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A compendious review on clay modification techniques for wastewater remediation

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ABSTRACT

Presence of significant quantities of toxic dyes has led to contamination of fresh water resources. The limited availability of fresh water has escalated the pressure on maintaining sustainable agricultural production to ensure food security. So , there is a need to recycle the wastewater and to explore the possibility to reuse it for irrigation purpose. Amongst different techniques, adsorption has been found to be the best way for the remediation of colored effluents. The concept of recycling and reuse of wastewater has propelled the exploration of potential inexpensive adsorbents. Clays are cheap, non-toxic abundantly available natural materials. Over the recent years, researchers have focused on clays modification to enhance their adsorption efficiency for the remediation of contaminants such as dyes from wastewater. Therefore, the present article is written with an aim to systematically summarize the recent advancements in clay modification and their potential as effective adsorbing agents for the removal of various dyes from contaminated wastewaters. A detailed description of various clay modification techniques such as treatment with surfactant, acid, heat, plasma, polymer, silane, metal oxide has been presented here. The effect of various physicochemical process parameters such as solution pH, initial dye concentration, adsorbent dosage and temperature on the performance of modified clays has also been presented. Based upon the final outcome of literature review, it can be concluded that modified clays are much better adsorbing agents in comparison to the natural clays. Hence, modified clays represent an economically viable and sustainable option for the purification of wastewaters containing dyes and it can be utilized for irrigating different crops at the places where fresh water resources have either depleted or limited.

Key words: Clay modification, Dyes, Wastewater, Surfactant, Silane

Rapid increase in industrialization and energy production in recent years has increased the pressure on freshwater resources. The generation of effluents from different industries containing numerous toxic pollutants is causing contamination of already limited water sources. Discharge of colored effluents by textile, paper, plastic, paint and pigment manufacturing industries without sufficient treatment creates problems for living organisms as these dyes have detrimental effects on all living beings. Dyes inhibit the penetration of sunlight into water and thereby negatively affect the aquatic flora through reduced photosynthetic activity (Ferreira *et al.* 2014).The dyes being used are highly persistent and recalcitrant in nature (Çakmak *et al.* 2017). Therefore, it becomes essential to remove these toxic dyes from the contaminated effluents before their discharge into the aquatic ecosystems.

Various estimates revealed that by the year 2050 about 60% increase in agricultural production is required to ensure global food security. This ever increasing food demand aggravates the pressure on available water resources.For achieving sustainable increase in agricultural productivity, optimum utilization of natural resource like water is of prime importance. Therefore, there is a need to find the ways where agricultural production continues to increase without facing water scarcity. One possible option to achieve it is the treatment/ recycling of dye contaminated effluents generated by numerous industries and utilizing the treated water for irrigation purposes.

Though there are different methods for the treatment of dyes but amongst available techniques, adsorption has been found to be the most effective due to its low installation cost and easy management. Activated carbon is commercially available for water treatment but its high regeneration cost has limited its use on a large scale. In the pursuit to find low-cost adsorbents, it was found that different types of adsorbents are available (Chopra and Singh 2019; Chopra *et al.* 2019) but clay mineral-based adsorbents are preferred amongst others being cheap, non-toxic and abundantly

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available, therefore, offer a good choice for the removal of various dyes from contaminated wastewaters. In this review, we have tried to present a comprehensive and demanding analysis of various clays, their modification and utilization for dye removal. Also, the factors affecting the adsorption process such as the effect of contact time, temperature, pH, initial dye concentration have been given due consideration in order to understand the interactions between adsorbent and dye molecule.

Structure and properties of clays

The term “clay’ generally refers to the naturally occurring inorganic crystalline materials found primarily in finer fractions of soil (<2 µm diameter) (Velde 1992; Velde 1995). The most commonly observed clays are layer silicates (kaolinite, illite, montmorillonite, vermiculite and chlorite) (Biswas and Mukherjee 1994) . Clays have a strong influence on both physical as well as chemical properties of soils because of their unique characteristic features such as smaller particle size, high surface to mass ratio and unique cation exchange characteristics (Anonymous 2002). Layer silicates also serve as an important component of coarser fractions (sand and silt) of soil and therefore, should not be restricted only to the clay fractions (Anonymous 2002) . Chemically, clay minerals are hydrous aluminosilicates comprising of two key building blocks; silica tetrahedral sheet $(SiO_4)^{4-}$ and octahedral sheet (di or tri-octahedral). Each silica tetrahedral sheet is formed through sharing of three basal oxide ions of each tetrahedron with two adjacent tetrahedral units leading to reduction in negative charge per unit tetrahedron. This type of arrangement leaves one unshared apical oxide ion in each tetrahedron, pointing upward from the basal plane accommodating the shared oxide ions (Anonymous 2002). This apical oxide ion is free to form a bond with other polyhedral atoms/ions. The octahedral unit formed either of aluminium, magnesium or iron; surrounded by equidistant oxygen or hydroxyl ion, leads to the formation of an octahedral sheet. Depending upon the valency of central cation (Al or Mg/Fe); octahedral sites can be filled in two ways. In case of trivalent ion such as in gibbsite $[Al_2(OH)_6]$; two-third of the ionic positions are filled to form the unit, resulting in the formation of dioctahedral structure, whereas in case of divalent ions such as in brucite $[Mg_3(OH)_6]$, all the positions are filled resulting in the formation of trioctahedral structure (Anonymous 2002) . Hence, it is clear that both dioctahedral as well as trioctahedral sheets are electrically neutral.The tetrahedral and octahedral sheets are bonded together through the sharing of an oxygen ion with silicon and aluminium in their respective sheets to form the basic crystal unit of a clay mineral. The spacing between the two layers of the crystal unit is the interlayer space.

Clay modification

Clay minerals contain various species of cations and anions, held onto their surface, that are usually available for exchange. This availability of exchangeable cations and anions on clay surface drew the attention of researchers all around the world to utilize their natural as well as modified forms as a potential adsorbent for wastewater treatment (Srinivasan 2011). Various scientific studies conducted during the recent past have revealed that naturally occurring clays are not much effective as an adsorbent for the removal of organic contaminants. This is primarily due to their hydrophilic nature, lower interlayer spacing and high surface energy (Hundal *et al.* 2001; Aggarwal *et al.* 2006). Therefore, modifications of natural clays are required to enhance the adsorption efficiency of clays. The modification results in an overall enhancement of the total surface area, pore volume and available active sites that ultimately result in the increase in adsorption efficiency (Uddin 2017). Modification of clays can be achieved through various processes and can enhance the adsorption efficiency to a great extent. The selection of modification techniques, materials used for modification and the purpose of modification can significantly affect the adsorption properties (Kausar *et al.* 2018) .Therefore, proper selection of modification technique and modification material is essential in order to achieve desired adsorption efficiencies for the intended purpose or application.

*Cationic surfactant modification for dye removal:*The modification of natural clays through cationic surfactants is among the most extensively explored approach. Natural clays contain loosely bound cations present between layers which can be easily replaced by other cations through ion exchange mechanism. This property of natural clays is successfully exploited to replace inorganic metal cations with the long chain hydrocarbon cationic groups of cationic surfactants. Ion exchange achieved through the replacement of interlayer cations with cationic surfactants can greatly enhance the adsorption of clays. Generally, natural clays are hydrophilic in nature. In order to enhance their adsorption potential for hydrophobic pollutants, the clays are typically modified with alkyl ammonium cationic surfactants through an ion exchange reaction (Sanchez-Martin *et al.* 2006). The alkyl ammonium cations preferentially remain present on the surface of the negatively charged clays, while the hydrocarbon chain extend into the interlayer spaces and render the original hydrophilic clay to become organophilic (Le Baron *et al.* 1999; Wang *et al.* 2010) . The adsorption characteristics of the resulting modified clay is greatly dependent upon the molecular structure of the organic modifier (Bartelt-Hunt *et al.* 2003). The surfactants used for modification commonly consist of a single or multiple long hydrophobic hydrocarbon chains which are attached to the central atom. This intercalation of clays through cationic surfactants not only alters the adsorption characteristics from hydrophilic towards hydrophobic but also increases the basal spacing between the layers to a great extent. Thus, the resultant surfactant modified clay becomes a more efficient adsorbent (Latifi *et al.* 2017; Patanjali *et al.* 2019; Patanjali and Singh

2020). It also enhances the overall surface area leading to improved intercalation of organic cation between the layers of modified clays (Singla *et al.* 2012: Patanjali *et al.* 2018). More often, the studies are focusing on the effect of length of alkyl chain, whereas the studies on the effect of the spacer length of surfactant are comparatively fewer (Yang *et al.* 2014; Luo *et al.* 2015).Wang and Wang (2008) modified montmorillonite with cetyltrimethylammonium bromide (CTAB). XRD patterns exhibited that untreated montmorillonite displayed a typical peak at 6.94˚ with a basal spacing of 12.74 Å. Although, montmorillonite modified with CTAB exhibited the peak shift towards lower angle (5.94˚) and an increase in corresponding basal spacing to 14.89 Å thereby indicating the formation of the intercalated nanostructures in the CTAB modified montmorillonite.

Anirudhan and Ramachandran (2015) modified natural bentonite clay by cationic surfactant (Hexadecyltrimethylammonium chloride) and studied its dye removal potential against methylene blue, CV and RB from the aqueous phase (Fig 1).The outcomes of the study revealed that modified bentonite exhibited higher dye removal efficiency than unmodified bentonite for all the dyes. Batch studies were performed to evaluate percent dye removal as a function of adsorbent dose of 400 micro mol L^{-1} at pH 9.0. The results revealed that modified clay is 1.6, 1.7 and 1.75 times more effective in comparison to the unmodified form for the removal of methylene blue, CV and RB respectively. This is due to the increase in surface area and porosity of bentonite as a result of the modification process. Increasing the dose led to the increase in active sites per gram of adsorbent. Therefore, number of adsorbate molecules were chemically bound to the adsorbent surface leading to an increase in adsorption.

Acid activation for dye removal: Chemical treatment of natural clays by various acids is extensively explored for the surface activation of different clays (Fig 2).This approach is more commonly explored in bentonite clays typically with hydrochloric acid or sulphuric acid. The natural clays are treated with mineral solutions in order to get a partly dissolved silicate material with enhanced surface properties such as specific surface area, a number of possible active sites, increased porosity and surface acidity (Carrado and Komadel 2009; Komadel and Madejová 2013) . The first effect of acid treatment of clays is the replacement of exchangeable cations with protons; thereafter they attack the interlayers (Amonette *et al.* 1994). The mineral structure is altered primarily due to the interaction between silicate structure of clay and inorganic acid leading to dealumination. This ultimately results in the formation of non-crystalline silicate layers (Zhao *et al.* 2008; Wang *et al.* 2011). The treatment of clays with acids such as hydrochloric acid or sulphuric acid also results in the removal of basic cations (e.g. Na^+, Ca^{2+}) from the interlayer spaces and edges. This will result in an overall increase in the negative charge of clays. Sulphuric acid is generally preferred over hydrochloric acid because it is comparatively cheaper and less harsh (Murray 2007).Consequently, these acid activated clays exhibit exceptional behavior which can be exploited for novel applications (Komadel 2016).The surface physicochemical characteristics of clay minerals can be successfully modified through treatment with various inorganic acids, i.e. hydrochloric acid (Yang *et al.* 2018), sulphuric acid and phosphoric acid (Toprak and Halisdemir 2015) .

Sarma *et al.* (2016) utilized different molar concentrations of sulfuric acid for modifying montmorillonite and studied their adsorption efficiencies in removal CV from aqueous solutions. Langmuir monolayer adsorption capacity revealed higher adsorption capacities of acid treated bentonite than raw bentonite. Moreover, increasing the molarity of acid resulting into enhanced adsorption capacity. Surface characterization of acid treated montmorillonite by BET revealed higher porosity and enhanced surface area per unit mass. Similar increase in specific surface area of clays and enhanced adsorption efficiencies has been reported by other authors also. Acid treatment of clays not only removes the impurities but at the same time substituting exchangeable cations with H^+ through ion exchange reactions. Acid treatment might result in cation leaching into the tetrahedral and octahedral sites to open up the platelet edges resulting in higher surface area and better pore dimensions for increased adsorption sites (Valenzuela Díaz and Santos 2001; Auta and Hameed 2013) .

Pillaring by metal cations for dye removal: Pillaring has evolved as a potential technique for the modification of clay surface through utilizing appropriate pillaring agents. This results in the widening of interlayer spaces of natural clays leading to highly resistant and thermally stable clays with improved porosity, basal spacing and increased

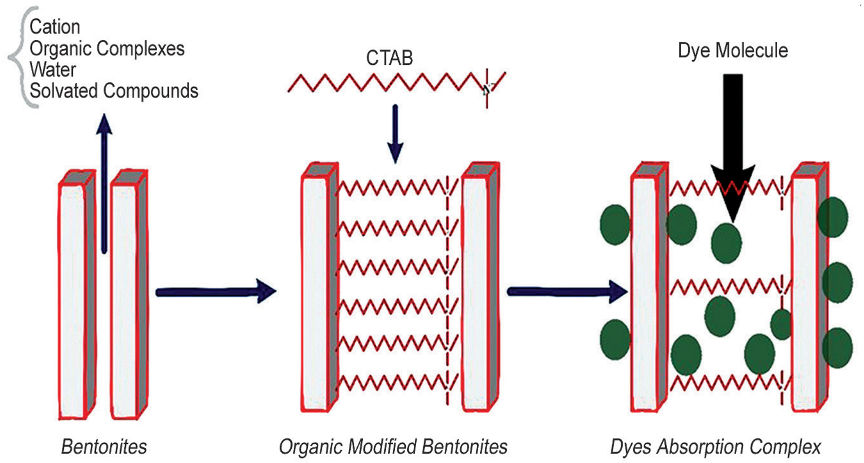

Fig 1 Adsorption of dyes through surfactant modified clays (Huang *et al.* 2017).

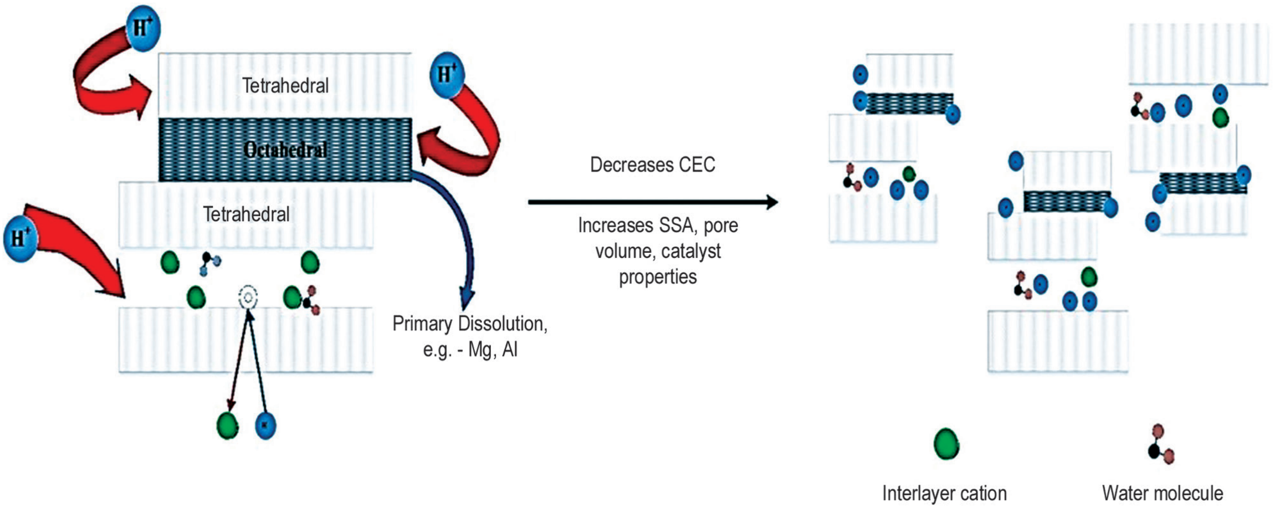

Fig 2 Effect of acid activation on the surface and interlayer spaces of bentonite clay (España *et al.* 2019).

surface to mass ratio (Zhou *et al.* 2014; Ye *et al.* 2016; Baloyi *et al.* 2018). The pillaring technique is fundamentally based on cationic exchange. In this technique, metallic cations are introduced in the interlayer spaces of the clay resulting in the formation of oxides that strongly bound to interlayers of the minerals (Fig 3) (Brigatti *et al.* 2006).In general, the preparation of pillared clays consisting of two key steps: firstly, the preparation of solution of the metal oxide pillaring agent and secondly, the mixing of this pillaring solution with a clay to form a suspension (Kloprogge *et al.* 2005).This method is time taking and needs a huge amount of water which represents a majorlimitation to scale-up this technique to industrial scale (Fetter and Bosch 2010) . Intercalation of natural clays with suitable pillaring agent leads to the formation of clays having enhanced porosity. The pillared clays are envisaged to exhibit enhanced adsorption properties. Due to high stability, cost-effectiveness, eco-friendly nature and great versatility in the application as adsorbents, pillared clays has emerged as one of the most intensively studied families of functional materials in the past few decades (Galeano *et al.* 2014). A wide range of naturally available clays and pillaring species are available. The proper selection of clay and pillaring species is, therefore, necessary to achieve the desired performance of the final resulting material. The factors that affect the adsorption performance of pillared clays and must be considered before utilization as adsorbents are as follows:

- thermal and hydrothermal stability of the pillared clay
- interlayer spacing
- pillaring density
- chemical nature and stability of pillars

The intercalation of clays in the pillaring process introduces two direct consequences on the properties of the clays. Firstly the d-spacing is enhanced as observed by XRD and secondly, the increase in the specific surface area (Gil *et al.* 2008; Gil *et al.* 2000).

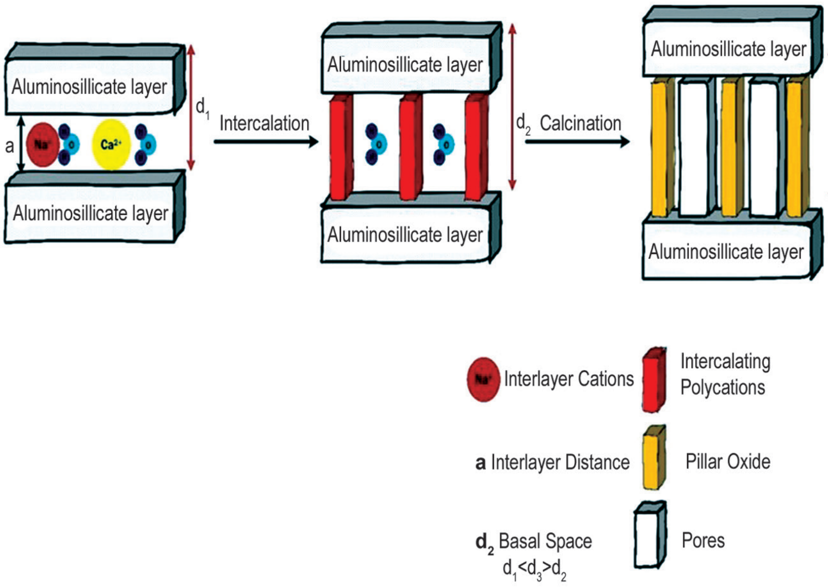

Fig 3 Schematic representation of pillaring by metal cations (Baloyi *et al.* 2018).

In a study, Gil *et al.* (2011) prepared aluminium (Al) and zirconium (Zr) pillared montmorillonite clays through intercalation and assessed their adsorption potential for the removal of two dyes such as MB and Orange II from the aqueous solutions. The maximum adsorption was attained after 5 h of contact time. In case of orange II both pillared clays showed almost similar adsorption capacities whereas, in case of MB higher adsorption capacity was exhibited by Zr pillared clay than Al pillared clay. Here, the restricted diffusion in micro-pores of size 0.8–1.4 nm is the major deciding factor for adsorption. Therfore, variation in adsorption capacities of two pillared clays can be explained on the basis of restricted diffusion.

In another study, Zeng and Liu (2005) utilized cation-exchange phenomenon to prepare mixed hydroxy Fe-Al-pillared montmorillonites having large basal spacing. These pillared clays, when utilized as adsorbents for the removal of direct green B from dye contaminated waterexhibited superior performance in comparison to the normal sodium montmorillonite. The pH of solution tends to exhibit high influence on the dye removal performance of pillared clays.

Titanium pillared montmorillonite was synthesized by Bouras *et al.* (2002) through the cationic exchange of polymeric titanium cations into the interlayers spacings followed by co-adsorption with cationic surfactant. These clays were then evaluated as adsorbents for the removal of anionic dye, sulfacid brilliant pink. Adsorption isotherms revealed that the organic modification of titanium pillared montmorillonite surfactant increased the dye removal capacity up to 1000 mg/g.

Plasma modification for dye removal: In the recent time, cold plasma techniques have fascinated many researchers due to their comparative advantages over the conventional modification techniques.Plasma modification techniques are energy efficient, easy to operate, non-polluting and are therefore emerging as a greener alternative (Şahin *et al.* 2015). Depending upon the type of gas used for the generation of plasma and other common reaction parameters of plasma treatment; it is possible to activate the clay surface differently. The manner in which clay surface can be modified through plasma includes the introduction of surface active groups, etching, surface abrasion, cross-linking or the combined effects in many cases (Ratner 1995; Guruvenket *et al.* 2004; Lixon Buquet *et al.* 2010; Fatyeyeva *et al.* 2011). Čapková *et al.* (2016) achieved montmorillonite surface modification with the help of plasma treatment and studied the structural changes that occured. The XRD and infrared (IR) spectroscopy results revealed that dehydration started at a discharge power 10 W and completed at 50 W. The dehydration was primarily due to the transfer of heat after collisions of montmorillonite grains with the ions from the plasma. The effects of plasma treatment were comparable to the effects of heat treatment of 8 h at 450˚C. Hence, plasma treatment might prove to be a much more energy efficient way for clay modification in comparison to the high energy consuming thermal treatment. In another study, Djowe *et al.* (2013) modified the smectite clay with the help ofgliding arc plasma. The results revealed that plasma treatment caused the breakdown of structural bonds at the surface of clay leading to the formation of hydroxyl groups (Si–OH and Al–OH) on the edges. The main mechanism behind this was the breaking of the Si–O–Si and Al–O–Al bonds at the edges and the formation of silanol (Si–OH) and aluminol (Al–OH) groups respectively.

In a study conducted by Yavuz and Saka (2013), kaolinite surface was modified through treatment with cold plasma in order to improve its adsorption properties for the removal of MB dye. After treatment of kaolinite with cold plasma, the maximum adsorption capacity increased by approximately 2.5 times (i.e. from 19.60 to 51.02 mg/g) in comparison to the untreated kaolinite. In another study, bentonite surface was modified through cold plasma treatment and its effect on adsorption characteristics was studied for the removal of MB from aqueous extracts. After cold plasma treatment, the specific surface area and the pore volume increased. Maximum adsorption capacity was evaluated through Langmuir adsorption isotherm and was found to be significantly higher than raw bentonite (Şahin *et al.* 2015).

Grafting of polymers/organic compounds for dye removal: Naturally occurring clays modified through grafting of polymers/organic compounds present a novel class of adsorbents that display superior adsorption properties in comparison to their unmodified counterparts. The grafting of clays with polymers/organic compounds not only provides an appropriate route for the synthesis of novel adsorbents but also helps in incorporating desirable structural changes and performance enhancement into the clays. The factors on which the grafting relies are composition and geometry of grafting material, its concentration and the nature of physicochemical interactions between them (Liu 2007). The surface grafting of clays with polymer/organic compounds leads to the improvement in interfacial interactions among the clay particles. Physical adsorption and chemical grafting are the key methods to achieve surface modification of clay minerals through polymers/organic compounds (Liu 2007).

Physical adsorption can be achieved via surface absorption or interaction of surface active sites with organic molecules, such as silane coupling agents (Fig 4). It is mainly controlled by thermodynamic factors and it can be enhanced through modification of clay surface. Surface modification of clay minerals through chemical grafting can be achieved by two methods: one step grafting (condensation of functionalized polymers with chemically active sites present on clay surface) and two step grafting (a monolayer of monomer is covalently attached to the clay surface) (Liu 2007). The two step grafting procedure is more advantageous in comparison to the one step grafting because desired properties could be incorporated in the grafted clay adsorbents through careful selection of the grafting monomers and grafting conditions (Kango *et al.* 2013).

Thermal activation for dye removal: The treatment of clays at elevated temperatures is a commonly employed method for enhancement of their surface properties and is known as thermal activation of clays.Thermal activation or heat treatment can increase the adsorption capacity of natural clays to a great extent e.g. palygorskite (Wang *et al.* 2007; Gan *et al.* 2009), bentonite (Toor and Jin 2012.; Toor *et al.* 2015). Different water molecules present in the intra-crystalline spaces can be selectively removed

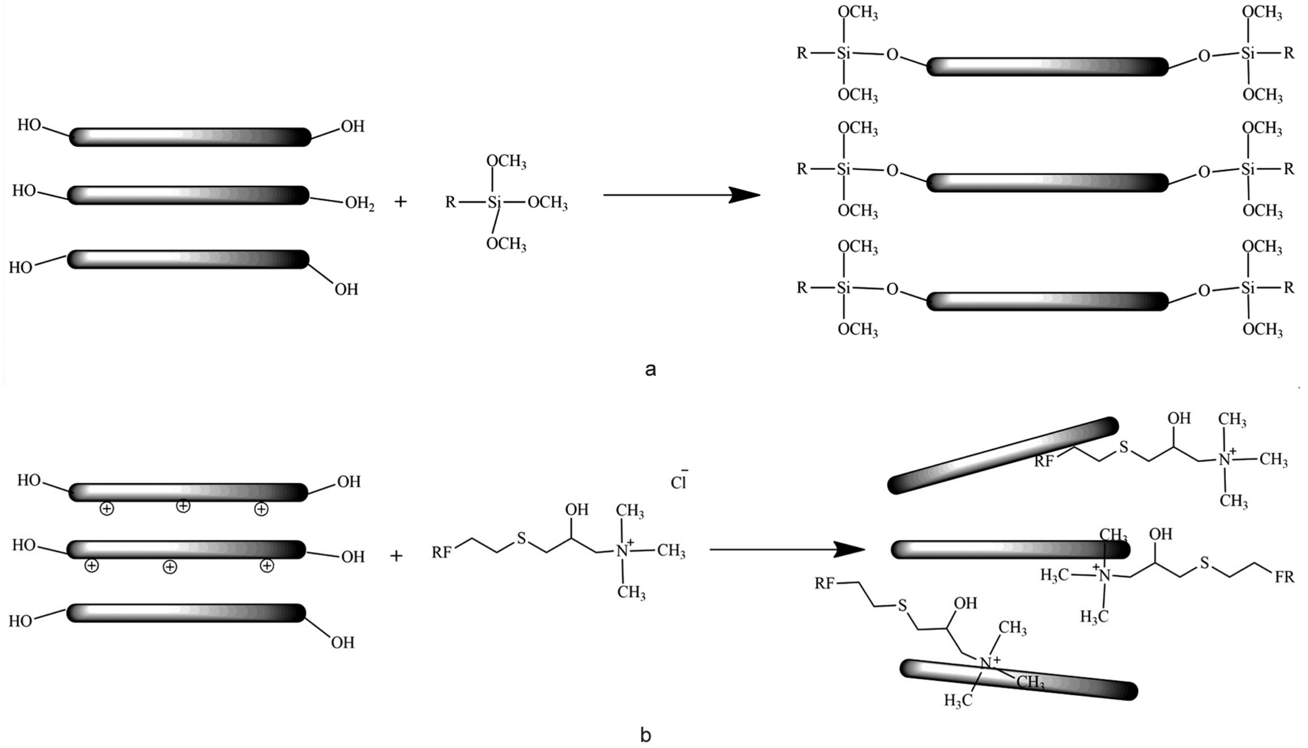

Fig 4 Modification of montmorillonite with (a) alkyl silanes and (b) fluorosurfactant (Khajehpour *et al.* 2015).

through the calcining of clays at variable temperatures, which correspondingly changes their porosity and surface properties (Kuang *et al.* 2004; Chen *et al.* 2011a). Therefore, high temperature treatment of clays has great influence on the surface area per mass unit of clay minerals which is one of the key determining factor for adsorption efficiency of any adsorbent (Wang *et al.* 2007).

Toor and Jin (2012) modified the surface of naturally occurring bentonite by thermal activation and the results revealed that bentonite structure became more porous after heat treatment. The scanning electron microscope (SEM) images of thermally activated bentonite indicated that the interlayer spaces collapsed, leading to the more tightly bound structure. The specific surface area of activated bentonite was increased nearly about 26% in comparison to the non-activated counterpart. The enhancement in surface area was primarily due to the exclusion of adsorbed and hydrated water present at different sites in untreated bentonite.

Chen *et al.* (2011) thermally activated polygorskite and studied their adsorption efficiencies for the removal of MB. During the study, it was observed that adsorption capacity increased to 78.1 mg/g with an increase in temperature up to 700˚C and thereafter decreases with further increase in temperature. A similar trend was also observed for cation exchange capacity which was maximum at 700˚C and decreased thereafter. This indicated that the cation exchange phenomenon is a main mechanism for the adsorption process. In a study, (Toor *et al.* 2015) evaluated thermally activated bentonite as low cost adsorbent for removal of congo red dye from wastewater. The adsorption performance of thermally activated bentonite for the removal of congo red was evaluated with respect to the temperature of activation and time of heating. The adsorption capacity of clay increased with the increase in time. The enhancement in congo red adsorption is primarily due to enhanced surface area per unit mass and the removal of trapped water from interlayer spaces. Contrastingly, the dye removal capacity of activated clay was reduced as temperature increased beyond 200˚C. This reduction in adsorption is possibly due to the reduction in surface area and the availability of active sites for adsorption. Under given physicochemical parameters, the thermally activated bentonite exhibited significantly higher adsorption of congo red than raw bentonite (Toor and Jin 2012) .

Some recent studies on the removal of dyes using modified clay minerals have been shown in Table 1.

Factors affecting adsorption of dye

Several factors such as pH of solution, initial dye concentration, temperature and amount of adsorbent etc. affect the adsorption of dye onto a matrix. Therefore, the effects of such parameters need to be considered. Optimisation of these parameters facilitates the development of large scale dye removal process (Yagub *et al.* 2014). In the subsequent section, various factors affecting the performance of clays for dye removal will be discussed.

Effect of solution pH: The pH of the solution is among the key factors which determine the adsorption performance of an adsorbent during the process of adsorption such as removal of dye from wastewater. The variability inthedegree of ionization of the adsorbate and the surface characteristics

Table 1 Recent studies on the removal of dyes using modified clay minerals

Clay mineral	Dye	Modification	Effect on adsorption capacity	Reference
Kaolinite and alpha quartz	MB	Sodium dodecyl sulfate (SDS) modified raw clay	Modification increased adsorption capacity from 23.13mg/g to 30.92 mg g	(Olusegun *et al.* 2018)
Vermiculite	AR and MB	Treatment with HNO_3 / H_2SO_4 / HCl followed by citric acid	Maximum adsorption capacities for AR and MB were 100.8 mg/g and 150 mg/g respectively	(Stawiński *et al.* 2016)
Vermiculite	AR and MB	Treatment of acid activated vermiculite with NaOH	Maximum adsorption capacities of AR and MB were 127 and 203 mg/g	(Stawiński *et al.* 2017)
Montmorillonite	MB	Iron oxide	Maximum adsorption capacity of 71.12 mg/g at 333 K	(Cottet *et al.* 2014)
Montmorillonite	MB	Dodecyl sulfobetaine surfactant-modified	Adsorption capacities for MB at 298 K and pH 5 was 254.0 mg/g	(Fan *et al.* 2014)
Bentonite	MB	Cold plasma treatment	maximum adsorption capacity of 303 mg/g at 30˚C.	(Şahin *et al.* 2015)
Montmorillonite	CV	H_2SO_4 treatment	Maximum adsorption capacity of acid treated clay was 400 mg/g	(Sarma *et al.* 2016)
Montmorillonite	Acid Red 1 and Acid Green 25	3-aminopropyl-triethoxysilane	Maximum adsorption capacity 364.1 and 397.0 mg/g for Acid Red 1 and Acid Green 25respectively	(Thue *et al.* 2018)
Kaolinite	CR, 4BS and 5R	Modification with TiO_2	Dye-removal efficiency increased from 25 to 95%, 11 to 90%, and 13 to 97% for CR, 4BS, and 5R, respectively	(Hai *et al.* 2015)
Kaolinite and Montmorillonite	CR	Treatment with 0.25 and 0.50 M H_2SO_4	Acid treatment of kaolinite and montmorillonite enhanced the adsorption capacity by 7-9%and 1.8-3.8% respectively	(Bhattacharyya *et al.* 2014)
Palygorskite and Sepiolite	MB and MY	3-aminopropyltriethoxysilane	Adsorption capacities were 49.48 and 47.03 mg/gfor grafted palygorskite and 60.00 and 59.78 mg/g for grafted sepiolite, for MB and MY dyes, respectively	(Moreira *et al.* 2017)
Vermiculite	Remazol Brilliant Blue RN	Ethylenediammine	Adsoption capacity was 11.02 mg/g	(de Queiroga *et al.* 2016)
Vermiculite	Pyronin B	Phosphoric acid	The adsorption capacities were 25.6 mg/gfor vermiculite and 30.0mg/g for modified vermiculite	(Toprak and Halisdemir 2015)
Montmorillonite	MO	Gemeni surfactants	The adsorption capacities ranged from 161.03 to 271.74 mg/g	(Luo *et al.* 2015), (Ren *et al.* 2018)
Montmorillonite	ARS and BG	HDTMA	Maximum adsorption capacities were 666.6 and 1250 mg/gfor Alizarin Red S and BG respectively.	(Biglari *et al.* 2018)
Montmorillonite	MB	HDTMA	Increase in adsorption capacity upon modification	(Jourvand *et al.*2015)
Sericite	Sulfur blue 11	HCl containing 2% (v/v) methanol	The adsorption capacity decreased from 145 to 64 mg/g withincreasein temperature from 283 K to 313 K	(Choi 2017)
Smectite	Bright green	HDTMA	The adsorption capacity of Bright green on HDTMA modified clay was found to be 45.5 mg/g	(Latifi *et al.* 2017)

Contd.

Table 1 (*Concluded*)

Clay mineral	Dye	Modification	Effect on adsorption capacity	Reference
Kaolin	MB	KT1-Thermal treatment KT2- thermal treatment followed by acid activation KT3- thermal followed by acid and alkaline treatments	The maximal adsorption capacity (111 mg/g) was observed for modified kaolin (KT-3).	(Boukhemkhem and Rida 2017)
Bentonite	Acid Blue 129	Magnesium	-	(Hussain *et al.* 2016)
Montmorillonite	BG	HDTMA	Maximum sorption capacity (460.15 mg g^{-1}) was achieved at a pH of 3.	(Omidi-khaniabadi *et al.* 2016)

of the adsorbent matrix may give rise to variation in pH of the solution (Nandi *et al.* 2009). In general, as a result of electrostatic attraction between the positively charged surfaces of adsorbent, the percent removal of anionic dye from solution increases at lower (acidic) pH ranges. The presence of electrostatic attractions among the positively charged molecules of dye and negatively charged adsorbent lead to the reduction in percent dye removal from the solution at higher (basic) pH ranges (Nadeem *et al.* 2016; Naeem *et al.* 2017; Rashid *et al.* 2016). On the other hand, when a solution has higher pH, the adsorption capacity as well as the removal of cationic dyes increases due to the interaction of the positively charged dyes with the anionic adsorbents (Ullah *et al.* 2013; Tahir *et al.* 2017) . Based on the results obtained from recently conducted studies the effect of solution pH on the adsorption performance of modified clays is compiled in Table 2.

Effect of temperature: Another physicochemical parameter which has a significant effect on dye removal efficiency of clays is temperature (Argun *et al.* 2008). Temperature has a considerable impact on dye removal efficiency because it can cause significant variation in the adsorption capacities of the adsorbent. In case of endothermic processes, the adsorption capacity tends to

Table 2 Effect of solution pH on the adsorption of dyes using modified clays

Adsorbent	Dye	pH range	Effect on adsorption	Reference
Surfactant modified bentonite	MB, RB and CV	2-11	Increase	(Anirudhan and Ramachandran 2015)
Silane modified palygorskite and sepiolite	MB	2-10	Decrease	(Moreira *et al.* 2017)
Silane modified palygorskite and sepiolite	MY	2-10	Increase	(Moreira *et al.*2017)
Silane modified montmorillonite	Acid Red 1 and Acid Green 25	2-10	Decrease	(Thue *et al.* 2018)
methylene esterified sericite	Sulfur blue 11	1-12	Increase for pH 1.0 to 6.0 and almost constant for pH 7.0 to 12.0	(Choi 2017)
Surfactant modified montmorillonite	MB	4-8	Nearly constant	(Fan *et al.* 2014)
Surfactant modified montmorillonite	Alizarin Red S and BG	3-11	Decrease	(Biglari *et al.* 2018)
Cold plasma modified bentonite	Methylene blue	2-12	Increase from 158 to 231mg/g	(Şahin *et al.* 2015)
Surfactant modified montmorillonite	BG	3-11	Decrease	(Omidi-khaniabadi *et al.* 2016)
acid-treated montmorillonite	CV	4-7	Increase from 25 mg/g to 165.0 mg/g	(Sarma *et al.* 2016)
Surfactant modified montmorillonite	MO	3-9	Decrease	(Ren *et al.* 2018)

increase withacorresponding increase in temperature.This is possibly due to the increase in kinetic energy of dye molecules leading to their higher mobility and increase in surface active sites for adsorption process to occur upon increase in temperature. A decrease in adsorption capacity with increase in temperature is observed for exothermic processes. This decrease in adsorption is possibly due to the diminishing adsorptive forces between the molecules of dyesand surface active sites present on the adsorbent (Salleh *et al.* 2011). Based on the results obtained from recently conducted studies the effect of temperature on the adsorption performance of modified clays is compiled in Table 4.

Effect of adsorbent dosage: The dose of adsorbent is a decisive parameter which governs the adsorption properties of an adsorbent at a particular quantity of the adsorbent under similar operating conditions. Usually, the percent dye removal increases with increase in adsorbent dose because the total number of surface active sites present on adsorbent tends to increase upon increasing the adsorbent dose. Therefore, the study of the effect of adsorbent dose on the adsorption process can provide a rough estimate about the quantity of a dye to be adsorbed with a minimum amount of adsorbent in order to assess the potential of adsorbent from an economic point of view (Salleh *et al.* 2011). The effect of adsorbent dosage on the dye removal performance of modified clay adsorbents as reported in various scientific literature has been presented in Table 5.

Application of textile wastewater in agriculture

The textile wastewater contains loads of pollutants and has high TDS, COD and BOD values. But after the treatment of these effluents, recycled water can be used as an alternative for irrigating the crops. Though there are many studies that have used textile effluents for irrigating the crops but the treated wastewater has found limited applications for its use for irrigation. Bhuiyan *et al.* (2016) used gamma radiation treated dye contaminated water for the irrigation of spinach and the plants exhibited overall better physiological growth than the underground water treated plants.

Challenges and future prospects

The comprehensive reviewing of literature till date has revealed that more comprehensive studies are required to

Table 3 Effect of initial dye concentration on the adsorption of dyes using modified clays

Adsorbent	Dye	Initial dye concentration	Percent dye removal	Reaction conditions	Reference
Mg-bentonite	AB129	1.0-6.0×10^{-7} mol/L	15.15 to 67.92 ×10^{-5}mol/g	pH 3.0	(Hussain *et al.* 2016)
Methylene esterified sericite	Sulfur blue 11	1-40 mg/L	Increased from 68 mg/gto 162 mg/g	pH 7.0	(Choi 2017)
Surfactant modified montmorillonite	ARS	20-100 mg/L	Increased from 18.18 mg/gto 81.89 mg/g	pH 3.0	(Biglari *et al.* 2018)
Surfactant modified montmorillonite	BG	50-500 mg/L	Increased from 36.23 mg/gto 468 mg/g	pH 3.0	(Biglari *et al.* 2018)
Phosphoric acid modified vermiculite	Pyronin B	15-35 mg/L	Increased from 14-30 mg/g	-	(Toprak and Halisdemir 2015)
Surfactant modified montmorillonite	BG	50-500 mg/L	36.23 to 468 mg/g	pH 3.0	(Omidi-khaniabadi *et al.* 2016)
Acid modified Kaolinite	RB	50-350 mg/L	Decrease in extent of adsorption from 34.1 to 14.4%	-	(Bhattacharyya *et al.* 2014)
Acid modified montmorillonite	RB	80–400 mg/L	Decrease in extent of adsorption from 43.1 to 11.3%	-	(Bhattacharyya *et al.* 2014)

Table 4 Effect of temperature on dye removal capacity of modified clays

Adsorbent	Dye	Temperature range (˚C)	Effect on adsorption	Type of process	Reference
Mg-bentonite	AB129	10-40	Decrease	Exothermic	(Hussain *et al.* 2016)
Silane modified montmorillonite	Acid Red 1 and Acid Green 25	25-50	Decrease	Exothermic	(Thue *et al.* 2018)
Iron oxide modified montmorillonite	MB	35-60	Increase	Endothermic	(Cottet *et al.* 2014)
Methylene esterified sericite	Sulfur blue 11	10-40	Decrease	Exothermic	(Choi 2017)

Table 5 Effect of adsorbent dosage on the percentage of dye removal

Adsorbent	Dye	Adsorbent dosage (g/L)	Percent dye removal	Reference
Acid base modified kaolin	MB	1.0 to 1.8	increases from 66% to 100%	(Boukhemkhem and Rida 2017)
Acid-treated montmorillonite	CV	0.2-0.8	Increase from 37.2 to 96.2%	(Sarma *et al.* 2016)
Surfactant modified montmorillonite	MB	1 up to 20	Decreased from 49.73 mg/g to 2.48 mg/g	(Jourvand *et al.* 2015)
Acid modified Kaolinite	RB	1.0 to 6.0	Amount adsorbed per unit mass decreased to 19.21 to 8.03 mg/g	(Bhattacharyya *et al.* 2014)
Acid modified montmorillonite	RB	0.2 to 0.6	Adsorption decreased from 98.99 to 74.34 mg/g	(Bhattacharyya *et al.* 2014)

improve the overall preparation and utilization of modified clay minerals as efficient adsorbents in dye removal from wastewater. Several aspects need to be addressed in upcoming studies related to modified clay materials as cost-effective and efficient adsorbents for dyes. The most important ones amongst these are improvements in adsorption efficiencies through the utilization of mechanistic modeling for anappropriate understanding of the adsorption mechanisms. The interactions among the adsorbates and adsorbents should be studied with further details in order to establish the relationships and roles of active sites/functional groups present in clays and dye molecules. Extensive research and analysis are required to assess the feasibility of these modified clay adsorbents and to bring the laboratory level efforts towards practically utilizable levels for dye removal at a large scale. The complications in the separation of adsorbate–adsorbent mixture after the adsorption process limit their practical utility as adsorbents. In addition, extensive work needs to be done to assess the behavior of different crops while using the treated wastewater for irrigation. As the demand of water is going to continually increase there is need to recycle and reuse the wastewater to ensure food security. As a greater number of clay minerals are available locally so researchers need to exploit these materials for colored effluent treatment and promoting the mantra ‘‘think globally, act locally’’.

Conclusion

After extensive review, it can be concluded that activation or modification of clays significantly enhance their surface properties. On the basis of various studies, it is well understood that modified clays are much more potent as adsorbents in comparison to their unmodified counterparts. It has also been observed that kinetics of adsorption of dyes depends on various physic-chemical properties such as solution pH, adsorbent dose, initial dye concentration and contact time.The development of superior modified/activated clay adsorbents is indispensable for their utilization in industrial applications. Although enough research has been carried out plentiful research is still required to attainanimproved understanding of the mechanism of dye adsorption through modified forms of clay minerals.

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