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REVIEW ARTICLE

WATER POLLUTION AND ITS CONTROL THROUGH ADSORBENTS OF CLAY-BASED MATERIALS: A REVIEW

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ABSTRACT

Water is an important material that is necessary for life on Earth. It is a sign of pureness, simplicity, and rejuvenation, and it possesses the ability to transform the environment and nurture and is a basic need of life. With the rapid increase in population and urbanization which discharge different chemicals and dyes to environment, the pure quality of water is going to become impure which ultimately results in causing diseases to aquatic, plants and animal life. Multiple methods are available for wastewater treatment are explained. This explains the ability of clay-based materials as adsorbents for water purification, different types of clay specially for water clean-up, their characteristics, the mechanism and type of attachment between adsorbate and adsorbent and methods of modification to enhance their abilities. Multiple types of clay-based materials used in past for wastewater treatment and their future predictions and possibilities are explained. Finally, clay-based adsorbents are one the most potential adsorbents for wastewater treatment.

KEYWORDS

Environmental Chemistry, Heavy metal removal by clay, Pollutant adsorption kinetics, Environmental Science, Sustainable materials

1. INTRODUCTION

The increase in human population and urbanization, affects the human life and natural environment adversely. Water is polluting everyday by men activities which cause different diseases both in animal and aquatic life. Number of deaths and diseases are caused by water pollution and almost 14000 people die every day because of water contamination and the quality of water is affected in different way (Chaudhry and Malik, 2017). Water pollution occurs when some untreated materials or wastes are excreted to water bodies which affects the aquatic and animal life directly and indirectly respectively. Based on survey of world health organization (WHO) nearly 80% of diseases are directly related to water. In some countries drinking and useable water does not meet the criteria of WHO protocols (Haseena, 2017). The release of materials such as chemical compounds, garbage, or micro - organisms into underground water or ponds, water sources such as rivers and oceans to the spot where the materials interact with advantageous water use or the natural workings of ecosystems is referred to as water pollution.

It also would include the discharge of energy into bodies of water in the form of heat. Sources of water pollution includes point source and non-point source. Pollution point sources are ones that can be directly identified. Examples include pollutants leaving companies, oil spills from tankers, and pipes connected to factories. Point sources of pollution primarily impact the vicinity of a point source, such as rain sewage overflow and wastewater from cities and factories effluent. On the other hand, non-point sources of pollution are those that reach the ecosystem through a variety of unknown pathways and come from many origins, allowing pollutants to infiltrate surface or groundwater. Examples include urban garbage and drainage from farming regions (Singh and Gupta, 2016). It is also explained by following Figure .

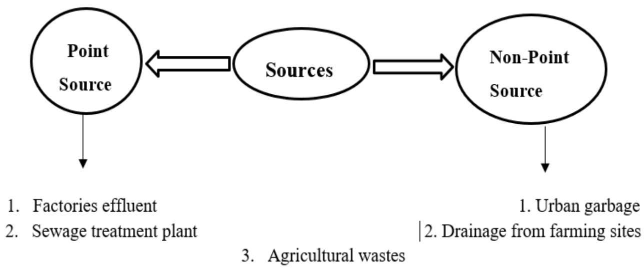

Figure 1: A chart shows the sources of water pollution.

The essential component of life is water. Of the total quantity of water on planet Earth, clean water makes up just three percent, and of that 3%, just 0.01 percent may be used to meet human requirements. Every person on the planet has the fundamental right and desire to access safe, clean water to consume. Water is an incubator of transmissible diseases since it is used excessively for drink and as an all-purpose solvent (Khan, 2023). Water pollution may be caused by a variety of factors, including pollutants released by various industrial enterprises, plants, and agricultural runoff. Household trash releases are the source of domestic water contamination. Wastes from toilets and bathrooms leak straight into bodies of water, where they remain and contaminate the water's natural balance. Similarly, the natural and pristine water is contaminated by pollutants released during the washing process (Sanda and Ibrahim, 2020). The majority of agricultural operations cause contamination of water by using huge quantities of pesticides and chemical-based fertilizers, which eventually seep into both surface and groundwater bodies. This alteration in the physical and chemical makeup of water brought on by agricultural practices harms the marine environment.

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The primary aquatic issue in water's surface bodies close to fields of crops is eutrophication. These nutrients are obtained by the landowner from drainage from their land use, which they employ to increase production and keep parasites away. Eutrophication has resulted in a bloom of algae on the outermost layer of the water's physique, which lower the oxygen level of the water and pose issues for aquatic creatures (Kumar, 2021). Industrial waste water can change the physical, chemical, and biological characteristics of the water that reaches the body, which has a significant harmful impact on polluting of the surrounding water body. Waste first causes the physical quality of the water to deteriorate. Subsequent biological deterioration manifests itself in the quantity, diversity, and arrangement of aquatic life. The well-being and security of people and animals are negatively impacted by the transmission of undesirable discharges from industry. The release of effluent from municipal and industrial sources is a significant source of contamination in bodies of water. It increases the concentration of nutrients and oxygen demand, fosters algae blooms that are harmful, and upsets the balance of the underwater ecosystem (Ewa, 2011). Health problems and water contamination are becoming more closely linked. Food and vegetables grown in contaminated water are used by 10% of the population. Polluted water poses a number of health risks, including disease related to respiratory system, sickness, dysentery disease and diseases related to heart and brain. It also imposes a bad impact on women who are pregnant and are more disclose to chemical substances, where it may enhance the danger of small for gestational (SGA) problems.

1.1 Heavy metals and water Pollution

Because they are arguably some of the most frequently discharged pollutants, ions made up of heavy metals are especially concerning. The substances found in the groups of copper (Cu), cadmium (Cd), zinc (Zn), lead (Pb), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), iron (Fe), and platinum (Pt) are considered heavy metals and metalloids because their atomic densities are larger than 4 g/cm3. Every day, a variety of man-made and natural sources discharge these metallic hazardous metals into the water. Because heavy metals cannot be broken down by the body, they have a tendency to collect over time and become more concentrated in living things. They can also have a lasting impact on a variety of species, in either a direct or indirect manner, as a result of biological magnification (Zamora-Ledezma, 2021). Around 40% of the world's lakes and streams are contaminated by contaminants such as heavy metals. These contaminants may originate from both natural and man-made sources. Eruptions of volcanoes and reactions with normally-occurring metal-containing rocks are examples of sources that occur naturally.

Different heavy metals caused different diseases like lead poisoning inhibits the production of hemoglobin, damages the kidneys, skeletal joints, genital system, and heart, Congenital deformities, GI problems, and accidental miscarriage are all brought on by inorganic mercury, Clinical manifestations of Zn toxicology encompass iron deficiency failure of the liver, renal failure, bloating, loose stool, and red pee and the body of a person collects cadmium, which has an adverse effect on its liver, renal the lungs, skeletons, the baby's place, mind, and central nervous system, among other organs (Sharma and Singh, 2015). Water contamination from heavy metals is especially concerning because it has risen dramatically over the past few centuries. Therefore, in order to address this issue and prevent its possibly disastrous impacts on both humanity and the environment, approaches, regulations, innovations, and products must be developed. It is also explained in Figure that the accumulation of heavy metals in aquatic and animal life.

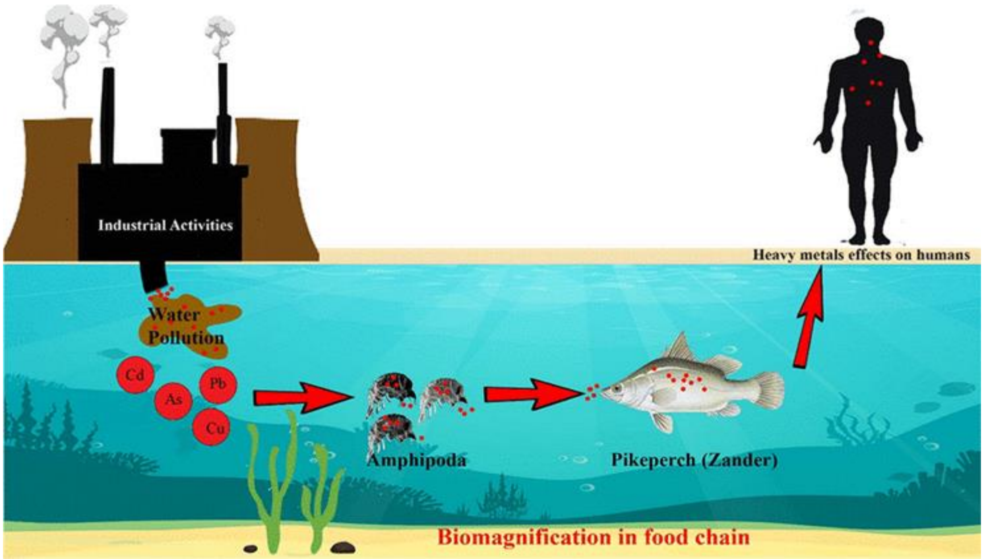

Figure 2: illustrates the schematic representation on accumulation of heavy metals

1.2 Dyes and Water Pollution

With the growth of contemporary industry comes a significant increase in the creation of dye waste water. Due to its complicated design, substantial amount, bright hue, and several challenging recoverable components, dye waste-water is difficult to biodegrade. The categorization of dye fractions may be separated into responsive dyes, acid dyes, and other 14 categories based on their use, with azo dyes making up the majority of the remaining eight groups based on chemical structure. The dye indicates that the color creates chromaticity pollution because the chemical structure contains a chromophore group. Because various dyes have distinct qualities, dye waste water has a varied composition (Liu, 2020). Multiple industries use acidic, basic, direct, disperse, reactive, Sulphur and vat dyes which release different type pollutant to natural environment and affect the environment directly or indirectly.

The textile business utilizes a lot of water, which contributes to widespread water contamination. The complicated chemical makeup of the colors used in the textile industry makes them not recyclable, which poses a hazard to pollution. The dye-laden wastewater has elevated salinity, temperature, color, BOD, COD, and floating particles. The cotton processing sector encompasses several steps and procedures such as scouring, bleaching, mercerizing, dying, printing purposes and completing (Yadav et al., 2014). Therefore, the removal of heavy metals, dyes and other pollutants are necessary.

2. Methods for Wastewater Treatment

The process of treating wastewater involves removing some of the particles and changing them slightly through decomposing from extremely complex, putrescible organic materials to mineral or somewhat durable organic matter. Most BOD and suspended particles in sewage are eliminated by two types of treatment: primary and secondary. This degree of treatment, nevertheless, has increasingly shown to be inadequate to safeguard the waters being received or to supply recycled water for home or commercial recycling. Consequently, extra treatment stages have been implemented in wastewater treatment facilities in order to remove more organic and solid contaminants, as well as nutrients and/or hazardous chemicals (Sonune and Ghate, 2004). Wastewaters are chemicals and sediments that are carried by water and dumped into drains; they are the leftovers from daily living in the area. There are two main methods for wastewater treatment which includes physical and chemical methods.

One of the earliest techniques to be utilized for sewage is screening. It filters out large contaminants from the waste water stream to minimize injury to subsequent machinery, reduce disturbance with facility operations, and keep unwanted floating particles out of the main settling tanks. It is the procedure for eliminating the bigger drifting and hanging debris, such as fibers, paper goods, filthy clothes, thread materials, and other things. There are several categories of screening like coarse screen, fine screen, very fine screen and micro fine screen. Each is categorized on the basis of size of their openings (Prabu et al., 2011). It is possible to remove particles from the flow route by using screens of different sizes. Following removal, anything left over may be crushed into smaller fragments and added back to the disposal stream, or it can be properly disposed of by burning or burying it. Comminution, the term for the technique of grinding used to minimize the dimensions of the particles while they are still in the flow of waste, is a substitute to actually removing the materials via screening (Deluise, 2005). Particulate are taken out of the fluid in a sedimentation tank during the processing of wastewater. Wastewater, or collected solids, build up at the sedimentation point of the tank's bottom and are routinely eliminated. Usually, prior sedimentation, coagulators are introduced to the stream to help in settlement (Singaravelu, 2023).

Membrane separation contributes to the efficient rejection of minerals and organic substances from sewage in a direct membrane filtering system, producing better filtrate purity with an elevated water extraction ratio. Since the direct membrane filtering system is often quite compact, little space is needed. Significantly, the direct membrane method uses less energy since it doesn't require an extra sludge activation step. Furthermore, during the direct membrane filtering process, the material that is eliminated organics and nutrients are concentrated at elevated ratios. These materials may then be post-digested to create renewable energy or turned into chemical fertilizers (Hube, 2020). One technology that has distinguished itself is floating treatment wetlands (FTW), which is effective and simple to set up and maintain. They are made up of macrophytes that emerge in a floating framework that maintains the roots of the vegetation in close association with the wastewater throughout time, allowing for the elimination of contaminants through a variety of mechanisms, even when the water flow varies.

Compared to the traditional centralized effluent treatment method, the use of FTWs for the purification of household wastewater has the benefit of cheap prices for fertilizer removal, as well as lower maintenance and energy expenses (Oliveira 2021). A straightforward procedure called flocculation or coagulation works well for recovering or eliminating contaminants. It has disadvantages like need a high dose and result in big particles and a lot of sludge (Sukmana, 2021). The transformation of elements dispersed in liquid into solid fragments is known as chemical precipitation in the procedure of treatment of sewage and water. Ionic components are extracted from the fluid by chemical precipitation, which lowers the dissolution of the ions by adding counter-ions. It is mostly used to remove metal cations, although it may also be used to remove organic compounds and anions including phosphate, cyanide, and fluoride (Wang, 2005). Two crucial steps in the purification of waste water and water are chemical neutralization and flow equalization. While flow equalization regulates the speed of flow and design, chemical neutralization is used to equalize the elevated alkaline or acidic substances in water. Chemical neutralization is, practically speaking, the process of adjusting pH to reach the intended treatment goal. In many urban and commercial treatment procedures, flow equalization is required to mitigate significant differences in circulation and water purity (Goel et al., 2005).

To eliminate pollutants and germs from water, advanced oxidation processes (AOPs) and advanced reduction processes (ARPs) have been created. The beneficial relationship involving oxidation and reduction is not fully utilized by these AOPs and ARPs, despite the fact that they can be quite effective. The suggested enhanced oxidation-reduction procedures may be useful for a variety of other sectors, in addition to water treatment. These include the creation and execution of electron transfer (Zhang et al., 2023). Humans are protected from being exposed to waterborne harmful bacteria by wastewater treatment. In these procedures, the hazardous microbial community undergoes induced metabolic alterations that result in microbial inactivation. The most popular technique for disinfecting wastewater treatment plant pollutants is chlorination (Collivignarelli, 2017). In wastewater treatment facilities, ion exchange resins are employed to replace a single ion with a different one in order to achieve removal of minerals. Anion interchange resins are the other form of ion exchange resin; the network of cationic resins is the first type (Kansara, 2016).

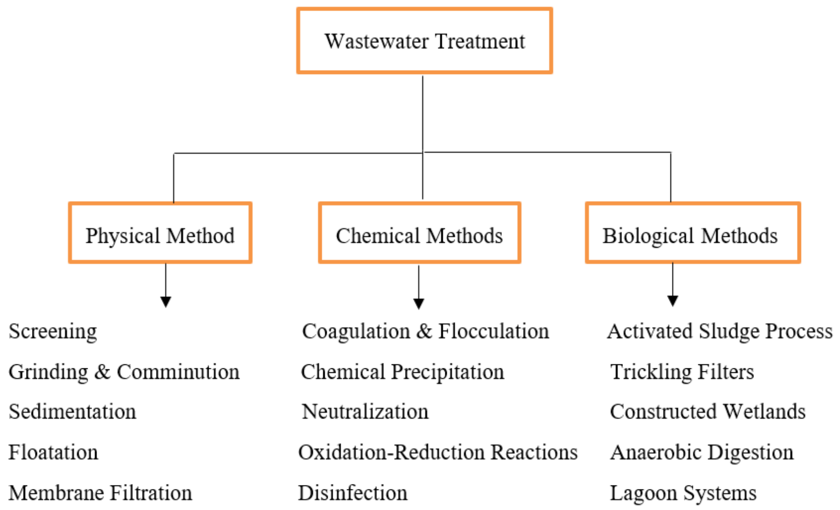

Figure 1: Shows a flowchart for multiple methods of wastewater treatment

2.1 Adsorption for Wastewater Treatment

The attachment of one substance on the surface of another substance is known as adsorption, which is a surface phenomenon. An adsorbate is a compound (pollutant) that clings to a solid surface, while an adsorbent is the solid surface itself. Temperature, the kind of adsorbent and adsorbate, the presence of additional pollutants, and ambient and experimental factors (pollutant concentration, pH, contact time, and adsorbent particle size) all have an impact on adsorption (Ali and Gupta, 2006). Adsorption is a quick, affordable, and versatile technique among the many water purification and recycling methods. The creation of inexpensive adsorbents has sparked a sharp increase in the amount of research being done in this area. Adsorption is essentially a mass transfer procedure that involves moving solutes or detachable species from a liquid phase onto a solid component's surface. The solid surface is the limit of adsorbed species due to physiochemical relationships. Adsorption is typically regarded as a dependable and reasonably priced wastewater treatment technique. Adsorption is typically regarded as a dependable and reasonably priced wastewater treatment technique. Adsorption can have the elimination effectiveness of up to 99.9%. The method of adsorption is one of the greatest methods for treating wastewater, according to the United States Environmental Protection Agency (USEPA) (Rashid, 2021). Adsorbate movement typically happens in three stages in this process: (1) adsorbate migrate to the adsorbent's outer body, (2) intraparticle dispersion into voids, and (3) solute adsorption and desorption.

The design of the adsorption process takes into account three factors: ions being exchanged, chemical adhesion produced by the presence of a chemical bond, and physical adhesion related to van der Waals force. Using isotherm models to describe adsorption equilibrium data is the most popular approach for studying adsorption processes. Different isotherms models are studied in order to explain and understand the mechanism of adsorption process. Some of these models are Henry's Isotherm Model, Freundlich Isotherm Model, Langmuir Isotherm, Hill Deboer Model, Temkin Isotherm Model and Dubinin-Kaganer-Radushkevich Isotherm Model (Ehiomogue et al., 2021). Researchers employed different materials as adsorbent for the treatment of wastewater like hydrogels, clay-based materials, activated carbon, zeolites, silica gel, biochar, activated alumina, polymeric adsorbent and magnetic adsorbents etc.

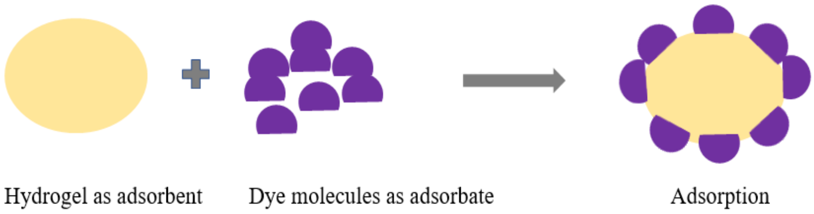

Figure 2: explains the general phenomenon of adsorption

The kinetics define how quickly the adsorption process works and are dependent on a number of physiochemical condition-related factors. Important features like kinetics enable the prediction of the ideal model and design for the adsorption process and offer insightful information about reaction pathways. Additionally, the kinetics provide information on the rate at which sorbents are absorbed, allowing for the monitoring of residence time at the solid-solution interface (Awad, 2019).

The elimination of dyes and ions made up of heavy metals from sewage has been the subject of much research on nanostructures. Many new types of tiny material adsorbents have been created recently to improve the effectiveness and absorbing capabilities of eliminating pollutants from wastewater. Because of their numerous distinctive morphological and structural characteristics, nanoparticles can be employed as efficient adsorbents to address a variety of environmental issues (Sadegh, 2017).

2.2 Clay-based materials for wastewater treatment

Clay's unique physicochemical qualities and attributes have sparked increased concentration for water purification. Many kinds of studies on clay-based nanocomposite have recently been completed with the goal of removing contaminants from water sources. One of the next steps toward efficiently using adsorbent nanoparticles in water and wastewater treatment is the creation of composite materials based on clay (Ayalew, 2022). Because of the size of their surface, permeability, surface charge, ability to exchange cations, acidity, and variety of active sites, clay minerals have been utilized as effective adsorbents. Numerous natural neutralizing mechanisms and pollution control are aided by these qualities. To improve the minerals' capacity for adsorption, clay must be modified. As a result, choosing the right modifier is essential to getting clays that work well as adsorbents (Rashid, 2021). Ther are different types of clay which are specifically used for wastewater treatment.

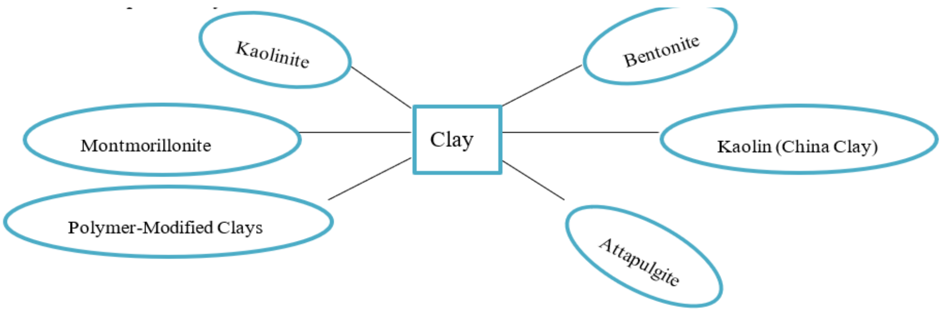

Figure 5: Represents different clay types specially used for wastewater treatment

Kaolinite consists of $Al_2Si_2O_5(OH)_4$ containing aluminum oxide, silicon dioxide and water. Montmorillonite having chemical formula of (Na, Ca)0.33$(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ having Na, Ca, Al, Mg, Si, O, OH and water. Bentonite is an absorbent clay mineral, and its composition is primarily composed of montmorillonite, a type of smectite group of minerals. Attapulgite is a clay having chemical formula of (Mg, Al)$_2Si_4O_{10}(OH)\bullet 4(H_2O)$ having Mg, Al, Si, O, OH and water.

Researchers employed different types of clay-based adsorbents for water purification. clay–poly(methoxyethyl)acrylamide (PMEA) composite was employed as adsorbent typically for the removal of lead (II) ions from aqueous solution which had adsorption capability of 81.02mg/g within the contact time of 60 min (Solener, 2008). A chitosan-g-poly(acrylic acid)/montmorillonite (CTS-g-PAA/MMT) nanocomposites used as adsorbent for the elimination of methylene blue from water which had adsorption capacity of 1859mg/g and also had the ability of reuse after the attachment of methylene blue (Wang et al., 2008). Activated attapulgite was utilized as bleaching agent or adsorbent for the removal of soyabean oil (Liu et al., 2008).

The charge composition at the clay's layer is closely related to the adsorption event that occurs there. Many mechanisms for the absorbency of ions containing metals by nano clay particles minerals have been reported. These include chemical adsorption, physical adhesion, micro-precipitation (which involves a transfer of ions at permanently charged places), and the formation of substances (complexes) at the boundary places with hydroxyl groups (Awasthi et al., 2019). The attachment of pollutants on clay surface occurs in many ways which is explained in Figure 3

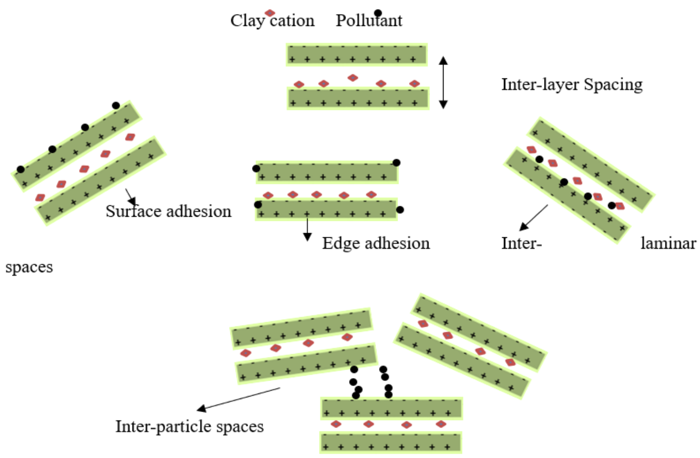

Figure 3: Shows different ways of attachment of pollutant on clay

Adsorbents made of natural clay compounds have a greater ability to adsorb than various other adsorbents for the elimination of heavy metals, and they are also more affordable and readily accessible. Clay soil is a popular adsorbent material due to its higher capacity to exchange cations, bigger surface area, and structural stiffness. The replacement of aluminum ions (Al3+) for silicon ions (Si4+) results in an overall negative charge on the clay framework and causes the formation of Bronsted acidity on the surface due to the dissolution of molecules of water. The adsorption capacity is improved by this acidity (Tiruneh, 2018). The following techniques are used to synthesize polymer–clay nano composite materials: polymer melt intercalation, polymer intercalation from solution, and intercalation of an appropriate monomer followed by in situ polymerization (Nguyen and Baird, 2006).

There are several methods for modifying clay materials especially for wastewater treatment like acid activation, thermal treatment and pillaring of clay. Activation is a physical or chemical procedure that makes clays more adsorbent. The chemical and physical characteristics, such as surface area and porosity, have both enhanced with acid activation. Thermal treatment centered around changing the small and large features of clay frameworks has been used to change the physic-chemical and structural properties of clay minerals and to boost the ability to absorb water in clay minerals. Heating the clay might alter its size, porosity, the formation of crystals and form. A potent method for enhancing the mechanical and thermal stability, particular surface area, porosity, and catalytic function of clay minerals is pillaring. Clay minerals are great adsorbents for protecting the natural world because of pillarization (Barakan and Aghazadeh, 2021).

Clay comes in a variety of forms, and each kind has special adsorption qualities. Kaolin clay, sometimes referred to as china clay, is a white or light-colored clay with a high capacity for adsorbing organic substances. It is frequently used to eliminate contaminants including heavy metals, organic colors, and oils from wastewater and water treatment procedures. Montmorillonite makes up the majority of the clay type called bentonite. It is highly adsorbent to organic molecules and some heavy metals, with a large surface area. Bentonite clay finds extensive application in the elimination of impurities from water and in the refinement of wines and edible oils. One kind of clay that has a lot of surface space and good expanding qualities is called montmorillonite. It is employed as an adsorbent in many different applications, including as the elimination of radioactive elements, organic matter, and toxic substances from soil and water (Khan, 2023).

In comparison to other adsorbents, clay-based customized adsorbent materials have remarkable capacity for regeneration and adsorption as well as selectivity. They are also inexpensive, porous, and have a large surface area. Several methods have been explored to regenerate wasted or dye-adsorbed clays, including chemical processing, supersonic extraction, heat, photocatalytic, and biological decomposition (Momina et al., 2018). Clay-based adsorbents have multiple environmental and economic considerations like natural abundance, biodegradability, low toxicity, renewability, and low cost, local availability, simple processing and versatility respectively.

Table Error! No text of specified style in document.: Clay- based adsorbents used for the removal of pollutants from wastewater

Adsorbent	Modification	Removed Pollutant	Condition	References
Moroccan clay		Methylene blue, Malachite green, Basic red 46	Room temperature	Bennani, 2015
Natural clays (Fouchana and Tabarka)		Reactive red 120, reactive orange 84, reactive blue 160	Room Temperature	Abidi, 2015
Sepiolite, kaolin, Synthetic talc		Reactive Yellow 138:1	Room Temperature	Rahman et al., 2015
Australian bentonite	Thermal activation, acid activation, combined acid thermal activation	Congo-red	Room Temperature	Toor, 2015
Attapulgite clay nanoparticle	Amino-functionalized & fabricated by hydrothermal carbonization of chitosan.	Methylene Blue (MB)	Room Temperature	Zhou, 2015
Bentonite clay		Reactive Black 5 (RB5)	shaking speed (100 rpm), temperature (323 K), pH (10), contact time (40 min)	Amin et al., 2015
Clay mineral originated from Morocco (Agadir city)		Nitrates Ions	pH 5.1	El-Ouardi, 2015
Nano clay	Achieved by bentonite treated with organic cation.	Orange GR, Black GN an African Brown	Room Temperature	Stagnaro et al., 2015
Papaya-clay combo, hybrid clay	Hybrid clay is synthesized from combination of Carica papaya seeds and Kaolinite clay.	methylene blue (MB)		Unuabonah, 2015
Pure bentonite clay balls, Surface modified clay balls	Modification is achieved by treatment with H_2SO_4 & calcination process.	Phosphate	Room Temperature	Lee, 2015
kaolin-bentonite clay (KBC)	bentonite blend with kaolin	Congo red	303-318 ±2 K	Ogunmodede, 2015
clay and sandy soil of Ikpoba river, Nigeria		naphthalene		Osagie and Owabor, 2015
Akadama clay	functionalized with $FeCl_3$	Cr(VI)		Ji, 2015
Montmorillonite (Mt), 4 organo-Mts (OMts)	with different octadecyl-trimethylammonium (ODTMA) loadings	Imazalil		Gamba, 2015
Brazilian bofe clay		Zn 2+ and Pb 2+	pH 3-5	Cunha et al., 2015
Palygorskite	Novel polyamidoamine (PAMAM) dendrimer-Functionalized	Pb^{2+} and Reactive Red 3BS		Zhou, 2015
Saponite, Palygorskite, and spondyle clay (Ukraine)	Magnetized by magnetic modifier Fe_3O_4 used in the form of magnetic fluid	Anionic surfactants and polyphosphates		Makarchuk, 2017

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Zeolite, smectite clay		Hg, As, and Cu	pH~2	Fiaizullina et al., 2017
kaolin clay	Fe_3O_4/kaolin magnetic nanocomposites	Direct Red 23 dye		Magdy, 2017
Exfoliated vermiculite, LECA		Gemfibrozil, mefenamic acid and naproxen		Dordio, 2017
Natural clay mineral from Algeria	Modified by iron oligocation called iron-pillared clays.	Diclofenac potassium		Mabrouki and Akretche, 2016
Sepiolite	Modified by coating of carbon nanoparticles & acid pre-treatment.	Phenol		Wu, 2017
Clay samples from Iran	conductive polyaniline was inflicted into the layers of clay	Pb(II) and Cd(II) ions		Piri, 2016
Montmorillonite	modified with different loadings Remazol Black B of CTAB (cetyltrimethyl-ammonium bromide)	Remazol Black B		Huang, 2017
Sand-clay mixture	Calcination	Phosphate	pH 10-12	Almily and Hasan, 2017
Sepiolite clay	Alginate hydrogel beads were impregnated with zinc oxide	congo red		Vahidhabanu, 2017
Natural clay from Turkey	Activated by treating with H_2SO_4	Astrazon golden yellow 7GL		Cakmak, 2017
Montmorillonite composite beads	Alginate–montmorillonite composite beads synthesized, cryogelation strategy utilized by deep-freezing alginate beads at –21°C	Methylene blue		Uyar et al., 2016
Granulated attapulgite (GAP)	Fe-impregnated charred GAP is synthesized by mixing 10g of charred GAP into 40 ml solution of ($FeCl_3.6H_2O$).	As (Ⅲ) & As (Ⅴ)		Yin, 2017
Metakaolin based geopolymer		Zinc (II) & Nickel (II)	25°C	Kara et al., 2017
Natural zeolite & Natural clay From Saudi Arabia	Modified using polyacrylamide	Cr(VI) and Toxic Ions		Sallam, 2017
Illite/Smectite (IS) clay	given clay is tear up & rebuilt as new porous adsorbent with enhanced surface area.	chlortetracycline (CTC)		Wang, 2017
Bijoypur clay (Kaolinite)	Clay-crystalline cellulose adsorbent synthesized by dissolution of cellulose in an alkali solution with additive.	chromium		Islam, 2017
Activated clay from Algeria		Methyl orange (MO)		Bendaho et al., 2017
Magnetic diatomite & illite clay	Modified by loading Fe_3O_4 NPs onto raw diatomite or illite clay surfaces	Phosphate		Chen, 2016
kaolinite, raw and sodium-	Charged Pharmaceutical products			Thiebault, 2019
Clay from Katiola and Fronan regions	Modified by treating with titanium oxide	Methylene blue & cadmium cations		Guilaume, 2018
Volcanic tuff (VT), natural clay and charcoal	Modified by treating with physical, chemical & thermal treatment	Phenols & Organic content		Azzam, 2018
Red clay soil (Utisol) Mbabane City	Combined clay adsorption-coagulation process	lead, Copper & Iron		Tiruneh, 2018
Montmorillonite nano clay		Ce (III) & crystal violet	room temperature	Parisi, 2019
Kaolinite/Smectite-A & Kaolinite/Smectite-B		lead (II)		El-Naggar, 2018
Novel montmorillonite	Modified into montmorillonite chitosan/poly (vinyl alcohol) (PVA) nanocomposite electro-spun nanofibrous membranes	Basic Blue 41 (BB41)		Hosseini, 2019

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Iranian natural clay and clay/Fe-Mn composite	composite is prepared by placing in water for 20 min, then $KMnO_4$ & $FeCl_3$ is added.	Arsenic (V)		Foroutan, 2019
Egyptian diatomite		Removal of different metal ion	pH 2-8 & 25°C	Elsayed, 2018
Colombian clay	modified with hexadecyltri-methylammonium bromide (HDTMA-Br).	Removal of chromium		Macias-Quiroga et al., 2018
3 Clays from Ivory coast region. whitish-coloured, gray colour & orange–red coloured.	Purified to get size particle less than 2 µm rich in clay minerals.	Humic acid	pH 3	Gueu, 2019
Natural & Modified Attapulgite	Modification is carried out Acid leaching.	Cr (VI)		Tichapondwa, 2019
Natural clay from Saudi Region with illite and Kaolinite as major parts		Methylene blue &	Crystal violet	Sakin, 2018
natural montmorillonite	Modified with 3-aminopropyl-trietoxisilane (APTES)	Acid Red 1 (AR-1) & Acid Green 25 (AG-25)		Thue, 2018
Hydrotalcites	Different adsorbents derived from hydrotalcites	Diclofenac		Rosset, 2019
Natural clay from Tunisia		Reactive red dye (RR 120)		Abidi, 2019
Aloji clay	Modified with acid concentration, Activation temperature & Activation time	Removal of Pb^{2+}		Obayomi and Auta, 2019
Natural clay (Sale-Morocco)		Cu, Co, Ni & Pb		Es-Sahbany, 2021
Clay from best way cement Industry in KPK (Pakistan)	Modified by acid loading into Given natural clay	Blue FBN (BFBN) & Rose FRN (RFRN)	pH~2 & 30°C	Kausar, 2020
Natural clay from Dashtestan city, Bushehr (Iran)	Modified into clay/starch/$MnFe_2O_4$ magnetic composite	Sunset yellow (SY) & Nile blue (NB)		Esvandi, 2020
Aluminosilicate rich clay soil from South Africa	Modified into Hydrothermally treated aluminosilicate clay (HTAC)	Fluorides & Pathogen		Obijole, 2021
Carbon-Clay (CSCC) biohybrid	Modified into Epichlorohydrin crosslinked chitosan/carbon–clay azo acid blue	Methylene Blue (MB), 29 (AB 29)		Marrakchi et al., 2020
Natural clay from BERCHID region	modified with cellulose acetate polymer (CA)	Crystal violet (CV)		Kouda, 2023

3. Recommendations & Future Outlook

Clay-based adsorbents have achieved attention worldwide due to versatile properties mainly in purification of wastewater due to enhanced adsorption capacity. Multiple types of clay like montmorillonite, sepiolite, Palygorskite, Bentonite and various others have been extensively studied for treatment of wastewater especially for dyes and heavy metals removal. Clay-based adsorbents possesses unique properties for water purification like enhanced surface area, having layered framework and cation exchange capacities. They have also advantaged of eco-friendly and economically feasible like they have no toxicity and they are not so expensive as compared to other adsorbents. There is still further research and developments on clay-based adsorbents to enhance adsorption phenomenon for wastewater treatment which involve exploration of alteration methods and techniques to enhance adsorption capacity and selectivity for different dye molecules and heavy metals. The ability of clay-based adsorbents for wastewater treatment can be further enhanced by integration of nanoparticles, polymer modification, functional group modification and surface modification. It may also be enhanced by hybrid-adsorbent system which may maximize the recyclability and reusability, minimizing the overall treatment cost and environmental impact. It may also be employed for the removal of pathogens and pharmaceutical wastes by modifying the clay-based adsorbents. Finally, clay-based adsorbents have the potential and ability for the purification of wastewater.

4. Conclusion

The availability of safe and clean water is the basic right of every individual and water treatment plays a significant role in ensuring that availability. Clay-based materials are considered as promising adsorbents in order to meet the requirements of water treatment. This review conducts a detailed analysis of different clay types, their properties, mechanism and potential for the treatment of wastewater. It begins with different types of clay which are mainly used for wastewater treatment. The clays have unique composition and discusses the type attachment of pollutant on clay-based adsorbent surface. The modification of clay-based materials for wastewater treatment is also explained and they also have no environmental and economic impact. Some raw and modified clay-based materials for specific dyes and heavy metals removal used in past have also been discussed. The possibilities and predictions about to enhance the capability of clay-based adsorbents for wastewater treatment is explained. Thus clay-based adsorbents are considered as one of the most suitable adsorbents for wastewater treatment.

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