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A critical review on clay-based nanocomposite particles for application of wastewater treatment

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ABSTRACT

Nanotechnology plays an important function in recent environmental aspects for the elimination of contaminants in the ecosystem. In recent times, nano-clay has initiated more concentration because of its distinctive physicochemical properties and characteristics. Recently, many types of research in clay-based nanocomposite were accomplished in the elimination of pollutants from water sources. Nanocomposite materials have advanced properties useful for contaminat removal such as higher surface area, thermal stability, selectivity to remove differ-ent contaminants, improved process ability, and fast decontamination. Thus, the development of clay-based composite materials is one of the upcoming directions to use effectively in water and wastewater treatment as adsorbent nanomaterials. This paper assesses the latest achievement in clay-based nanocomposite preparation, material property analysis and function for various pollutant removals. In particular, great consideration was paid to the recent progress in clay/metallic, clay-polymer, and clay-carbon composites presenting their application in the removal of different kinds of pollutants. Moreover, the mechanism of adsorption, the challenges and future perspective were also dis-cussed to reach the optimum performance of the nanomaterials adsorbent. It is confirmed that clay-based nanocomposite materials are more cost-effective technology than conventional treatment methods.

Key words: clay, metallic oxide, nanocomposite, polymer, wastewater

HIGHLIGHTS

- Nanocomposite materials have advanced properties useful for contaminate removal.
- Clay based nanocomposite can overcome the restrictions of individual clay and other constituents such as low selectivity, pH dependency, small specific surface area, and low water wettability.
- Clay based nanocomposite can be utilized as a cost-effective and novel adsorbent for the adsorption of organic contaminants from water and wastewater.

1. INTRODUCTION

Nowadays, the rapid development of advanced technologies results from one of the thoughtful global concerns in environ-mental degradation (Jaishankar *et al.* 2014). The wastewater that comes from several industrial processes is one of the main sources of pollution in natural water sources (Siddeeg *et al.* 2019). A clean source of water is an elementary requirement for every human community. The release of harmful constituents into water sources is rising significantly. Nevertheless, the increased use of poisonous materials has considerably raised a load of undesirable chemicals in freshwater through the bio-sphere. Connected to the rapid growth of industrialization, scientists reported the existence of more than 700 carcinogenic and highly toxic inorganic and organic micro-contaminants (Nguyen *et al.* 2020; Naidu *et al.* 2021). These are considered persistent ecological contaminants, which are not degradable. Toxic inorganic elements include Cr (VI), Hg, Cd (II), Pb (II), As (V), etc. while organic contaminants include dyes, pigments, and others.

The contamination of drinking water with toxic and heavy metals such as As (V), F^-, and a high load of dissolved solids are major concern. Pathogenic organisms are the main cause of water-borne disease for children (Forstinus *et al.* 2016). It is just not possible to get rid of these dangerous toxic pollutants. The easiest method to resolve this inclusive crisis is to grow cost-

effective and competent water and wastewater treatment expertise, which requires eco-friendly and non-contaminating materials.

The Conventional water and waste water treatment techniques have definite drawbacks such as high operational and maintenance cost, residual toxicity, non-recovering of materials, and so on. To address these concerns, researchers began to find a solution to solve these challenges. Among all the wastewater testament technologies, nanotechnology is the preferential solution for wastewater treatment and water purification. Furthermore, the use of clay-based nanocomposites in water and wastewater treatment has been confirmed to be valuables due to their great characteristics and recycling potential of the nanomaterial, which creates them to desirable than the traditional treatment techniques (Mukhopadhyay et al. 2020).

Nanotechnology encompasses the development of along materials at the nano stage by either extending up from single sets of particles or breaking large materials into small particles (Chen & Caruso 2013). Nanotechnology-based methods have developed competent approaches and materials for the solution of various tricky problems that were not addressed by earlier technologies and usual techniques. It needs an arrangement of natural materials, nanomaterials, and nanocomposites for a valuable and effective treatment manner for the removal of contaminates (Theron et al. 2008). From previous centuries, several nano-based technologies were used for the management and treatment of wastewater. Nano-sized particles have enormous prospective to be used in water and wastewater treatment because of unique materials chart eristic of surface area for removal of microbial, inorganic, and organic contaminants from water (Meyer & Upadhyayula 2014). A variety of types of nanomaterials are also offered to be competent for water and wastewater treatment such as carbonaceous nanomaterials, zeolites, polymers, and metal-containing nanoparticles.

Previously, investigators have used different adsorbent materials to eliminate toxic pollutants from water and wastewater including adsorption (Unuabonah & Taubert 2014; Das et al. 2018; Arora et al. 2019; Gu et al. 2019; Moreno-Sader et al. 2019; Sahmoune 2019; Malatji et al. 2021), electrolysis (Chebotareva et al. 2020), electrodialysis (Al-Amshawee et al. 2020), chemical oxidation (Fadillah et al. 2020), reverse osmosis (Yang et al. 2019; Couto et al. 2020), membrane (Caprarescu et al. 2017), conventional coagulation (Narayanan et al. 2020; Skaf et al. 2020), and chemical precipitation (Verma & Balomajumder 2020). Many of these methods are expensive and cannot be applied in low-economic nations. Coagulation techniques and chemical precipitation cause secondary pollutants to need extra treatment and raise the treatment cost. Interestingly, adsorption is the largest part of the contaminant removal process because it is inexpensive and easy to operate, and provides maximum removal capacity for various pollutants. The chosen adsorbent material must be freely accessible, cheap and simply generable, and contain higher selectivity into target pollutants. Efficient adsorbents of biological, organic, or mineral origin have been developed for water treatment.

The most-used adsorbent materials include polymeric resin products (Khan et al. 2020), biomass (Coelho et al. 2020), agricultural wastes (Joseph et al. 2021), industrial by-products, natural clay minerals (Ayalew 2020; Thiebault 2020), zeolites (Aragaw & Ayalew 2019; Chen et al. 2020), and activated carbon (Nam et al. 2014). Because of their free accessibility and contrasted to other adsorbent materials, natural clay and kaolinite minerals have strongly selected as a new adsorbent for the taking away of different contaminants from water (Amari et al. 2021).

Nevertheless, the efficiency of this material is lowered as compared to other adsorbent materials. Commonly, the real use of clay materials as adsorbents is limited due to many influences such as the minor specific surface area, the small electron attraction between the adsorbent surface and the adsorbate molecules, and the problem of adsorbent recovery. To solve these limits, researchers have developed clay-based nanocomposite materials combining the beneficial properties of both natural clay minerals and other composite materials.

A new composite adsorbent material has high adsorption efficiency, high thermal stability, high specific surface area, and better regeneration efficiency than individual components (Pavlidou & Papaspyrides 2008).

This review paper provides the latest experimental data regarding nano-clay composite materials that have been arranged and used for the removal of water pollutants.

1.1. Structures and kinds of clay minerals

Clay materials naturally exist in plentiful sedimentary rocks in hydrated phyllosilicate form. The simple unit of clay mineral is interrelated by SiO_4^- tetrahedron with three oxygen molecules, shared one tetrahedron to another tetrahedron. Clay minerals have a great adsorption capability, which relates to the higher specific surface area caused by their sheet assembly and a net negative charge on their configuration. This offers to adsorb and grasps cations, such as cationic particles and heavy metals. Currently, there are different types of nanoclay materials including kaolin, bentonite, montmorillonite, illite, micas, and

kaolinite. Nanoclay minerals are pretty, inexpensive, and freely available. Moreover, they have remarkable characteristics such as high porosity, greater particle surface area, and capability to retain contaminants on the surface.

1.2. Application of nanomaterial in water and wastewater treatment

Recently, nanotechnology is a developing field and contributes an extensive set of tools that are currently under the process of advance at the nanoscale (Thomé *et al.* 2015). It plays a chief part in the development of new approaches to reduce environmental degradation as well as improving the rate of environmental protection (Zhang *et al.* 2016). Nano-technological methods are frequently being studied to increase traditional water treatment systems. This requests less in cost and is more operative than the current existing methods for the elimination of pollutants from water sources (Abdelbasir & Shalan 2019). Nanoparticles are used as powerful adsorbents combined with magnetic units to adsorb contaminants in wastewater. Furthermore, nanoparticles can be utilized in the photochemical destruction of pollutants. Nanoparticles have countless prospective applications in water management because of distinctive physicochemical characteristics including higher porosity and good thermal and mechanical stability, which can be used competently in the removal of microbial, inorganic, and organic contaminants from water bodies (Meyer & Upadhyayula 2014).

2. CLASSIFICATION OF NANOCOMPOSITE MATERIALS

In nanocomposite material preparation, one of the stages is the range of nanomaterials, and they vary from conservative composite within microscale configuration because of their tiny particle size and the greater specific surface area (Awasthi *et al.* 2019). Nanocomposite components contain more than one phase of nano-size substances, and each segment has different dimensional properties. The nanocomposite materials have advanced material characteristics such as electrochemical, conductivity, and thermal. Based on the matrix difference and structure arrangement, natural clay nanocomposite can be categorized into three main classes such as metallic-based nanocomposites, polymer-based nanocomposites and carbon-based nanocomposites.

2.1. Metallic-based nano-clay composites

Metallic-based clay composites are consist of metallic nanomaterials such as Fe/Al_2O_3, Ni/Al_2O_3, magnetic iron oxide/clay nanocomposite, zinc oxide clay-based (ZnO/clay), titanium oxide clay-based (T_2O/clay). They have improved magnetic properties such as high electrical and chemical resistance, superparamagnetic, saturation magnetization, strong mechanical properties, and high specific surface area. Having these extra physiochemical properties, metallic-based nanoclay composites have a great application for the adsorption of different pollutants from water and wastewater.

2.1.1. Magnetic iron oxide/clay nanocomposite

Currently, researchers are focused on the nanoscale and they propose that nanomaterials have unlimited potential to diminish water pollutants. Among those nanocomposite materials, magnetic materials, particularly iron oxide nanoparticles have been documented since earliest times to now. They have distinctive characteristics for water and wastewater treatment (Abdullah *et al.* 2019). Some of these characteristics are included higher mobility, higher reactivity, high adsorption capacity, high reactivity, and catalytic activities. Moreover, magnetic nanoparticles have also distinctive properties such as optical, magnetic and electrical properties. Magnetite (F_3O_4) and maghemite ($\gamma\text{-}Fe_2O_3$) are the largest type of magnetic nanomaterials typically considered because of the exceptional characteristics that display at nanomaterial scales such as excellent thermal stability, good mechanical properties, chemical resistance, high specific surface area, and superparamagnetic properties (Zhu *et al.* 2018; Qiao *et al.* 2019). It is known that magnetic iron oxide nanoparticles (MNPs) are the most selected nanomaterials for adsorbents and photocatalysts. The magnetic iron nanocomposites are cost-effective method for photocatalysis and adsorption due to their excellent saturation magnetization, simple recovery, and reusability.

A material's adsorbent ability and selectivity for an identified pollutant can be improved by surface-modifying its entire surface and joining it with structures of other supporting materials. Currently, researchers found that there are different materials used as supporting magnetic nanoparticles. Among these likely composite resources coupled together with the magnetic nanoparticles, nanoclay materials have been received attention from researchers. Clay minerals have higher adsorption ability, which derives from the higher specific surface area caused by their structural arrangement and a net negative charge on their alignment. These properties can be used to grip positively charged contaminants.

Clay minerals are found naturally and have an attractive adsorption property for the elimination of pollutants from wastewater due to their high specific surface area and porosity. The layer of silicate configuration and porosity of particle allocation

of the nanocomposite, and cation exchange capacity are the main factors for the removal of specified molecules in water treatment.

2.1.1.1. Synthesis of magnetic iron oxide/clay nanocomposites. Overall, there are two key preparation methods for the synthesis of magnetic iron oxide/clay nanocomposite namely co-precipitation and intercalation of MNPs towards a clay configuration (Fadillah *et al.* 2020). The co-precipitation technique is conducted based on the entire chemical reaction and interaction between the clay minerals in aqueous dispersion used to synthesize MNPs. Thus, the formation of nucleation and development of the nanoparticles' crystal happens *in situ* in solution diffusion of clay crystals, as shown in Figure 1.

The synthesis of magnetic iron oxide/clay nanocomposites through co-precipitation combines a clay mineral with magnetic nanoparticles in the alkaline situation to produce a sol-gel pattern. In this preparation, NH_4OH or $NaOH$ is usually used to produce the alkaline state, which openly synthesizes the precipitate of the composite (Orolínová & Mockovčiaková 2009; Zong *et al.* 2013; Tokarčíková *et al.* 2017). The reaction and interaction between the clay mineral and the magnetic nanoparticles to produce a composite through the sol-gel method can be strengthened by using some methods including heating by using a reflux system or by other techniques such as microwave irradiation. Once the reaction is formed, the sample is then allowed to dry and calcinate. The preparation of the γ-Fe_2O_3 phase by using Slovakian bentonite at temperature of 85 °C was conducted and a magnetization of 35–42 emu/g was obtained. The mixture of oxidation and co-precipitation could be also be performed to invent a homogeneous magnetic nanoparticles phase (Chang *et al.* 2016; Chen *et al.* 2016; Wan *et al.* 2016; Belachew & Bekele 2020).

Natural kaolinite is one of the most commonly used types of clay minerals as an adsorbent in wastewater treatment. It has a one-to-one structural arrangement and contains the minor ability for the adsorption process (Tireli *et al.* 2014). The magnetic nanoparticles and kaolinite were prepared through the co-precipitated reaction technique (Fayazi & Ghanbarian 2020). During the precipitation reaction, the magnetic particles can be spread to both the external and interlayer surface of the clay (Tsoufis *et al.* 2017). During the synthesis of clay with MNPs, different important features that influence the composite particles should be considered (Mahdavinia *et al.* 2017; Goncharuk *et al.* 2020).

2.1.1.2. Adsorption mechanism of magnetic iron/clay nanocomposite. Magnetic iron clay nanocomposite has been extensively utilized for the elimination of contaminants from aqueous solutions including adsorption, chemical, oxidation, and photo-oxidation processes. The diminishment and elimination of pollutants including chemical elements, such as dye, pigments, heavy metals, and other organic toxins from water and wastewater have been stated. The use of magnetic iron clay nanocomposites for the treatment of water and wastewater by using adsorption is more effective than advanced oxidation processes and photocatalysis. The mixture of the adsorption behaviors of natural nanoclay materials with the magnetic properties of MNPs from novel magnetic iron clay nanocomposites adsorbents is a favorable method for the elimination of contaminants from water.

Table 1 shows several magnetic iron clay nanocomposites along with their target contaminants and prohibiting processes. As seen in Table 1, several alterations have been tried to improve the adsorption competency of magnetic iron clay nanocomposites, principally through surface functionalization. The use of polymers, surfactants, and other chemical compounds comprising functional groups onto nanocomposites is operative for attracting the adsorbate. To designate the adsorption performance, studies have adopted isotherm models, such as the Freundlich, Langmuir, and Dubinin-Radushkevich models. The
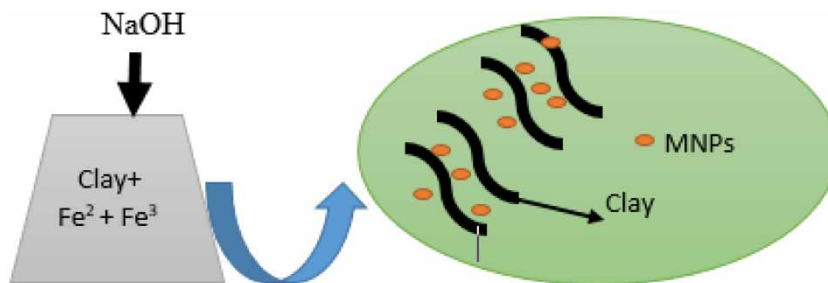

Figure 1 | Diagram representation of the co-precipitation method.

Table 1 | List of magnetic iron oxide/clay nanocomposite used for adsorption of various pollutants

Magnetic iron oxide/clay nanocomposite	Adsorbate	pH	Removal capacity (mg/g)	Isotherm of adsorption	References
Bentonite/iron oxide magnetic	Co(II)	8.0	10.7	Langmuir	Chen et al. (2011)
Fe_2O_3/bentonite	Picloram	5.5	–	Langmuir	Marco-Brown et al. (2012)
O,O′-bis(2-aminopropyl) Polypropylene glycol-γ-Fe_2O_3/montmorillonite	Methylene orange	–	9.8	–	Yu & Yang (2010)
Montmorillonite-Cu(II)/Fe(III) oxides	Humic acid	6.1	98.0	Langmuir	Peng et al. (2006)
Clay/polyaniline/Fe_3O_4	Methylene blue	–	184.0	Langmuir	Mu et al. (2016)
Fe_3O_4/kaolinite	Copper	5.0	106.0	–	Lasheen et al. (2016)
	Cadmium	7.0	100.0	–	
	Nickel	7.0	95.2	–	
	Chromium	6.5	97.0	–	
	Pb (II)	6.5	98.0		
Magnetic attapulgite-biochar composite	Oxytetracycline	10.0	33.3	Langmuir	Wang et al. (2019)
γ-Fe_2O_3/halloysite	Ag nanoparticles	–	67.9	Langmuir	Janacek et al. (2018)
Magnetic and anionic–cationic modified montmorillonite	Methylene blue	–	246	Langmuir	Rahmani et al. (2020)
Fe_3O_4/halloysite	Naphthol green	3.0	11.2	Langmuir	Riahi-Madvaar et al. (2017)
Polyethylenimine functionalized magnetic montmorillonite clay	Cr(VI)	2.0	62.9	Langmuir	Fayazi & Ghanbarian (2020)
montmorillonite clay (MMT-Fe_3O_4-PEI) Fe_3O_4/sepiolite	Safranin	7.9	18.5	–	Fayazi et al. (2015)
Magnetic core-shell dodecyl sulfate intercalated layered double hydroxide (Fe_3O_4)	Methylene blue and methylene orange	–	18.5 and 225.0	–	Li et al. (2019)
Fe_3O_4/montmorillonite	Methylene blue	7.37	59.9	Langmuir	Chang et al. (2016)
Graphene/magnetite/montmorillonite	Methylene blue	11.0	225.0	Langmuir	Zhang et al. (2019)
Fe_3O_4/Al-pillared bentonite	Hg(II)	3.5	26.0	Dubinin Radushkevich	Zou et al. (2018)
Fe_3O_4 NPs/diatomite and	PO_4^{3-}	2.0	11.9	Langmuir	Chen et al. (2016)
Fe_3O_4 NPs/illite	PO_4^{3-}	2.0	5.48	Langmuir	
Fe_3O_4/bentonite	Enrofloxacin	3.54	180.0	–	Peng et al. (2019)
Chitosan/clay/magnetite	Cu(II) and As(V)	9.0 3.0	17.2 5.9	–	Cho et al. (2012)
Fe_2O_3–palygorskite	Fenarimol	–	27.8	–	Ouali et al. (2015)
Fe_3O_4–sepiolite	Bisphenol A	–	12.8	–	Tsoufis et al. (2017)
Fe_3O_4/sepiolite	Atrazine	7.7	15.9	Langmuir	Liu et al. (2014a, 2014b)
Fe_3O_4/bentonite	Cr(III)	7.0	11.7	Langmuir	Shah et al. (2018)

Langmuir isotherm model signifies the monolayer adsorption taking place on a vigorously homogeneous exterior, on which adsorbed pollutants non-interaction with the adsorbent surface. The adsorption process of contaminates by using magnetic iron/clay nanocomposite is listed in Figure 2.
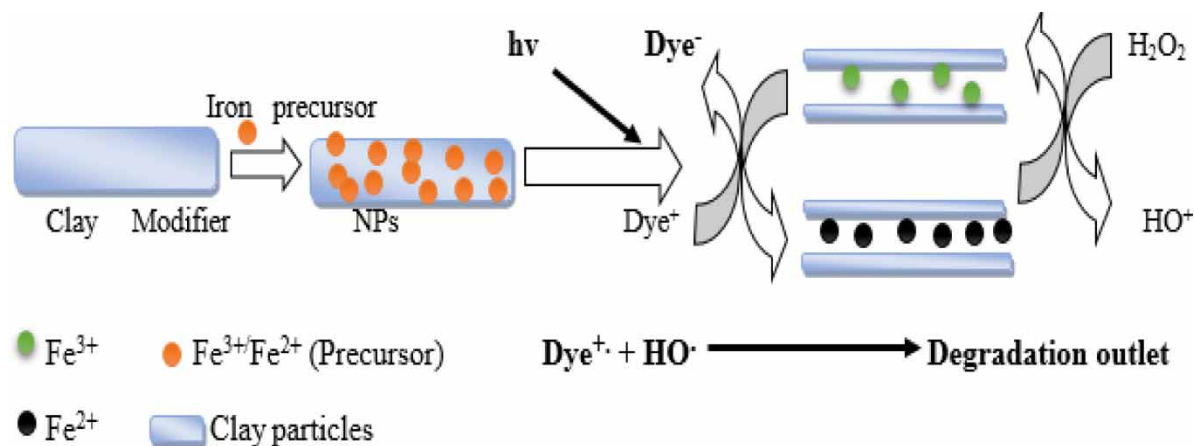
Figure 2 | Pictorial exhibition of the adsorption mechanism of contaminates by using magnetic iron/clay nanocomposite.

2.1.1.3. Physicochemical characterization of magnetic iron clay nanocomposite.   The pore size distribution and specific surface area are imperative factors in adsorbent and photocatalyst applications for water and wastewater treatment (Lasheen *et al.* 2016). The superior specific surface area brings additional adsorption sites for highly bonding with the target contaminates. The Brunauer-Emmett-Teller method calculated from the N_2 adsorption/desorption isotherm data is a usually acceptable technique for specific surface area calculation. But porosity of particle allocation and specific surface area are not the most significant parameters for removal proficiency but also the presence of water-loving and water-hating are the other adsorbent surface interactions (Fatimah & Nurkholifah 2016). In molecules, numerous aspects influence concentrated adsorption including adsorbent/catalyst dose, contact time, pH, adsorbent particle size, and so on. For instance, pH value is one of the factors for the adsorption process during surface infarction. The zeta potential is also the basic parameter related to capacity magnetization. It measures the charge magnetism or repulsion between particles under the magnetic field. The larger magnetic field strength produces higher adsorption (Tireli *et al.* 2014; Peng *et al.* 2019). Magnetic fields employed higher effects on the adsorption of contaminants, as revealed by their surge of elimination and adsorption ability. Moreover, the size of nanoparticles has a significant effluent for magnetic field strength as analyzed by using a transmission electron microscope (TEM) (Siregar *et al.* 2018).

2.1.2. Kaolin/ZnO nanocomposite

In the latest time, different kinds of adsorbents including graphene oxide, zeolites, activated carbon goethite, agricultural wastes, industrial by-products, metals/metal oxides nanomaterials, and many more were fruitfully used to eliminate noxious waste from wastewater. Among these listed remarkable adsorbents, a zinc oxide nanoparticle is a type of semiconductor metal oxide that shows outstanding adsorption and photocatalytic activity in the presence or absence of light (Kamaraj *et al.* 2020). It is considered high resistance to optical and chemical corrosion, high catalytic activity, high stability in chemical properties, and non-toxic properties (Shakir *et al.* 2016; Akkari *et al.* 2018; Wang *et al.* 2018).

Zinc oxide nanoparticles can be synthesized from different precursors such as zinc sulfate, zinc nitrate, hexahydrate, zinc acetate dihydrate, zinc chloride, and zinc acetylacetonate by using either chemical or physical approaches. The disadvantages of using zinc oxide nanoparticles alone include fast agglomeration formation, small particle size distribution, low specific surface area, which make recovery from the aqueous phase very hard. Moreover, the release of zinc oxide nanoparticles into the atmosphere could pose prospective health and environmental hazards. Thus, the hold of zinc oxide nanoparticles on the appropriate medium could help to block these problems (Akkari *et al.* 2017). The reinforced nanoparticles typically possess tremendous adsorption capacity, thermal stability, high specific surface area, and good mechanical properties as compared to non-reinforced metal oxide nanoparticles.

Clay minerals are very appropriate for this drive due to their inexpensive and extensive accessibility. Moreover, their entire molecular configurations determine valuable in chemical and physical properties including water holding capacity, reactivity, specific surface area, and ion exchange capacity (Bel Hadjltaief *et al.* 2016; Uddin 2017). The exchangeable ions aid the adsorption of natural contaminants in wastewater through the adsorption and ion exchange methods. But the charge

should be a vital parameter to be considered for their application. Hence, the need to know the capacity of the adsorption method for impurities removal in wastewater under numerous experimental situations is very imperative. So it is a vital need to exhaustively examine the possibility of using kaolin and hybrid clay based on kaolinite clay and zinc oxide nanoparticles for the adsorption of contaminants from water and wastewater.

Currently, efforts have been made to host zinc oxide nanoparticles on the whole surface of natural clay minerals to investigate the capacity of the nanocomposite as an adsorbent for the removal of wastewater contaminates. Azizi et al. (2017) produced zinc oxide nanoparticles to eradicate lead ions (Pb) from wastewater and attained optimum adsorption ability and the removal efficiency was found to be 19.65 mg/g and 93% respectively. The most favorable excremental situation was found to be pH value of 5.0, lead initial concentration of 10 mg/L, and contact time 1 h, adsorbent dose of 0.1 g, and the temperature was 70 °C.

Correspondingly, Zolfaghari et al. (2013) have gained the highest sorption ability of 2.5 mmol/g for zinc oxide coated nanoporous carbon and it was accountable for the removal of 90% of Pb (II) compared to ZnO with 2.38 mmol/g and 78% removal efficiency. Salehi-Babarsad et al. (2020) investigated the elimination capability of toxic contaminate metals including Cu^2, Fe^{3+}, Cr^{6+}, and Cr^{3+} in an aqueous solution by using zinc oxide/graphene oxide and zinc oxide/polyaniline composites. The authors recognized that support materials of graphene oxide and polyaniline polymer provided the greater adsorptive capability of zinc oxide nanoparticles. In the same way, Sonawane et al. (2017) also described that the composite of zinc oxide/bentonite was effective for the exclusion of safranine dyes in an aqueous solution. Sani et al. (2017) studied the taking away of Cu (II) and Pb (II) molecules from wastewater by using zinc oxide/montmorillonite nanocomposites. It was shown that the surface area and the sorption capacity of zinc oxide nanoparticles were improved by the addition of nanoclay particles.

2.1.2.1. Synthesis of kaolin-supported zinc oxide nanoparticles. Zinc oxide/clay nanocomposites can be synthesized through wet impregnation, and the sol-gel method technique (Vahidhabanu et al. 2017). The author found the prepared zinc oxide/clay nanocomposite had amazing adsorption capacity and was credited to the occurrence of zinc oxide nanoparticles in the inserted nanocomposites. About 5.0 g of Zn $(C_2H_3O_2)_2$ was primarily dissolved in 50.0 cm^3 distilled water and then 0.5 M of NaOH solution was added into the solution dropwise to regulate the pH to be 6, 8, 10, and 12. After stirring for 30 min, a white colloidal suspension was formed.

Around 0.5 g of the beneficiated kaolin clay particles were dispersed into the solution and were actively stirred at 150 rpm for a maximum of 1 h. A zinc oxide/clay uniform gel was produced and permitted to age in condition. The result was then washed by using distilled water and dried out at 80 °C overnight using the oven. Lastly, the product sample was calcined at 450 °C for 3 h using the furnace. The zinc oxide nanoparticles are dispersed on the kaolin matrix as shown by using X-ray diffraction pattern. The XRD exhibited the existence of diffraction related to the zincite hexagonal structure. The small intensity value at 2θ of 31.79°, 34.42°, 36.25°, and 56.60° with conforming the Miller-Bravais catalogs (100), (101), (102), and (110) crystal structure, which further confirmed the presence of zinc oxide nanoparticles in the kaolin clay nanocomposite sample. The diffraction pattern and analogous crystal structure are faithfully fitted with the normal JCPDS file of the zincite phase of the zinc oxide nanoparticles (No.36-1451). The phase of zinc oxide nanoparticles described in this investigation is in good concurrence with earlier studies (Cao et al. 2019; Le et al. 2019). The result of the XRD pattern confirmed the real formation of a mixed phase of zinc oxide/kaolin nanocomposite.

Besides, Singh et al. (2013) discovered assorted phases of zinc oxide/Fe_3O_4 nanocomposites prepared by using the co-precipitation technique. The result mainly notified that there was no confirmation of peaks extending and shifting of diffraction peaks to upper angles within the studied pH choice. This auxiliary displayed that the synthesized zinc oxide/kaolin nanocomposites were extremely crystalline. The small and high-intensity diffraction at 12.0° and 26.9° peaks showed the existence of kaolin clay in the numerous nanocomposite trials.

Except for zinc oxide/kaolin nanocomposites synthesized at a pH value of 8.0, which exhibited the average consideration of pure zinc oxide at 2 theta values of 25.1° and others revealed a mixture of zinc oxide and kaolinite. Thus, the characteristic reflection structure of zinc oxide for kaolin/zinc oxide nanocomposite at pH 8.0 fits the high-resolution TEM characterization as revealed in the FTIR spectra of kaolin/zinc oxide nanocomposite prepared at different pH values followed by calcination at 450 °C for 3 h.

2.1.3. Titanium dioxide/kaolin clay nanocomposite

2.1.3.1. Titanium dioxide/kaolin nanocomposite preparation. According to Tokarský et al.'s (2014) description, titanium dioxide/kaolin nanocomposite was synthesized by using grounded kaolin clay less than 5-micrometer particles. Firstly, the

powder was treated with HCl at room temperature and stirred for 3 h. Afterward, a yellow-red solution was separated through decantation. Later, the kaolin clay units were treated with 15% NaOH under automated stirring for about 30 min. White powder result was found through decantation, filtration, and washing by using distilled water. Finally, the sample was dried using the oven at a temperature of 80 °C for 4 h drying time. The gained titanium dioxide/kaolinite nanocomposites powder was exposed to chemical investigation such as XRD, SEM, and XRF. Based on the authors' report, the main composition of raw kaolin mineral and the synthesized titanium dioxide/kaolinite nanocomposite by XRF examination has been obtained as: 23.46% Al_2O_3, 2.66% Fe_2O_3, 1.56% TiO_2, 63.17% SiO_2, 0.84% CaO, 0.19% MgO, 0.22% Na_2O, 0.27% K_2O, and 7.43% loss of ignition.

X-ray fluorescence investigation displayed that the ratio of SiO_2/Al_2O_3 equals 2.69 for raw kaolin clay and 3.87 for the synthesized titanium dioxide/kaolinite nanocomposite. The outcome of XRF and XRD measurements has shown that the raw kaolin clay is composed mainly of kaolinite and metal oxides. The use of HCl and NaOH solution towards kaolin minerals is to remove the other components and oxides. On the other way, the prepared titanium dioxide/kaolinite nanocomposite is composed mainly of aluminum silicates and titanium dioxide. This technique directed that the elimination of the allied metal materials from the raw kaolin clay by hydrochloric and sodium hydroxide introduced a change into the chemical structure of kaolin clay and increases the surface area and adsorption capacity.

Zhang et al. (2011) successfully synthesized titanium dioxide/kaolinite nanocomposites with diverse phase titanium dioxide (anatase and brookite) at the intermediate reaction temperature. The crystal and mineral type of titanium dioxide nanoparticles could be controlled by the kaolin clay matrix, develop outstanding catalytic performances. Similarly, Hai et al. (2015) prepared acid-activated clay through calcination and chemical activation of coal-bearing kaolin and then improved it by using titanium dioxide nanoparticles to advance its capacity to absorb and thus eliminate dyes. Mamulová Kutláková et al. (2011) prepared nanocomposite kaolinite/titanium dioxide by using hydrolysis of titanium oxide sulfate in the existence of clay, and calcined titanium dioxide/kaolinite composite at 600 °C using the furnace. Since thermal treatment was advantageous to the upgrading chemical reaction of titanium dioxide/kaolinite nanocomposites. The precipitation of titanium dioxide/kaolin nanocomposite has mainly emphasized the crystal assembly modifications of titanium dioxide on a substrate but disregards the influence of morphological matrix on properties of titanium dioxide.

So synthesis catalysts with clay that have naturally changed morphology are a very significant investigation to illuminate the influence of clays structurally on the photocatalytic performance and interfacial features of titanium dioxide/kaolinite.

The titanium dioxide/kaolin clay simultaneously confined their owing characteristics of titanium dioxide and clay displayed unlimited adsorption photocatalytic properties. This new material has a bright view in degradation of organic contaminants (Aliou Guillaume et al. 2018). Hence, kaolin clay with several morphologies can be utilized as auxiliary materials for the development of titanium dioxide nanoparticles. The distribution of titanium dioxide nanocrystal towards clay has fine dispersal and plentiful minor particle size than that of individual titanium dioxide sample, causing from the close edge and decent interfacial interaction. Thus, the titanium dioxide particles size can be organized by kaolin clays and create effective contact with clay surface, which would lead to showing more catalytic reaction active sites and improving the photocatalytic properties.

2.1.4. Clay/polymers nanocomposite

Recently, natural minerals such as kaolinite and clay are mainly used to improve the performance and mechanical properties of polymeric materials. The combinations of polymers and kaolinite materials are measured as promising reinforcements to produce clay-polymer nanocomposites with higher properties useful for contaminant elimination. Up to now, there are three chief group clay/polymer nanocomposites including exfoliated nanocomposites, intercalated nanocomposites, and phase-separated micro-composites (Othman et al. 2014).

In the case of exfoliated nanocomposites, the clay particle is completely distributed in the interior of the polymer matrix. They are composed of approximately 1 nm clay layers separated within the matrix of the polymer. The clay/polymer nanocomposite is formed by filling the silicate crystalline into the polymer chain. The phase-separated micro-composite, obtained from fixed polymer surrounded by silicate layers, have parallel properties to the conservative nanocomposite. This nanocomposite polymer shows outstanding properties concerning deformation, biodegradability, chemical resistance, mechanical strength, and thermal stability. Clay polymer nanocomposites may contain numerous polymers chains in their preparation such as polyesters, chitosan, polyvinyl chloride, polypropylene, epoxies, polystyrene, and polyurethane.

2.1.4.1. Preparation technique of polymer/clay-based nanocomposite. Overall, there are three different ways used for the synthesis of polymer-clay nanocomposites such as the solution-blending technique, melt-bending method, and in-situ polymerization technique.

2.1.4.1.1. Solution-blending technique

In this process, the polymer is commonly permitted to solidify in appropriate solvent primarily. Concurrently, the clay material is also spread in the same solvent separately. Afterward, the clay-solvent distribution is moved into a polymer-solvent solution. The combination of clay/polymer/solvent solution is permitted to become homogenized for a consequent period. Lastly, the mixture is cast onto level support and the solvent eliminated through evaporation (Ahmad *et al.* 2011). The solution-blending technique is displayed in Figure 3.

2.1.4.1.2. Melt-bending method

The second type of preparation method is called the melt-bending method. This technique permits for the good mixing of the clay and the polymer materials as compared to the solution-blending method. In this case, the clay particles are openly reinforced towards the polymer matrix through a melt-integration approach. In this way, the clay/polymer is permitted for the strengthening process, which is commonly prepared at a greater temperature than the polymer melting temperature (Guo *et al.* 2018). A representation image of stages involved in the melt-blending technique can be seen in Figure 4.

2.1.4.1.3. In-situ polymerization technique

The third kind of preparation method is the in-situ polymerization technique. This technique aids to improve the compatibility between the polymer and the clay units. This method helps to achieve uniform dispersion of clay molecules into the polymer matrix. This is due to the well disperse of clay molecules initially in the solution having monomers, which is then exposed to the following polymerization. Lastly, the clay atoms are imbedded with a tinny sheet of the polymer as supporting to the entire polymer matrix, which is appropriate for the next processing methods including extrusion and compression casting (Abbasian & Mahi 2014). A graphic presentation stages included in the in-situ polymerization process can be observed in Figure 4.

Based on their developed routines, clay/polymer nanocomposite exhibited the capacity to remove various contaminants such as metal ions, microorganisms, phenols, pesticides, pigments, and dyes from water and wastewater. Intake water includes different microorganisms that are accountable for hazardous water-borne diseases such as typhoid, diarrhea, and
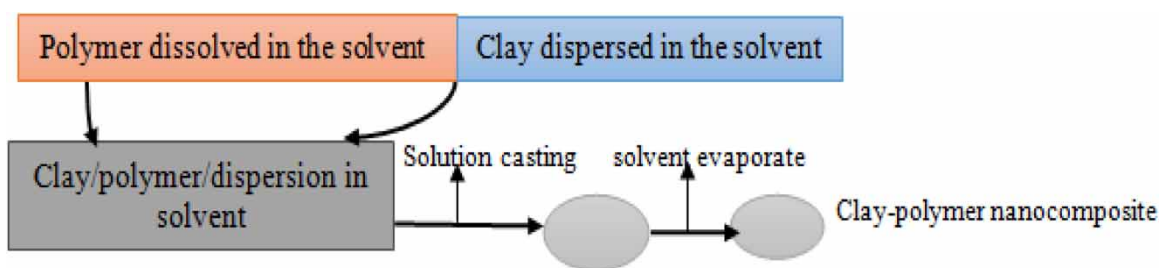

Figure 3 | The synthesis process of clay-polymer nanocomposite adsorbent using the solution method.
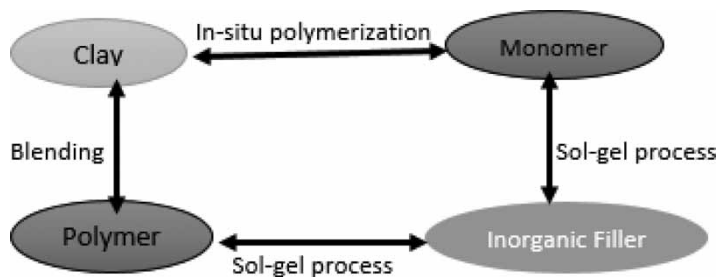

Figure 4 | Three general methods for synthesis of clay/polymer nanocomposite.

dysentery (Wołejko et al. 2020). Chlorination technology was applied traditionally to discount the pathogen population. However, currently, this expertise become less used because of the presence of some soluble organic impurities that endorsed the formation of secondary toxic pollutants such as haloacetic acids, trihalomethanes, and chlorophenols (Kaya et al. 2020). Also, the chloramination process displayed a greater potential to create nitrosamines than chlorination. Previously, the use of different materials such as sand slow filtration was proposed but with restricted competence due to delaying with some blocking (Farré et al. 2020). Remarkably, the use of clay/polymers composite was attractive for the removal of bacteria and other contaminates. The capacity of copper-doped montmorillonite polyethylene composite was examined for the removal of Escherichia coli bacteria (Bruna et al. 2012). The synthesized clay polymer composite comprises a montmorillonite-Cu^{+2} compound that permitted greater antimicrobial activity and found 99% removal capacity for E. coli. Likewise, other clay/polymer composites including clay/polydimethyloxane/chitosan/silver, and montmorillonite/polydimethyloxane/chlorhexidine acetate exhibited the capacity to slow down the growth of different bacteria (Kang et al. 2013). Bentonite clay with surface modified by starch-graft was used to remove E. coli.

The microbial removal was attained due to the existence of cationic molecules on the surface of the clay (Undabeytia et al. 2014). The presence of monomer improved the nanocomposite with positive charges that electrostatically attracted the negative phospholipids of the microbial cell tissue initiating cell interference. Hence, clay/polymer composites are more effective than individuals for microbial eliminations. Moreover, chitosan/montmorillonite nanocomposites are shown to have antibacterial activity. Fascinatingly, the composite of chitosan/montmorillonite was more effective for the elimination of E. coli and Staphylococcus aureus than chitosan and montmorillonite (Han et al. 2010). The composites of chitosan-montmorillonite and chitosan/clay with surface modified by Ag+ nanoparticles were investigated in microbial activity (Deng et al. 2011).

Clay/polymer composites can be reused for microbial elimination by using several reagents such as HCl, steam, and sodium hypochlorite (Unuabonah et al. 2017). Due to higher antimicrobial activity, clay/polymer composites can be used effectively to decontaminate polluted water. The existence of hazardous poisonous organic and inorganic contaminants including phenols, dyes, pesticides, and organic acids may cause environmental harm even in small amounts. Interestingly, these organic and inorganic pollutants were eliminated by using clay/polymer composite materials as nanoadsorbents, because of the presence of high polymeric hydrophobic pieces on the nanocomposite surface (Hernández-Hernández et al. 2018). In this viewpoint, numerous clay/polymer nanocomposites in the type of tablets or powder were synthesized by using the thin-coated layer techniques. This approach offers an improvement of the adsorbent for reusability after adsorption of noxious pollutants (Shahadat & Isamil 2018). As shown in Table 2, several organic and inorganic pollutants can be removed from wastewater through the adsorption process using clay/polymer composites.

The straight discharge of organic, microbial and inorganic contaminants in water sources significantly affects the atmosphere. Among these contaminants are polyphenolics, tannic acid, dyes, pesticides, chromes, and pigments that come from disintegrated organic materials, which are extremely dangerous for creatures in the marine environment. Usually, the tannic acid compounds occur in water and soil surface. Subsequently, it is vital to discover the appropriate way for their elimination. In this perspective, clay layered with chitosan polymer was used as a novel adsorbent for the removal of tannic acid with an adsorption capability value of 95.3 mg/g. The sorption resulted from H-bonding, electrostatic exchanges, and Van der Waals force attractions (Deng et al. 2012). Interestingly, the synthesized nanocomposite was better to absorb more tannic acid molecules obtained as 456 mg/g adsorption capacity by using the solid medium of protonated clay with chitosan resin polymer dispersion (Wu & Chen 2013).

Correspondingly, organic phenolic materials including phenols and 4-chlorophenol were eradicated by using polymer reinforcement combined with clay surface reformed with a surfactant of hexadecyl trimethyl ammonium. This adsorbent showed an elimination capacity of 0.335 mg/g and 0.119 mg/g respectively for phenols and 4-chlorophenol (Hernández-Hernández et al. 2018). Similarly, trinitrophenol and trichlorophenol were eliminated by using montmorillonite prepared from poly-4-vinylpyridine-co-styrene with elimination efficacy of 99.6, and 60% respectively. In this work, it has been proposed that a weak Van der Waals force is elaborated in the adsorption mechanism (Ganigar et al. 2010). Similarly, (Zhu et al. 2011) were studied the removal of phenolic materials by using a nanocomposite of cetyltrimethylammonium poly (diallyldimethylammonium) to modify the montmorillonite clay. The adsorption capacity into phenols was improved. The elimination of dyes from water and wastewater by using clay/polymer nanocomposite was informed through many studies. In this study, numerous researchers stated the exploit of chitosan polymer as an effective adsorbent (Bée et al. 2017). (Wan Ngah et al. 2010) prepared the clay/polymer nanocomposite of bentonite/chitosan for the removal of azo dye tetrazine, identified by its dangerous influence on aquatic organisms. In this study, pH is the main factor that affects the adsorption process. With a small pH value,

Table 2 | Removal of various pollutants from wastewater using clay-polymers nanocomposite adsorbent

Adsorbent type	Adsorbate	pH	Temp (°C)	Adsorption capacity (mg/g)	Isotherm model	Kinetic model	Reference
Chitosan/bentonite	Tartrazine	2.5	47	294.1	Langmuir	Pseudo-second-order	Wan Ngah et al. (2010)
Chitosan-coated attapulgite	Tannic acid	5.5	–	95.2	Freundlich	Pseudo-second-order	Deng et al. (2012)
Chitosan-g-poly (acrylic acid)/montmorillonite	Methylene blue	6.5	–	1,895.0	Langmuir	Pseudo-second-order	Wang et al. (2008)
palygorskite/chitosan resin microspheres	Tannic acid	8.0	–	455.0	Langmuir	Pseudo-second-order	Wu & Chen (2013)
Chitosan/montmorillonite	Congo red	4.0	30	–	Langmuir	Pseudo-second-order	Wang & Wang (2007)
Humic acid-modified bentonite	2,4dichlorophenol Cu (II)	6.5 6.5	30 30	14.23 22.41 mg/g	– –	– –	Jin et al. (2016)
montmorillonite /layer double hydroxide	Methylene blue	–	–	74%	–	–	Zhou et al. (2014)
Chitosan/bentonite	Amido Black 10B	2.0	20	323.6	Langmuir	Pseudo-second-order	Liu et al. (2015a, 2015b)
polyaniline/montmorillonite clay nanocomposites	Green 25	6.0	20	100%	Langmuir	Pseudo-second-order	Kalotra & Mehta (2021)
Chitosan/bentonite	Malachite green	6.0	37	435.0	Langmuir	Pseudo-second-order	Ngah et al. (2010)
Hydrogels of Kappa-carrageenan-gpoly(acrylamide)/sepiolite	Crystal violet	10.0	25	74.0	Langmuir	Pseudo-second-order	Mahdavinia & Asgari (2013)
poly(AA-co AMPS)/montmorillonite	Methylene blue	10.0	25	214.0	Redlich–Peterson	Pseudo-second-order	Hosseinzadeh & Khoshnood (2016)
Amino-modified polyacrylamide–bentonite	Malachite green	6.0	30	656.5	Freundlich	Pseudo-second-order	Khalil & Kenawy (2020)
Chitosan/attapulgite	Cr (III)	5.0	30	65.37	Langmuir	Intraparticle diffusion	Zou et al. (2011)
	Fe (III)	3.0	45	62.51	Langmuir	Intraparticle diffusion	
Chitin/bentonite nanocomposite	Cr (VI)	4.0	–	443.72	Freundlich	–	Saravanan et al. (2013)
Alginate–montmorillonite nanocomposite	Pb (II)	6.0	–	244.7	–	–	Shawky (2011)
Chitosan and montmorillonite	Se (VI)	–	–	18.5	–	–	Bleiman & Mishael (2010)
Na-montmorillonite/cellulose	Cr (VI)	5.5		22.3	Langmuir	Pseudo-second-order	Kumar et al. (2012)
Polyaniline modified bentonite	U(VI)	6.5	20	14.1	Langmuir	Pseudo-second-order	Liu et al. (2017)
Chitosan immobilized on bentonite	Pb (II)	–	35	26.39	Freundlich	Pseudo-second-order	Futalan et al. (2011)
	Mn (VII)	4.0	–	14.82	Langmuir		

(*Continued.*)

Table 2 | Continued

Adsorbent type	Adsorbate	pH	Temp (°C)	Adsorption capacity (mg/g)	Isotherm model	Kinetic model	Reference
Bentonite/ thioureaformaldehyde						Pseudo-second-order	El-Korashy et al. (2016)
Chitosan grafted poly acrylic acid bentonite composites	Cu (II)	6.0	25	88.6	Langmuir	–	Kumararaja et al. (2018)
	Ni (II)	7.0	25	49	Langmuir	–	
Attapulgite/poly(acrylic acid)	Pb (II)	5.0	–	38	Freundlich	Pseudo-second-order	Liu et al. (2014a, 2014b)
Chitosan/clinoptilolite	Ni (II)	5.0	25	247.04	Langmuir	Pseudo-second-order	Dinu & Dragan (2010)
Poly(acrylic acid-coacrylamide)/attapulgite	Cu (II)	6.0	–	69.76 mg/g	–	–	Liu et al. (2015a, 2015b)

a positive charge was formed, which permits the electrostatic interaction between nanocomposite surface and dye molecules. Whereas at maximum pH, the charge becomes negative and resulted in a falling adsorption process because of the occurrence of repulsion forces between the dye molecules and nanocomposite surfaces. The entire cross-linked chitosan in the composite is epichlorohydrin, which becomes insoluble in the water and thus increases the capacity of the adsorption process.

Similarly, methylene blue dye was detached from the aqueous solution by using clay/chitosan charming drips at a pH range of 3–12 and mass ratio of clay to chitosan greater than 0.5. The maximum removal efficiency and adsorption capacity for methylene blue were found as 50% and 83 mg/g respectively (Bée et al. 2017). The adsorption mechanism has occurred through electrostatic interaction between the positive charge of the dye molecule and the negative charge of clay particles with a broad pH range.

Also, Vanamudan & Pamidimukkala (2015) prepared clay/chitosan nanocomposites for the elimination of Rhodamin-6 G dye with a sorption capacity of 446.4 mg/g. The adsorption chemical kinetics of the dye molecules was explained by the pseudo-second-order kinetic model. Furthermore, Xu et al. (2018) investigated the elimination of methylene blue by using clay/chitosan nanocomposite. In this investigation, the greatest removal efficiency was obtained as 99.99% and the optimum adsorption capacity was found as 152.3 mg/g. The adsorption performance was mainly effluent by the pH value and the adsorption equilibrium experimental data was followed by the Langmuir isotherm. Vanaamudan & Sudhakar (2015) also synthesized chitosan-modified nanoclay for the removal of two dyes including reactive blue-21 and reactive red-141 dyes. The adsorption capacity for the reactive blue-21 and reactive red-141 was found as 477 mg/g and 440 mg/g respectively. The equilibrium experimental adsorption data of the two dyes followed the pseudo-second-order kinetic model. Peng et al. (2013) compared the adsorption capacity of modified and unmodified clay matter for the removal of reactive dyes. Overall, the chitosan-modified clay nanocomposite's adsorption capacity was 71.39 mg/g for reactive yellow-3 RS dyes, which is considerably greater than the unmodified clay materials, which obtained 6.4 mg/g. In this study, at maximum pH value, the adsorption process decreased because of the repulsion forces among like charges, whereas at a small pH value, the positive charge was produced at the chitosan surface due to the presence of some amino groups that improved the adsorption process through electrostatic attraction. In recent times, De Sousa et al. (2020) prepared a composite of clay-polymer by using sodium bentonite and ureasil-poly (ethylene oxide) through the sol-gel technique for the elimination of methylene blue from aqueous solution. Fascinatingly, methylene blue was detached quickly and proficiently over the adsorption process.

Like dyes, microbial metalloids and toxic metals are the main sources of water-poisonous metalloids and heavy metals such as Cr, As, Cd, Ni, Sb, Cu, U, Se, and Pb. Heavy metals and metalloids constitute a severe hazard for humans and organisms. These contaminants can collect inside various organisms causing destructive effects. Thus, their elimination from water sources is critical for the good environment (Jordão et al. 2002). Recent research has shown that efforts have been piloted to remove the contaminated heavy metals from the water source by using clay mineral as their reinforcement and chitosan also as the polymer (Rusmin et al. 2015; Azzam et al. 2016).

(Azzam et al. 2016) prepared clay-chitosan/silver nanocomposite for removal of copper Cu (II) ions. The maximum adsorption capacity was found as 181.5 mg/g at a pH value of 7.0. The maximum adsorption at pH 7.0 occurred due to the

interaction between Cu (II) ions and the chitosan molecules. Khalek et al. (2012) synthesized a nanocomposite of poly/methacrylic acid attached with chitosan/bentonite, for removal of Hg (II), Pb (II), and Cd (II) ions. In this study, the removal efficiency for Hg (II), Pb (II), and Cd (II) values was obtained as 94, 89, and 78%, respectively were obtained at high pH. Similarly, a composite of chitosan/attapulgite was prepared and confirmed to remove Fe (III) and Cr (II) ions from an aqueous solution. The optimum adsorption capacity was obtained at 10.41 mg/g and 11.65 mg/g for Fe (III) and Cr (II) at the adsorbent doses of 0.2 g/L respectively. Usually, the adsorption mechanism of metal is organized by the process of electrons shared among adsorbent surfaces and metals through covalent bonding (Zou et al. 2011). In the same way, (Wang et al. 2016) investigate the chitosan/Al-pillared montmorillonite composite to eliminate Cr (VI) with an adsorption capacity of 15.7 mg/g. Moreover, Cu (II) and Pb (II) ions were removed using a similar composite synthesized from clay/chitosan with a ratio of 1:0.45 to eliminate Cu (II) and Pb (II) at a pH value of 6.5 with a removal efficiency of 96% and 99.5% respectively through chemisorption mechanisms (Kumararaja et al. 2018). Also (Rusmin et al. 2015) synthesized different mass clay to chitosan ratio of including 1:1, 1:2, and 2:1 for removal of lead molecules from aqueous solution. The optimum removal capacity was obtained as 201.5 mg/g using the ratio of 1:1. The presence of pores and high surface area from both polymer and clay is the main reason for the high removal of lead ions. In an alternative study, the adsorption of Pb (II) was increased via using different molding from an aqueous solution when the clay weight enlarged by 5% with respect to polystyrene polymer composite (Alsewailem & Aljlil 2013).

Similarly, various metals including Cd (II), Zn (II), Ni (II), and Cu (II), were removed using chitosan-grafted polyacrylic acid bentonite nanocomposite. The optimum removal was found at pH values of 6, 8, 6, and 7, respectively, for corresponding Cd (II), Ni (II), Cu (II), and Zn (II) (Kumararaja et al. 2018). The occurrence of a negative ion at the adsorbent surface with a positive charge of heavy metals allows maximum adsorption to occur at a higher pH value. Also, Grisdanurak et al. (2012) studied the removal mechanism of Pb (II), Cu (II), and Ni (II) from water by using chitosan impregnated on bentonite clay using ethylene glycol diglycidyl ether as an immobilizer. The maximum adsorption capacity of 26.38 mg/g, 21.55 mg/g, and 15.82 mg/g respectively for Pb (II), Cu (II), and Ni (II) ions (Futalan et al. 2011). In this study, an exothermic adsorption process has occurred for both metals and also the entropy behavior becomes decreases as shown from thermodynamic parameters (Liu & Lee 2014).

3. NANO-CLAY ADSORPTION MECHANISM IN WATER TREATMENT

Recent studies displayed that nano-clay as an adsorbent confirmed more consideration for the adsorption of several contaminants from water and wastewater because of the improvement of the surface adsorption mechanism. Former studies have been established that the nanoclay adsorbent low-cost materials are non-toxic with the higher outlook of ion-exchange capacity and plentifully existent. Numerous kinds of clay minerals such as kaolinite (Jiang et al. 2010), bentonite (Bereket et al. 1997), illite (Echeverría et al. 2005), pyrophyllite (Gupta et al. 2009), sepiolite (Lazarević et al. 2007), and montmorillonite (Ijagbemi et al. 2009) have been listed to be effective for the elimination of pollutants from wastewater. Nano-clay minerals have greater specific particle surface area and higher pollutant removal performance that offers suitable structural, chemical resistance, thermal stability, and mechanical properties to the adsorption of numerous contaminates. The adsorption manner at the entire surface of the clay is openly connected to the charged molecule existent at the surface. Several kinds of mechanisms have been informed for the adsorption of metals ions by using nanoclay materials such as micro-precipitation, physical adsorption, and chemisorption. The development of organic polymer/clay can be attained by the exchange of organic molecules and cation (Stathi et al. 2007). The adsorption of contaminates might be at the different surface locations of the adsorbent materials as shown from Figure 5.

4. CONCLUSION AND FUTURE PROSPECTIVE

Nano-clay materials are the best minerals for the synthesis of novel materials and afford a cost-effective sustainable solution to various industries for health and environmental safety. Replacement of traditional approaches for decontamination of water and wastewater by advanced inexpensive materials has been confirmed as an encouraging tool in the water treatment process. Composites of clay used for coating with different materials have a superior perspective for decontamination pollutants. As reported in the literature, the proficiency of clay minerals can be increased by the incorporation of new materials at the nanoscale for the development of stable clay nano-composites with advanced properties. In recent years, clay-based nanocomposites getting more consideration in different areas such as water and wastewater treatment. Modification of surface,
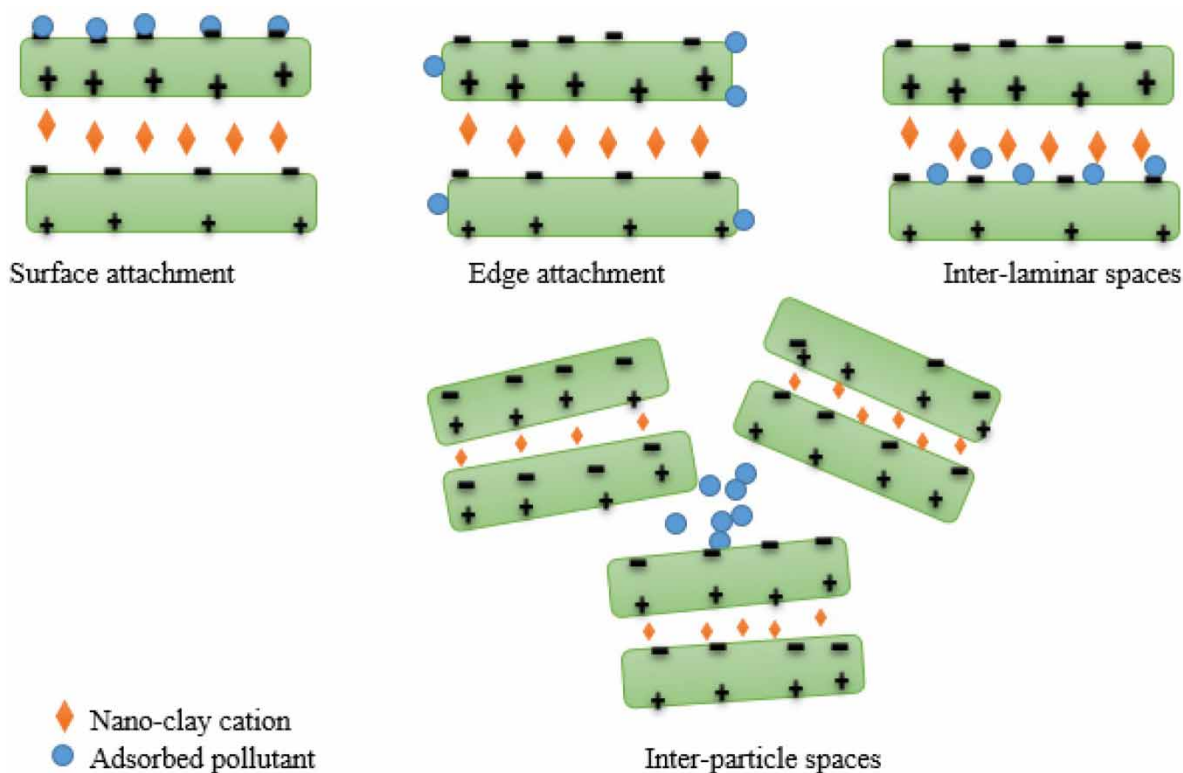
Figure 5 | Different kinds of surface location adsorption mechanisms of pollutants.

alteration of particle geometry, and increased particle surface area make compatible nanomaterials for modifications in the surface geometry and increment in the surface area make them a well-suited material for the adsorption process.

Clay-based nanocomposites and their application in wastewater treatment have been well investigated and have been used in several ways to compact with contaminate-containing water. As shown from previous research, incorporating functional and active materials into nano-clay surfaces has caused stable adsorbent, photocatalyst, and catalyst nanomaterials, which have improved adsorbent recovery and sustainability in the wastewater treatment process. But, practically, research works have not yet been achieved in the large-scale production and implementation of this advanced technology. Besides, researchers have been carried their experiment only using synthetic wastewater solution. However, there is a necessity for more investigations to test which the performance evaluation of clay-based nanocomposite materials on industrial wastewater. So it is greatly recommended that researchers should investigate large-scale production and industrial application.

DECLARATION OF COMPETING INTEREST

The author declares that he has no known competing for financial interests or personal relationships that could have appeared to influence the work reported in this work.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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