The biocompatible nonionic polyoxyethylene sorbitan monolaurate surfactant was chosen for its pharmacological properties such as anti-inflammatory, antibacterial, antimalarial, antioxidant, antidiabetic, and anticancer effects, as well as its non-toxic nature, enabling its use in drug delivery systems [62, 63].

Research has effectively incorporated natural surfactants into montmorillonite to displace water molecules in interlayer gaps. This method lowers organic content more efficiently than unmodified montmorillonite in adsorption. The results met the criteria for creating an effective drug delivery system and can be used as a key component in developing a new drug delivery system.

Previous research has employed clay swelling inhibitors derived from sodium montmorillonite/triterpenoid saponin in the petroleum industry, specifically in enhanced oil recovery (EOR) and drilling fluids areas [64]. Triterpenoid saponin is a natural surfactant extracted from Glycyrrhiza glabra. Glycyrrhiza glabra is a plant in the Fabaceae family [65]. This plant species is well-known for its ability to thrive in agricultural and plantation settings as weeds, which are readily available. It is noteworthy for its high saponin content, which ranges from 22.2% to 32.3%, and it is recognized as a potent biological herb.

The primary purpose of EOR is to enhance the oil recovery factor. It is also utilized in the drilling fluid sector for many purposes, including shale stability, emulsification, aphronization, penetration rate enhancement, water inflow decrease, and lubrication [66].

Various substances are combined with specific compositions in the production of cosmetics. Cosmetic formulations designed for topical application on hair, eyelashes, and face skin. Cosmetics are formulated with materials such as powder as the primary component, surfactants, scents, herbal oils, antioxidant compounds, colors, etc., as additives varying from 0.01 to 10%. The cosmetic composition of the present invention contains many herbal extracts, each at a concentration of no more than 2%. An intriguing herbal extract to consider for this combination is Chestnut Seed extract (*Aesculus hippocastanum*). It possesses anti-inflammatory effects that benefit the skin.

Lipophilic compounds can be beneficial cosmetic ingredients when used safely and effectively. In addition, cosmetic formulations might include microspores, liposomes, micelles, and microspheres. Combining various types of natural and synthetic surfactants is necessary to create micelles because of their differing polarity properties.

Cosmetics should be able to spread and be absorbed quickly by the skin, hair, and scalp when used. Top cosmetic formulations consist of liquid or solid emollients, solvents, humectants, thickeners, and powders. The cosmetic compositions in this invention contain various powders such as chalk, talc, kaolin, starch, Smectite clays, chemically modified magnesium aluminum silicate, organically modified montmorillonite clay, hydrated aluminum silicate, fumed silica, aluminum starch octenyl Succinate, and combinations of these.

Rhamnolipid is a natural surfactant widely utilized for its biodegradable nature, low toxicity, and capacity to create microemulsions and surface-active characteristics. Rhamnolipids are appropriate for usage as foundational components in emulsions and nanoemulsions for many applications in industries like food, beverage, personal care, and pharmaceuticals. Rhamnolipids have been created as cosmetic ingredients, and there is ongoing research on producing liposomes and emulsions, including patents [67]. This recent advancement is gaining significance in the cosmetics sector.

IV. Conclusions

This review paper demonstrates that utilizing clay material/natural surfactant composites for adsorption is a viable alternative to traditional adsorption processes employing only clay materials, effectively eliminating dyes and heavy metal ions. Natural surfactants have certain benefits compared to chemical surfactants. Based on its natural surfactant properties, it can be inferred that it is biodegradable due to its uncomplicated chemical composition, ecological suitability, little toxicity, and ability to endure harsh temperatures, making it suitable for various sectors. This study field has significant potential for advancement to enable the practical application of clay material/natural surfactant composites beyond just laboratory experimentation.

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