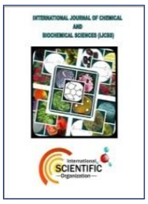
International Scientific Organization

International Journal of Chemical and Biochemical Sciences
(ISSN 2226-9614)

Journal Home page: www.iscientific.org/Journal.html



Clay and other natural Inorganic materials effectiveness in wastewater treatment: A review

Sana Yaqoob* and Ayesha Mushtaq

Department of Chemistry, University of Agriculture Faisalabad, Pakistan

Abstract

In recent decades, expanding domestic and commercial activity has resulted in the discharge of a variety of toxic pollutants into aquatic systems. Therefore, there is a crucial need for a reliable and environmentally acceptable method of eliminating these contaminants from wastewater. Adsorption is regarded as a simple, affordable, and environmentally friendly technique among the available technologies. Among the natural adsorbents, clay minerals have drawn more attention because of their distinctive properties: large surface area, better cation exchange capacity, and environment friendly material. They act as effective adsorbents with good adsorptive ability for highly toxic water-soluble dyes. This review article emphasises the significance of various clays (in raw and modified forms) that are being employed as an adsorbent for the removal of different dyes from industrial effluents. Different modification methods used to modify the clay to get better results are discussed in detail. Appropriate conditions for a clay-dye system are illustrated, as are the adsorption capacities of various clays, and the adsorption process is critically examined. This article will also examine the use of inexpensive, naturally occurring inorganic adsorbents other than clays to remove toxic heavy metals and dyes from industrial effluents. This study suggested that modified clays are more efficient materials for the purification of dye-polluted water than other abundantly formed natural adsorbents.

Keywords: Wastewater, Clays, Adsorption, natural adsorbents, Clay Minerals

Full length article **Corresponding Author*, e-mail: gillsana823@gmail.com

1. Introduction

The last few decades have shown a dramatic increase in human population and industrialization that ultimately incases the demand of consumption of freshwater Hence the water quality is deteriorating day by day because of the heavy metals /dyes (cationic, ionic dyes) that are released from the industries. So as a result bulk amount of industrial contaminated water is directly discharged into the natural environment and water reservoirs. These dyes or heavy metals are very toxic in nature and highly stable in aqueous environment [1-2]. These hazardous heavy metals /dyes can enter into the human body through biological food chain and accumulate in the body and cause many diseases including gastric dysfunction, anemia, bone softening and many others. These synthetic dyes /metals have detrimental impact on aquatic organisms as well. These dyes contain chromogenic groups that form a layer on the water surface, and does not allow the light to enter the water, hence lower the photosynthesis rate of aquatic plants and disturb the other vital activities of aquatic organisms [3-4].

Therefore this polluted water must be treated to remove contamination before discharge into the water streams [5-6]. Numerous methods, including ion exchange, electrochemical oxidation, Fenton oxidation, reverse osmosis, coagulation/flocculation, zonation, electrocoagulation, biodegradation, and adsorption, have been developed for the treatment of dye polluted water. These treatments have high removal efficiency but at the same time have many disadvantages like high energy utilization, cost, huge waste etc. [7-8]. Adsorption is considered to be the most effective method for the removal of dyes/ heavy metals from industrial effluents due to its advantages such as high removal efficiency, cost effectively, easy to use etc. There are many natural adsorbents such as egg shells, wool, volcanic ash, and sand but the most abundant of all are clays and clay minerals due to their excellent properties such as high CEC (cation exchange capacity), surface charges, high absorbance capacity, and high surface area etc. Clays are hydrated phyllosilicate minerals that naturally found in sedimentary rocks during the process of weathering [9-10]. One unit is made up of $SiO^{-}_{4,}$ and oxygen molecules arranged themselves in a tetrahedron order. These tetrahedrons connected to the next tetrahedron to form a sheet like structure [11-12]. Clay are considered to be a natural scavengers for pollutants like heavy metals or dyes. The presence of exchangeable ions on clay surfaces makes it possible for the clay to absorb the ions through adsorption and the ion exchange process. Mg^{2+}, Cl^{-}, and H^{+} ions are found on the surface of clay minerals. Clays have a very strong attraction for dyes /heavy metals and exchange the ions on its surface without effecting the its other structure. Modification of clays by physical or chemical treatments enhance its adsorption ability, this absorptive property makes the clay minerals a novel adsorbent. Modified clay by several treatments show excellent result for the removal of contaminants from wastewater. Acid treatment, thermal treatment, clays pillaring are the methods used for the modification of clays [13-14]. Swelling properties, physiochemical properties and their 2D (two dimensional) structure enable the clay minerals to trap the heavy metals and other contaminants from industrial wastewater on their surfaces using the process of adsorption. This review article emphasizes the removal of organic, and inorganic contaminants from wastewater and the brief structures of different clay minerals belongs to different classes. The adsorption capacities of raw and modified clays for dyes /heavy metal removal also review in this article [15-16].

2. Clay's

Clay's are very fine-grained minerals with plastic properties. They have a high water content and can solidify when dried or fired. Clays generally consists of phyllosilicates, but some other components could impart plasticity or hardening. [17]. Clays can be differentiated from other (fine grained) soils from size, and morphology of the clay. The main classes of clay include Montmorillonite semactic. Talc, Pyrophyllite, sauconite, and vermiculite, saponite, nontronite, and montmorillonite are all members of the smectite group. The clay micas are part of the illite group. illite is the most common mineral among all [18]. Chlorites are often classified as a distinct group of phyllosilicates rather than clay. In these categories, there are about 30 various types of pure clays, and that most natural clays are a combination of these and other weathered minerals [19].

Clay differences offer an opportunity to study the effect of framework and different layer charges on metal- ion coordination to fixed charge sites. Moreover, these mineral selection offered a variety of surface hydroxyl- site structures for aluminol and silanol. The surface charges (negative charge) in the structure of fine grain minerals is related to clays adsorption abilities. Adsorption of positively charged dyes, can neutralise these negative charges on clays surfaces. The clays also had great surface area, approximately 800 m^2/g,that contribute significantly to their high adsorption ability. With compared to other clays montmorillonite clay are expected to have greatest sorptive capacity [20]. Modification of clay minerals improve its efficiency in removing contaminants from water and industrial water. Zeolites are silicate minerals that occur naturally but can also be synthesised commercially. Clinoptilolite is the most common natural zeolite species. The ion exchange abilities of zeolites decide their adsorption properties [21].

3. Classification and general properties of clays

Clay minerals are materials particle with the size smaller than 2 µm as well as a family of minerals with similar chemical compositions and crystal structural characteristics. Plasticity, fineness of the grain, shrinkage, swelling and many others are the physical properties of the clay. Clays are fine-grained aluminosilicates mineral crystals, and metal oxides [22]. Clay minerals are classified into different classes based on their properties, such as mica, smectites, kaolinite, and vermiculite etc. [23]. Electrostatic repulsion, crytallinity, adsorption, and specific cation exchange reactions all contribute to these interactions. More the porous surface of clay more will be its binding power for ions [24-25]. China clay is a primary ancient and pure clay that was first used by the Chinese. It is primarily composed of kaolinite clay, but it is also composed of mineral mixture containing montmorillonite, feldspar, and illite clays etc. Clays are classified as "Amorphous or Crystalline" on the basis of differences in inter-layer structures (see flow chart. 3). The crystal structures of crystalline Clays can be divided further into groups based on the layer structure of the clays including 1:1, 1:2, and mixed layer- type clay, which is illustrated in fig.1 (a) and 1(b).

4. Basic structure of the Clay

Clay particles have a diameter of 2mm and remain suspended in aqueous solutions due to their particle nature [7][26]. Clay minerals are classified as layers of silicates and phyllosilicates because they are mainly composed of silica and alumina sheets. Clay minerals can be classified further based on types of layer structures. Clays are composed of a silicate sheet that is interconnected to the second sheet through the combining of metallic atoms, hydroxyl groups, and oxygen groups. Sheets of silica, brucite, and gibbsite are the basic structrual units of clay mineral. One tetrahedral and an octahedron as shown in fig.2 (a) and fig.2 (b) is composed of two hydroxyl ion planes separated by a plane of magnesium or aluminium ions, which is usually coordinated by hydroxyl sheets. Magnesium and aluminium ions are the basic sheets of octahedrons that is separated by hydroxyl ions. These sheets in octahedrons are arranged hexagonally to form octahedral sheets. The 2:1 (three layer) layer lattice silicates are made from two silica tetrahedral sheets separated by an octahedral sheet as in fig. 1(b). Among the 2: 1 clay minerals the mica, smectite groups are the most abundant clay minerals [27]. The basic structural unit of the 1:1 layer minerals consists of one tetrahedral and octahedral sheets (Fig. 1(a).

5. Types of Clay Minerals

5.1. Montmorillonite Clay

Montmorillonite's clay forms microscopic crystals and are phyllosilicate mineral in nature. Montmorillonite is a smectite group mineral and consist of 2:1 crystal lattice that expands latice Monoclinic clay minerals are nonmetallic clay, that usually contain smectite group (hydrated- sodium calcium, and silicates) (Grim 1962). The major components of montmorilonite are K, Fe, and some other ions that varies according to the source **[28]**. Montmorilonite consist of multiple layers with an alumina (octahedral sheet) and tetrahedral sheet pointing inward in the center. These multiple layers are expand in all directions (length, width direction), while the bond are weak and can break easily, and allow water molecues to enter between the layers and swell also known as swhp-elling. Substitution of various types of smectite and that result in the separation of charges in such a way, allowing water to move between crystal lattice sheets, resulting in reversible cation exchange and very plastic properties [29]. Montmorillonite is the component of Bentonite clay. The volume of this clay greatly varies when it adsorb water, water absorbing property also known as "swelling of clay". Monmorillonite swell (swelling capacity) more as compared to other clays, because of its interlayer space that allows the water molecule to enter between these layers of the clay. Its expansion property can be easily estimated by its exchangeable ions in the material. When sodium is dominant exchangeable cation, the clay can swell to several times its original volume. Monmorilonite has very large specific area, which gives them important sorptive properties. Metal ion uptake mechanisms on smectites are affected by ionic strength, pH, and the type of ion being adsorbed [30].

5.2. Bentonite Clay

Bentonite is an impure clay that normally contain montmorillonite and is an aluminium phyllosilicate material. A gibbsite layer is sandwiched between two silica sheets to constitute the structural units of montmorillonite. The octahedral layer substitutions occur primarily in Mg^{2+}, Fe^{2+} and lesser extent in silicate layer Al^{3+}, Si^{4+}. The clay mineral's chemical structure is based on a hydroxyl-aluminosilicate framework. Clay minerals' crystal structures are made up of sheets of silica and alumina that arranged octahedrally or tetrahedrally . In some cases, divalent Mg or Fe replace some of the trivalent Al [31]. To provide charge balance, substitution is followed by the addition of alkaline metal including Na, K and alkaline earth metals such as Mg and Ca. on the basis of these elements including calcium, aluminium and sodium bentonite can be divided in to several types. As a result of volcanic ash, weathering in the presence of water, results in the formation of bentonite clay minerals. The two most common types of bentonite including calcium and sodium bentonite, both of which are used mainly in commercial processes. Calcium bentonite is an excellent adsorbent due to its excellent colloidal properties, and swelling properties and can effetely use in oils and fats solutions [32].

5.3 Kaolinite Clay

Kaolinite clay has general formula $Al_2SiO_2.5(OH)_4$. Trioctahedral and dioctahedral are the forms of kaolinite clay. Dioctahedral clay minerals include nacrite, halloysite while the Trioctahedral clay mineral includes cronstedite, chryosite etc. [33]. The basic structure of the kaolinite group is consisted of silicate sheets (Si_2O_5) which is tightly bounded to aluminum oxide or hydroxide layers ($Al_2(OH)_4$) which also termed as gibbsite layer. It is a silicate mineral, which consists of an alumina tetrahedral sheet that is joined by oxygen atoms to form an octahedral sheet. The principal structural unit of this group is a layer composed of one octahedron connected with tetrahedral sheet. . Aluminium occupies octahedral sites in octahedral mineral while magnesium and iron occupy these sites in trioctahedral minerals. Kaolinite and halloysite are singlelayer structures [34]. Kaolinite clay is the least reactive form of the clay with heterogeneous charge surfaces [35].

6. Adsorption mechanisms of different clays

Several steps are involved in the mechanism of adsorption process of dye removal. The processes involved in the mechanism of adsorption include dye diffusion, intracellular diffusion, and adsorption of particle on the surface of the clays. The equation below explain the adsorption of dyes (cationic) on clay adsorbents

$$\mathbf{R_4N^+Cl \longrightarrow R_4N^+ + Cl^-}$$

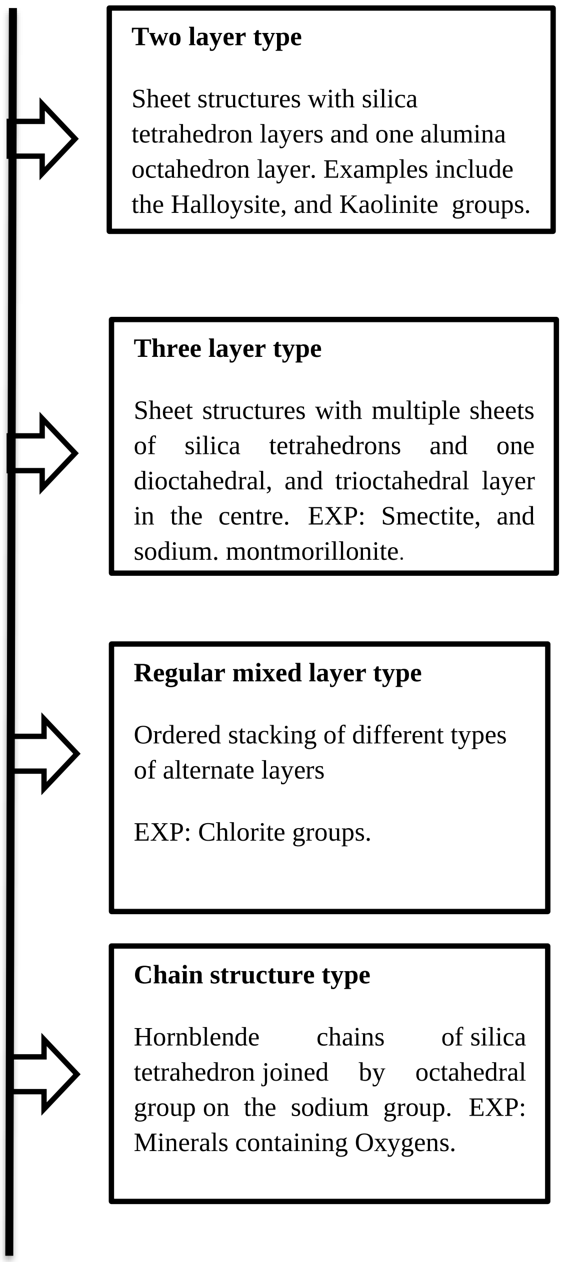
$$\mathbf{Na{-}{-}{-}Clay \longrightarrow Clay^- + Na^+}$$

$$\mathbf{R_4N^+ + (clay)^- \longrightarrow R_4N{-}{-}{-}{-}clay}$$

In the first step of the above reaction, dyes dissociates into the positive and negative ions. In the second step, addition of clay exchange the position of cation. In the third step the surface of clay left negatively charged, and the dyes are positively charged compounds that are attracted towards the negatively charged sites of the clay surfaces. This attraction maybe of electrostatic interaction, or ion exchange process [36].

7. clay minerals [27]

Clay minerals classification based on the layering of the clays (Flow chart 1).



Flow chart 1: Classification of clay minerals

8. Modification methods for different Clay's group

Modification of clays using several physical and chemical treatments enhance the adsorption properties, and porosity of clay minerals. Different methods are used to modify the clay minerals some of them are pillaring of clays, polymer modification, acid treatments and many others [37].

8.1. Nano-clay

Layerd tubes, fibrous crystal, and negative charged sites are the properties of various clay minerals. Kaolinite and mica clays can be exfoliated into nanorods and nanotubes **or** nanosheets. Exfoliation of clays give an advantage of complete dissociation of clays and formation of nano-scale clay units while the modification of clays via pillering can only increase distance between the layers of clays. Exfoliated nano-clays gives another advantage of high surface area and largly exposed surface sites for the process adsorption. Modification of clays with fuctional polymers and other coupling agents to make it nanocomposite material, increase its adorption capacity [38]. Nanocomposites materials can be synthesized by many functional-polymers and chelating groups. Nanocomposite clay minerals serve as cost effective adsorbent for the removal of organic inorganic pollutants from industrial effluents .The industrial effluents contain dyes, heavy metals or many other inorganic ions. Varieties of nano-composites can be prepared from nanoclays with different morphologies including (1D,2D nano sheets and nano tubes) and NPs [39].

8.2. Polymer modification of Clay

Modification of clays using polymers enhance adsorption capacity of clays. -OH, -COOH, and -NH2 functional groups can be easily introduced in the interlayer space and surface of clays via the process of polymerization. Selective adsorption can be achieved by polymer modified clays, and form strong attraction with heavy metals**.** Epicholorohydrin dimethylamine modified bentonite clay shows selective adsorption from wastewater containing different ions like lead, cadmiumand mercury, because of selective adsorption properties of the modifye clays, it can adsorb mercury specifically. This provides a new method of selective removal of heavy metals from wastewater with specific functions [1-40].

8.3. Acid activation

Acid solution with strong acids like HCl, HNO_3, and H_3PO_4 are used to exchange protons from interlayer using the process of activation to enhance the porosity and SSA of the clays. The edges of the layered clays are open to escape ions from the tetrahedrons and octahedrons during the process of pickling SSA of clay minerals. Inorganic and organic acids are usually used for acid activation of clays and gives better results as compared to others The two important factors that affect the properties of the acid washed modified clays are acid dosage, and its treatment time. Acid modification of clays using thermal and acid treatment increase the surface area of the clay minerals. The 48.3 mg/g is the adsorption capacity of the tungsten clay that is much higher than other natural clays minerals [41].

8.4. Pillared clays

Native clays can be modified in a variety of ways, allowing the improvement in their properties like porous structure of the clay. Modification of clays via pillaring involves various stages. Metal salts are hydrolysed by alkali agents that lead to the formation of hydroxocation, this is the first step for the synthesis of pillaring solution. The interlayer cation of clay is exchanged with the polynuclear hydroxocation (pillaring solution cation), in the second step of pillaring. This exchange of cation increase the space between the layers and allow the clay to swell. The last step is thermal treatment, which includes dehydration and dehydroxylation of interstitial polyhydroxocations. Metal oxides are formed between the layers of montmorillonite, that form strong oxygen bridge with alumosilicate layers of clay. Columnar or pillared clays are those that have been modified using pillaring technique [42].

8.5. Organosilane modification of Clays

Organosilanes are chemicals with monomeric silicone-based compounds that resemble hydrocarbons in structure. Organosaline modification of clays is achived by grafting of organosilane on clays. Condensation of clays occur due to the transfer of alkoxy group into silanol group in the process of hydrolysis. The varying functional group of organosilane modified clays give the clays some additional functions. Hydrogen bonds are formed between the OH group and silanol group on the surface of the clay. Amino siloxane incorporate between the layers of monmorilonite clay and forms a cubic structure. The amino groups with high affinity(metal-bonding sites) enhance the adsorption capacity for several ions such as cupper, and lead [43].

8.6. Organic modified clays

Organic modified clays are classified into three different types, based on the process of modification and the molecular structure of the modifiers. Type I is related to surfactants, mainly including cationic, anionic and non-ionic/zwitter-ionic surfactants. Type II is associated with polymers and type III is associated with organosilanes.

9. Removal of heavy metals by Kaolinite Clay

9.1 Raw Kaolinite Clay

Kaolinite clays have a low ion exchange capacity, but despite this property, they can be used to remove heavy metals. This behaviour can also be formed by modifying appropriate treatment techniques. It was reported that raw kaolinite clay minerals can be used to remove heavy metals, including Pb, Ni, Cu, and Cd, from industrial wastewater. Kaolinite clays use the ion exchange and adsorption processes to remove heavy metals. The adsorption of metal ions is decreased as the concentration of electrolyte increases because this causes the shielding of the surface negative ions by electrolyte ions. So it was determined that the process of adsorption slows down as the concentration of electrolyte increases [44]. It was observed that the adsorption process of kaolinite is changed after thermal treatment. The adsorption potential of kaolinite for eliminating pb ions from aqueous solutions was studied. Temperature-related increases in retention capacity were observed [45].

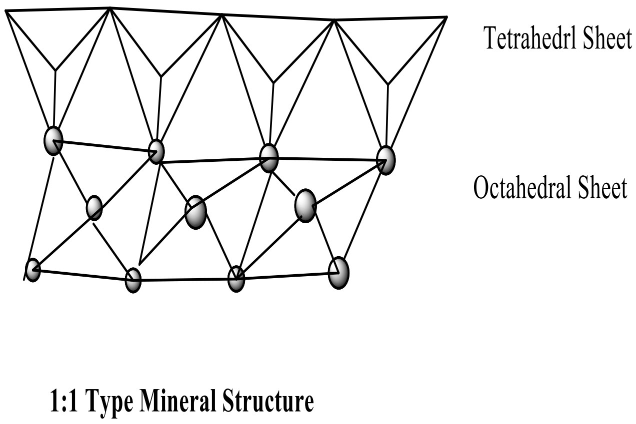


Figure 1 (a). The 1:1-layer minerals contain one tetrahedral and one octahedral sheet in their basic structural unit

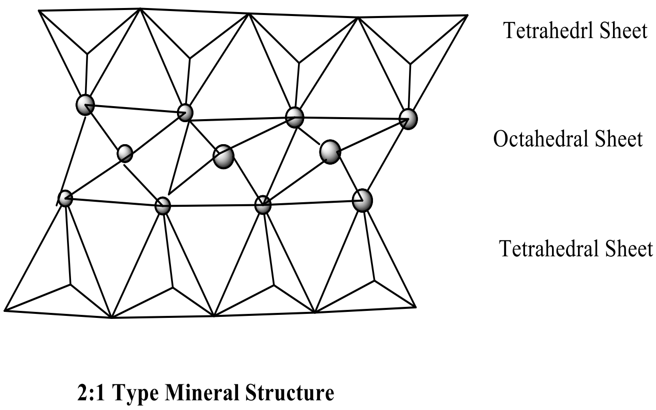


Figure 1 (b). \The crystal units (layers) of these minerals are characterized by an octahedral sheet sandwiched between two tetrahedral sheets.

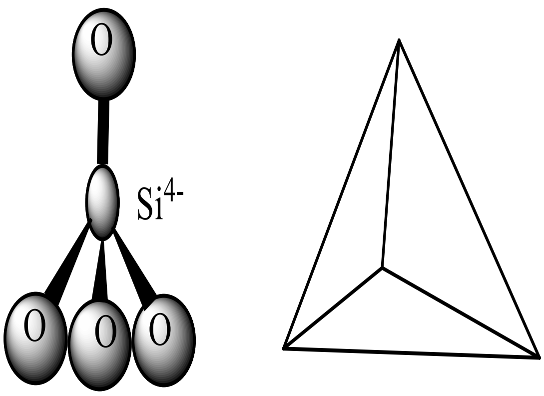


Figure 2 (a). The basic building block of tetrahedral sheet is a unit of Si atom surrounded by four oxygen atom known as silica tetrahedral

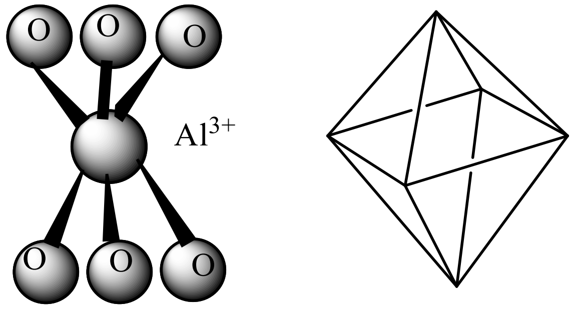


Figure 2 (b). Octahedral unit is comprised of closely packed oxygens and hydroxyls in which aluminum, iron, and magnesium atoms are arranged in octahedral coordination

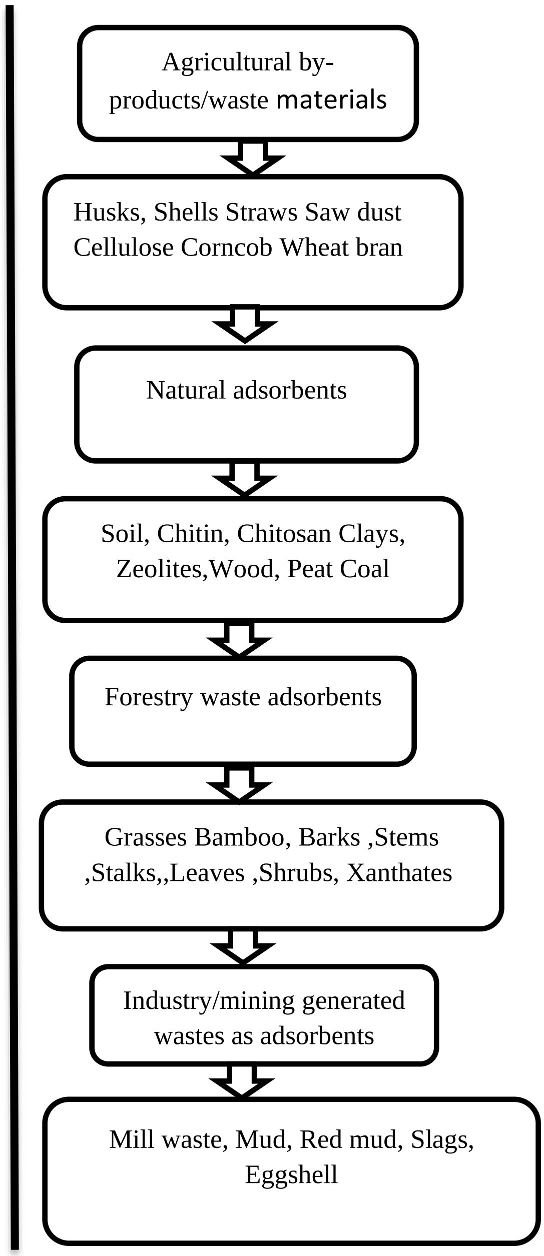


Figure 3. Some natural inorganic adsorbents from different sources

9.2. Modification of kaolinite Clay

Adsorption of Pb ions on the tripolyphosphate form of modified kaolinite was 'optimised' into two stages. Pb ion adsorption usually occurs at O-P-O negatively charged sites. The adsorptive ability of TPP-modified kaolinite clay increases as the presence of "negatively charged sites" per molecule increases [46-48].

The study's mechanism revealed that clay minerals act like chelating sorbents with humic acid as compared to "inorganic ion exchangers" for heavy metals removal. It was observed that the SPP-modified clay will effectively be used as an adsorbent for the removal of Pb, Zn, and Cd ions from industrial effluents. The adsorption capacity of SPP-modified kaolinite increases at different temperatures for metals including Pb, Zn, and Cd. The adsorption capacity of kaolinite clay in its unmodified form is compared with that of aluminium sulphate-modified clay for the removal of lead from different aqueous solutions. Under favourable conditions, the adsorption of Pb ion on modified kaolin clay is much greater than (4.5) folds that of unmodified kaolin clay. The process of adsorption starts increasing with an increasing level of Ph**.** Natural and raw kaolinite produced excellent results. The majority of results found that increasing concentration resulted in increased adsorption. Adsorption increased with pH and decreased with precipitation. The optimal pH for many metal adsorptions was in the 5–6 range. Many studies reveal that the process of adsorption is fast when initiated and at high temperature. Its equilibrium was reached after a few hours of initiation [49-51].

10. Raw vermiculite

Vermiculite is a naturally occurring adsorbent with the potential of removing hazardous heavy metals from wastewater in its raw form. Vermiculite clay's ability to adsorb Pb ions from aqueous solutions was studied. It was noted that the ionic strength of the electrolyte affects the adsorption of metal ions on the surface of the adsorbent because ions are competing for their adsorption. It was noted that the "coexisting" heavy metals have to compete for their adsorption on the same adsorptive site. The adsorption capacity of trivalent metals is greater than that of divalent metals. When these metals are added to the solution, they replace the already adsorbed divalent ions [52]. It was noted that cesium can be removed from aqueous solutions using vermiculite as an adsorbent at various temperatures. According to the experimental results, it was revealed that the adsorption process of cesium on vermatite is a very slow process, and the yield is also very slow. So it was concluded that vermiculite can only be used at high temperatures [53].

10.1 Modified vermiculite

A vibration mill was used to perform mechanochemical treatment on vermiculite. The mechanochemical treatment reduced particle size while significantly increasing the "surface area" of the clays. The "mechanochemical treatment" of vermiculite's clay improved its Pb adsorption capacity. Modified vermiculite was prepared to increase the heavy metal adsorption capability of vermiculite clay. In a study, the adsorption capacities of chitosan-g-poly," also known as acrylic acid, were compared with "CTS-Gpaa/VMT" hydrogel to remove lead and cadmium from industrial aqueous solutions. About 90% of the total adsorption was completed in just 3 min. at 303 k for lead and cadmium ions from aqueous solutions. The removal of Pb and Cd from aqueous solutions using the process of adsorption follows the ion exchange, electrostatic attraction mechanism [54]**.** For the effective removal of cesium ions from industrial effluents, large surface area and highly porous modified clay (ethylamine-modified vermiculite) was prepared. The adsorption capacity for cesium is highly increased after modification. According to the results it was found that the (Ethyl-VER,) modified clay with excellent surface area, and highly porous structure shows better results as compared to the raw clay [55].

11. Some natural inorganic adsorbent

Expensive treatments cannot be employed on large scales due to high energy consumption. Therefore, the need for developing adsorbents with low cost and high efficiency is getting attention. Adsorption is considered to be the most efficient technique to remove dyes and heavy metals from wastewater and can be employed on large scales as well. Natural materials from various industries and agricultural waste are considered low-cost adsorbents. Some of them are grouts, egg shells, seeds, straws, and many more. They are used as an adsorbent for the removal of pollutants from wastewater **[56]**. Some natural inorganic adsorbent derived from different sources enlisted in figure.3.

11.1. Red mud

Red mud can be used as an adsorbent to treat phosphorus-containing water, like phosphates. Red mud driven from Bayer's process in the refining industry has high removal efficiency in wastewater treatments. RMA is a modified form of red mud and can be effectively used as an adsorbent for phosphate removal. This clay is modified by using nanocrystaline material (akaganeite) **[57].** RMA (modified red mud) has a wide pH range and a high rate of adsorption as compared to ferric hydroxide-modified clay many experiments demonstrate that the granules and RMA-modified clays effectively remove sulphate from wastewater (without affecting phosphate uptake). Granules-modified clays lost half of their phosphate adsorbed on their surface while the RMA did not **[58].**

11.2. Fly ash from industries

Fly ash driven from paper mills can be used as a base material to create efficient bioadsorbents. Wood ash is the most commonly used ash as an adsorbent. The composition of ash reveals that it can be used as an adsorbent for the removal of inorganic contamination from industrial effluents**.** Arsenic can be selectively removed from wastewater using ash as an adsorbent. This method is also used to reduce the concentration of arsenic in the aqueous solution to an acceptable level. Iron-modified ash can also be used as an arsenic removal adsorbent. The adsorption capacity of fly ash is nearly equal to that of activated carbon. It was found that the modified ash fly gave better results as compared to the raw ash fly [59].

11.3. Fruit waste

Fruit waste (cellulose-based waste) can be used as an adsorbent for the removal of dyes from wastewater. Juice and soft drink industries from around the world discard fruit peel and pith, which can be used as adsorbents in adsorption treatments of wastewater. India is the largest consumer of fruits, which results in huge waste that can be used as adsorbents [60].

11.4. Wood shaving

Spruce wood shvings (Picea abies) are used for the adsorptive removal of both basic and acid dyes from wastewaters. Na_2CO_3, HCl, and Na_2HPO_4 are used for the modification of adsorbents. The wood sorbents, when treated with either an alkaline solution of carbonate or phosphate solution, enhance the ability for sorption of MB, a basic dye; however, when treated with any mineral acid, there is a reduction to a certain extent observed in the sorption capability of MB, with a Langmuir Freundlich value range of 0.060 to 0.165 mm. The total opposite results were obtained for Egacid Orange, an acid dye that obtained the sorption maximum in a range from 0.045 to 0.513 mmol/L. In addition, the sorption efficiency for a basic dye decreases with lowering the pH, while the acid dye shows an increase in the sorption capacity with a decrease in pH value when estimated using the mechanism of ion exchange for measuring sorption. Although dye sorption ability is mildly affected by any inorganic salt or the presence of surfactant [61].

12. Conclusions

Clay minerals have gained significant attention as highly effective adsorbent materials due to their properties, such as high cation exchange capacity (CEC), large surface area, and porosity. Modified clay minerals exhibit enhanced removal efficiency compared to raw clay minerals. Various experimental parameters, including temperature, dye concentration, and pH, have been explored to compare the adsorptive performance of different clays in different forms (raw, modified, etc.) belonging to different classes for removing dyes and heavy metals from aqueous solutions. However, some studies lack comprehensive characterization of different clay classes used as adsorbents, warranting further investigation in future studies. Characterization techniques like scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), and Fourier transform infrared (FTIR) are commonly employed. To advance the field, future research should focus on evaluating the working conditions and optimization of "clay-based reactors" to scale up the adsorption process. Emphasis should also be placed on developing potential methods for regenerating adsorbents, ensuring reusability, and refining the adsorption process to enhance the performance of clay-based adsorbents. Additionally, further research is needed to understand the surface morphologies of different clays, different modification methods (e.g., interlayer pillaring), and the mechanisms underlying dye and heavy metal adsorption on activated clays.The adsorption capacity of clays depends on factors such as size, volume, and shape of the clay particles. Furthermore, the adsorption performance of various adsorbents is influenced by the surface morphology of the inorganic materials used. The pH of the solution plays a crucial role in the adsorption process of inorganic adsorbents. Altering the pH can modify the surface charges of the adsorbents, affecting their interaction with dyes. Generally, a higher pH favors adsorption of positively charged dyes onto negatively charged surfaces through ion exchange and electrostatic forces of attraction. The optimal pH range for inorganic material adsorbents is typically around 5-8, which facilitates maximum adsorption of dyes. Consequently, the morphology of the adsorbent's surface significantly influences the removal of dyes from industrial effluent. Modified clays exhibit superior adsorption performance compared to raw clays, as various activation methods enhance their properties, surface area, and selectivity

.

References

[1] T. Zhang, W. Wang, Y. Zhao, H. Bai, T. Wen, S. Kang, G. Song, S. Song, S. Komarneni. (2021). Removal of heavy metals and dyes by clay-based adsorbents: From natural clays to 1D and 2D nano-composites. Chemical Engineering Journal. 420: 127574.

[2] I. Ahmad, M.A. Hanif, R. Nadeem, M.S. Jamil, M.S. Zafar. (2008). Nutritive evaluation of medicinal plants being used as condiments in South Asian Region. Journal of the Chemical Society of Pakistan. 30(3): 400-405.

[3] F. Asghar, A. Mushtaq. (2023). The Future of Nanomaterial in Wastewater Treatment: A Review. Int. J. Chem. Biochem. Sci. 23: 150-157.

[4] M.A. Dutt, M.A. Hanif, F. Nadeem, H.N. Bhatti. (2020). A review of advances in engineered composite materials popular for wastewater treatment. Journal of Environmental Chemical Engineering. 8(5): 104073.

[5] M. Khan, I.M. Lo. (2016). A holistic review of hydrogel applications in the adsorptive removal of aqueous pollutants: recent progress, challenges, and perspectives. Water research. 106: 259-271.

[6] I. Akbar, M.A. Hanif, U. Rashid, I.A. Bhatti, R.A. Khan, E.A. Kazerooni. (2022). Green Nanocomposite for the Adsorption of Toxic Dyes Removal from Colored Waters. Coatings. 12(12): 1955.

[7] T. Ngulube, J.R. Gumbo, V. Masindi, A. Maity. (2017). An update on synthetic dyes adsorption onto clay based minerals: A state-of-art review. Journal of environmental management. 191: 35-57.

[8] A. Hanif, S. Ali, M.A. Hanif, U. Rashid, H.N. Bhatti, M. Asghar, A. Alsalme, D.A. Giannakoudakis. (2021). A novel combined treatment process of hybrid biosorbent–nanofiltration for effective Pb (II) removal from wastewater. Water. 13(23): 3316.

[9] Q. Imran, M. Hanif, M. Riaz, S. Noureen, T. Ansari, H. Bhatti. (2012). Coagulation/flocculation of tannery wastewater using immobilized chemical coagulants. Journal of applied research and technology. 10(2): 79-86.

[10] A. Javed, A. Mushtaq. (2023). A critical review of electrocoagulation and other electrochemical methods. Int. J. Chem. Biochem. Sci. 23: 98-110.

[11] Y. Chauhdary, M.A. Hanif, U. Rashid, I.A. Bhatti, H. Anwar, Y. Jamil, F.A. Alharthi, E.A. Kazerooni. (2022). Effective removal of reactive and direct dyes from colored wastewater using low-cost novel bentonite nanocomposites. Water. 14(22): 3604.

[12] T. Fatima, A. Mushtaq. (2023). Efficacy and Challenges of Carbon-based Nanomaterials in

Water Treatment: A review. Int. J. Chem. Biochem. Sci. 23: 232-248.

[13] M. Zahid, N. Nadeem, M.A. Hanif, I.A. Bhatti, H.N. Bhatti, G. Mustafa. (2019). Metal ferrites and their graphene-based nanocomposites: synthesis, characterization, and applications in wastewater treatment. Magnetic nanostructures: environmental and agricultural applications. 181-212.

[14] T.M. Ansari, S. Shaheen, S. Manzoor, S. Naz, M.A. Hanif. (2020). Litchi chinensis peel biomass as green adsorbent for cadmium (Cd) ions removal from aqueous solutions. Desalination and Water Treatment. 173: 343-50.

[15] A.A. Ayalew. (2022). A critical review on clay-based nanocomposite particles for application of wastewater treatment. Water Science and Technology. 85(10): 3002-3022.

[16] M. Khalil, M.A. Hanif, U. Rashid, J. Ahmad, A. Alsalme, T. Tsubota. (2023). Low-cost novel nano-constructed granite composites for removal of hazardous Terasil dye from wastewater. Environmental Science and Pollution Research. 30(34): 81333-81351.

[17] A. Ehsan, H.N. Bhatti, M. Iqbal, S. Noreen. (2017). Native, acidic pre-treated and composite clay efficiency for the adsorption of dicationic dye in aqueous medium. Water Science and Technology. 75(4): 753-764.

[18] H.H. Murray. (2006). Applied clay mineralogy: occurrences, processing and applications of kaolins, bentonites, palygorskitesepiolite, and common clays. Elsevier: pp.

[19] S. Nausheen, H.N. Bhatti, M.A. Hanif. (2017). Enhanced Removal of Golden XGL Dye by Clay Composites: Batch and Column Studies. Polish Journal of Environmental Studies. 26(5).

[20] I. Chaari, M. Medhioub, F. Jamoussi. (2011). Use of clay to remove heavy metals from Jebel Chakir landfill leachate. Journal of Applied Sciences in Environmental Sanitation. 6(2): 143-148.

[21] A. Espantaleon, J. Nieto, M. Fernandez, A. Marsal. (2003). Use of activated clays in the removal of dyes and surfactants from tannery waste waters. Applied Clay Science. 24(1-2): 105-110.

[22] A. Odoma, N. Obaje, J. Omada, S. Idakwo, J. Erbacher. (2013). Paleoclimate reconstruction during Mamu Formation (Cretaceous) based on clay mineral distributions. J. Appl. Geol. Geophys. 1: 40-46.

[23] T. Shichi, K. Takagi. (2000). Clay minerals as photochemical reaction fields. Journal of Photochemistry and Photobiology C: Photochemistry Reviews. 1(2): 113-130.

[24] I. Javed, M.A. Hanif, U. Rashid, F. Nadeem, F.A. Alharthi, E.A. Kazerooni. (2022). Enhancing functionalities in nanocomposites for effective dye removal from wastewater: Isothermal, kinetic and thermodynamic aspects. Water. 14(17): 2600.

[25] A. Tariq, A. Mushtaq. (2023). Untreated Wastewater Reasons and Causes: A Review of Most Affected Areas and Cities. Int. J. Chem. Biochem. Sci. 23: 121-143.

[26] Z. Rehman, A. Mushtaq. (2023). Advancements in Treatment of High-Salinity Wastewater: A Critical. Int. J. Chem. Biochem. Sci. 23: 1-10.

[27] M.K. Uddin. (2017). A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chemical Engineering Journal. 308: 438-462.

[28] S.N.S. Jaafar. Adsorption study-dye removal using clay. Kuktem, 2006.

[29] A. Günay, B. Ersoy, S. Dikmen, A. Evcin. (2013). Investigation of equilibrium, kinetic, thermodynamic and mechanism of Basic Blue 16 adsorption by montmorillonitic clay. Adsorption. 19: 757-768.

[30] Y. Han, S. Sheng, F. Yang, Y. Xie, M. Zhao, J.-R. Li. (2015). Size-exclusive and coordination-induced selective dye adsorption in a nanotubular metal–organic framework. Journal of Materials Chemistry A. 3(24): 12804-12809.

[31] S. De Gisi, G. Lofrano, M. Grassi, M. Notarnicola. (2016). Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. Sustainable Materials and Technologies. 9: 10-40.

[32] R. Zakaria, I. Hassan, M. El-Abd, Y. El-Tawil In *Lactic acid removal from wastewater by using different types of activated clay*, Thirteenth international water technology conference (IWTC), Hurghada, 2009; 2009; pp 403-416.

[33] A. Miller. (2010). Homogenized behavior from increasingly heterogeneous systems: uranium transport experiments at the intermediate scale. 2010-Mines Theses & Dissertations.

[34] M. Menkiti, O. Onukwuli. (2011). Studies on dye removal from aqueous media using activated coal and clay: an adsorption approach. NY Sci J. 4: 91-95.

[35] A.W. Miller, Y. Wang. (2012). Radionuclide interaction with clays in dilute and heavily compacted systems: a critical review. Environmental science & technology. 46(4): 1981-1994.

[36] E. Errais, J. Duplay, M. Elhabiri, M. Khodja, R. Ocampo, R. Baltenweck-Guyot, F. Darragi. (2012). Anionic RR120 dye adsorption onto raw clay: Surface properties and adsorption mechanism. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 403: 69-78.

[37] J. Cecilia, C. García-Sancho, E. Vilarrasa-García, J. Jiménez-Jiménez, E. Rodriguez-Castellón. (2018). Synthesis, characterization, uses and applications of porous clays heterostructures: a review. The Chemical Record. 18(7-8): 1085-1104.

[38] F. Wahid, C. Zhong, H.-S. Wang, X.-H. Hu, L.-Q. Chu. (2017). Recent advances in antimicrobial hydrogels containing metal ions and metals/metal oxide nanoparticles. Polymers. 9(12): 636.

[39] A. Gil, F. Assis, S. Albeniz, S. Korili. (2011). Removal of dyes from wastewaters by adsorption on pillared clays. Chemical Engineering Journal. 168(3): 1032-1040.

[40] M.A. Hanif, H.N. Bhatti. (2015). Remediation of heavy metals using easily cultivable, fast growing,

and highly accumulating white rot fungi from hazardous aqueous streams. Desalination and Water Treatment. 53(1): 238-248.

[41] P. Komadel, J. Madejová, Acid activation of clay minerals. In *Developments in clay science*, Elsevier: 2013; Vol. 5, pp 385-409.

[42] T. Kon'kova, M. Alekhina, A. Mikhailichenko, G. Kandelaki, A. Morozov. (2014). Adsorption properties of pillared clays. Protection of Metals and Physical Chemistry of Surfaces. 50(3): 326-330.

[43] N.J. Vickers. (2017). Animal communication: when i'm calling you, will you answer too? Current biology. 27(14): R713-R715.

[44] M.-q. Jiang, X.-y. Jin, X.-Q. Lu, Z.-l. Chen. (2010). Adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) onto natural kaolinite clay. Desalination. 252(1-3): 33-39.

[45] W. Omar, H. Al-Itawi. (2007). Removal of Pb? 2 Ions from Aqueous Solutions by adsorption on kaolinite clay. American Journal of Applied Sciences. 4(7): 502-507.

[46] J. Hizal, R. Apak, W. Hoell. (2009). Modeling competitive adsorption of copper (II), lead (II), and cadmium (II) by kaolinite-based clay mineral/humic acid system. Environmental progress & sustainable energy. 28(4): 493-506.

[47] T.M. Ansari, M.A. Hanif, T. Rasool, M. Ali, R. Nadeem, M. Yaseen. (2016). Reclamation of wastewater containing Cu (II) using alginated Mentha spicata biomass. Desalination and Water Treatment. 57(23): 10700-10709.

[48] M.A. Hanif, H.N. Bhatti, M. Asgher, M.I. Jilani, I.A. Bhatti. (2015). Remediation of Pb (II) using Pleurotus sajor-caju isolated from metal-contaminated site. Desalination and Water Treatment. 56(9): 2532-2542.

[49] Z. Danková, A. Bekényiová, I. Štyriaková, E. Fedorová. (2015). Study of Cu (II) adsorption by siderite and kaolin. Procedia Earth and Planetary Science. 15: 821-826.

[50] A. Hanif, H.N. Bhatti, M.A. Hanif. (2015). Removal of zirconium from aqueous solution by Ganoderma lucidum: biosorption and bioremediation studies. Desalination and Water Treatment. 53(1): 195-205.

[51] H.N. Bhatti, A.W. Nasir, M.A. Hanif. (2010). Efficacy of Daucus carota L. waste biomass for the removal of chromium from aqueous solutions. Desalination. 253(1-3): 78-87.

[52] A. El-Bayaa, N. Badawy, E. Abd AlKhalik. (2009). Effect of ionic strength on the adsorption of copper and chromium ions by vermiculite pure clay mineral. Journal of hazardous materials. 170(2-3): 1204-1209.

[53] X. Wu, H. Zhou, F. Zhao, C. Zhao. (2009). Adsorption of Zn2+ and Cd2+ ions on vermiculite in buffered and unbuffered aqueous solutions. Adsorption Science & Technology. 27(10): 907-919.

[54] X. Wang, A. Wang. (2012). Equilibrium isotherm and mechanism studies of Pb (II) and Cd (II) ions onto hydrogel composite based on vermiculite. Desalination and Water Treatment. 48(1-3): 38-49.

[55] H. Long, P. Wu, L. Yang, Z. Huang, N. Zhu, Z. Hu. (2014). Efficient removal of cesium from aqueous solution with vermiculite of enhanced adsorption property through surface modification by ethylamine. Journal of colloid and interface science. 428: 295-301.

[56] G. Atun, G. Hisarli, W. Sheldrick, M. Muhler. (2003). Adsorptive removal of methylene blue from colored effluents on fuller's earth. Journal of colloid and interface science. 261(1): 32-39.

[57] Q. Sun, L. Yang. (2003). The adsorption of basic dyes from aqueous solution on modified peat–resin particle. Water research. 37(7): 1535-1544.

[58] Z. Li, Y. Kong, Y. Ge. (2015). Synthesis of porous lignin xanthate resin for Pb2+ removal from aqueous solution. Chemical Engineering Journal. 270: 229-234.

[59] K.V. Thomas, L. Bijlsma, S. Castiglioni, A. Covaci, E. Emke, R. Grabic, F. Hernández, S. Karolak, B. Kasprzyk-Hordern, R.H. Lindberg. (2012). Comparing illicit drug use in 19 European cities through sewage analysis. Science of the Total Environment. 432: 432-439.

[60] F.A. Pavan, E.C. Lima, S.L. Dias, A.C. Mazzocato. (2008). Methylene blue biosorption from aqueous solutions by yellow passion fruit waste. Journal of hazardous materials. 150(3): 703-712.

[61] P. Janoš, S. Coskun, V. Pilařová, J. Rejnek. (2009). Removal of basic (Methylene Blue) and acid (Egacid Orange) dyes from waters by sorption on chemically treated wood shavings. Bioresource Technology. 100(3): 1450-1453.