Adsorption of Dyes Using Natural Minerals: A Review

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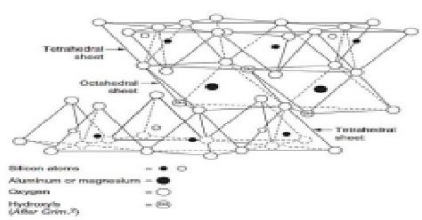
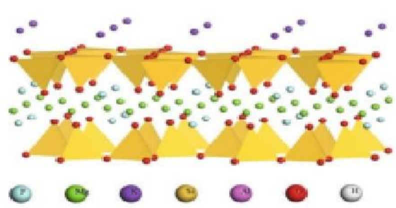
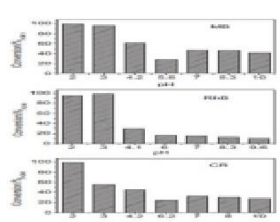
GRAPHICAL ABSTRACT



Montmorillonite Structure


Schematic mica platelet structure



Influence of pH on the catalyzed declorization of (MB, RhB and CR)

Abstract

Adsorption is an effective and widely technique used for separating many pollutants from wastewater. Pollution of water with color materials such as dyes is of environmental concern due to their toxicity and cause carcinogenic effects on human and aquatic life. These dyes are presented into the water bodies from the effluence of several industries such as textile, paints, cosmetics, paper, food, and others causing water pollution. Adsorption technique using low cost adsorbents has gained a lot of attraction of many researchers for years. The purpose of the present study is to investigate using natural minerals as inexpensive adsorbents for removal of dyes from wastewater. This investigation can be made by reviewing the major topic researches that applying natural mineral materials as cheap adsorbents for treating of colored wastewater. Natural materials such as vermiculite, sepiolite, montmorillonite, kaolinite, perlite, diatomite, zeolite, and others, are categorized as permeable minerals, multilayer minerals and other based on structural properties. These adsorbents can be used as is or changed to enhance adsorption properties.

Keywords: Dyes; waste water treatment; adsorbents; adsorption; natural mineral

1. Introduction

Water resource, as the most precious resource for human survival, is facing unprecedented challenges so, one of the most significant worldwide challenges is water contamination. Consumption waters have become increasingly important in treating, reusing, and recycling as a result of population increase, the enhancement of various species, healthy water lack and agriculture. Industrial waste generates a large amount of wastewater. As a result of the rapid development of numerous industries, waste was dumped into water and soil systems. Many pollutants are typically found in wastewater, including anionic and cationic ions, oil, and organics, all of which are damaging and poisonous to ecosystems (Shaobin Wanga and Yuelian Peng,2010).

To eliminate these contaminants, cost-effective solutions are required, and a variety of wastewater treatment procedures have been developed over time. Advanced oxidation, Adsorption, ion exchange, coagulation ,flocculation, ,ozonation, precipitation, liquid-liquid extraction and membrane filtering are all examples of wastewater processing (Rafatullah *et al*.,2010),(Sivakumar and Rao,2003) Because of its ease of operation, low capital cost, and lack of sensitivity to contaminants, adsorption has been employed as an attractive way of wastewater degradation., Adsorption is generally viewed to be an useful and practical method of water and wastewater processing, also the creation of an efficient adsorbent is critical to the technique's effectiveness (Sokolowska *et al*.,1996),(Naser G.F. *et al*. 2021).

The development of an efficient adsorbent is key to the technique's success. Conventional adsorbents, such as ion exchange resins and activated carbon, are prohibitively expensive for commercial use. The adsorption technique using cheap natural minerals from the cost side is appealing due to its active elimination levels for pollutants at noticed quantities. Natural minerals are widely used in numerous fields of pollution remediation because of their unique structure, characteristics, and perfect environmental harmony. Several natural metals have a large sorption capability for diverse pollutant species due to the existence of tiny holes and canals in the structure, as well as a high specific surface and elongated character. Furthermore, treating wastewater with natural minerals has the benefits of a large source, low cost, low energy consumption, and improved removal efficiency. At the moment, this has piqued the curiosity of both domestic and international environmental protection experts. Natural mineral categorization has been devised based on the structural properties of natural materials as: Firstly: filmed minerals, with a packed sheet body, constitute a viable material for wastewater treatment. Due to their unique structural qualities, as well as their diversity in texture, morphology and architecture ,due to their individual constitutional qualities, as well as their diversity in composition, morphology, and architecture (topological change, intercalation, and personality with other useful materials), Secondly: Porous minerals: Natural porous metals are developing as a composite with the potential to reduce pollution. Accessible pores, a large surface area, chemical and mechanical stability are all features of natural porous minerals. These characteristics usually result in high permeability and significant selectivity against many pollutants, such as (Diatomite, Zeolite, Sepiolite, Attapulgite and Halloysite). In addition: As adsorbents, different minerals usually have a higher surface activity. Capability and sort of interactions that occur between mineral surfaces and contamination are determined from the surface side and chemical properties of minerals such as (Calcite, Tourmaline, Magnetite, Rutile/Anatase). However, the problem persists; every year, a considerable size of wastewater is created and thrown inside the surface waters. Dyeing wastewater demands special Large volumes of dyes have been released into the environment throughout the last century as the printing and dyeing industrialization process has progressed. Dyes are common chemical compounds that are commonly used to color a variety of items, including textiles, leather, paper, rubber, printing, and plastics. A typical textile mill consumes roughly 1.6 million liters of water per day (Petcu *et al.*,2016)and about 200 liter of water is required to manufacture one kilogram of textile. The considerable volume of dye contaminants in wastewater poses a significant environmental danger. Because dyes can impede sunlight transmission, they can have a negative influence on both aquatic organisms and humans(Crini, and Badot, 2008).Heavy metals (such as lead, chromium, and others) in addition to aromatics are common contaminants (Ramanath,2005) .Dyes components in wastewater cause mutagenicity, carcinogenicity, liver, kidney and centric nervous system malfunction in humans. Throughout the years, a variety of approaches have been used to remove colors from dyeing effluent. (Gupta and Suhas , 2009) Dyes, on the other side, are usually less degradable because of their complicated chemical texture. They are nearly uniform in a variety of limitations, like light, oxidizing operators and aerobic digestion (Crini, 2006) . As a result, because the adsorption technique is both cost-effective and efficient, it has been widely employed to manage dyeing wastewater (Qadeer,2007) Because of its outstanding adsorption capability, activated carbon considered as most extensively used traditional adsorbents in practice. However, the expensive cost and difficult regeneration techniques have limited its application (Deniz, 2016). Furthermore, traditional activated carbon is inefficient and selective against dispersed vat dyes (Crini and Peindy,2006).To reduce costs and improve adsorption effectiveness, many novel replacements to standard activated carbon have been discovered. Multiple adsorbents, such as (clays / zeolites) and their compounds, bio sorbents, agricultural solid wastes and various materials have been organized and adjusted for dye degradation from unreal wastewater by a large number of researchers over the last few decades (Demirbas ,2009) .

2. Mineral Adsorbents

2-1. Montmorillonit

The chemical formula was $(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2.nH_2O$ and The crystalline structure of a 2:1 aluminosilicate is defined by one octahedral aluminum-centered layer sandwiched by two tetrahedral silicon-centered sheets. Fig. 1 was utilized in a variety of sectors and has piqued interest because of its rheological, colloidal, swelling, and electric characteristics. Various pollutants, including heavy metal cations and cationic dyes have been removed using original montmorillonite adsorbents (Den *et al.*,1992),(Missana *et al*.,2008),(Almeida *et al*.,2009),(Gürses,2006),(Abollino *et al*.,2003),(Chen *et al*.,2015). Modifications to montmorillonite can improve its propensity to attract and hold pollutants. Attractive processes such as thermal treatment ,acidification and (organic/inorganic) intercalation are the most common procedures for modifying montmorillonite (Bhattacharyya et al ,2006),(Teng and Lin,2006),(Aytas *et al*.,2009),(Al-asheh *et al*.,2003),(Tian *et al* .,2009),(Lee, S.Y *et al*.,2004),(Zhu, R et al.,2009). Acid-treated montmorillonite, which has been washed with hydraulic or sulfuric acid sharing on removing impurities and replacing commutable cations with H^+, raising montmorillonite's active surface area and improving its adsorption capacity against a number of contaminants. Acid-treated montmorillonite has a better capacity for adsorption of “methylene blue” dye from wastewater than unprocessed montmorillonite (Banat, 2007)Thermal processing of montmorillonite can change its physico - chemical properties by dehydrating and de-hydroxylating it, as well as resulting octahedral cation migration inside the octahedral sheet. Thermal processing can also alter the compositional qualities of montmorillonite and affect its water degradable. These modifications may improve the sample's adsorption ability for cationic pollutants and hydrophobic organic molecules (Aytas *et al.*,2009),(Al-asheh *et al.*,2003),(Tian *et al* .,2009),(Lee, S.Y *et al.*,2004).

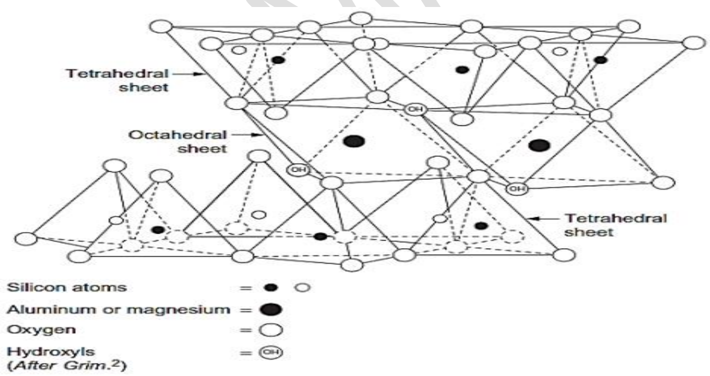


Figure 1: Montmorillonite Structure (A.R. Rahmani *et al.*, 2018)

For decades, montmorillonites have been widely employed in a variety of industrial applications. They're used in therapeutic and medicinal items as raw ingredients. The antibacterial activity of montmorillonite nanocomposites has been used to treat cutaneous conditions (S.M.R. Shaikh *et al*.2017). The clay mineral can potentially be used to improve innovative medicine delivery methods. Montmorillonites are utilized in the gas and oil sector to make water-based -drilling muds for deep good drilling. They're also used in iron and steel foundries as a foundry-sand bond. Montmorillonite entourage for holding radio-active wastes take use of their swelling and drying capabilities. Montmorillonites can be acid-activated to improve their catalytic efficacy by changing their insertion and ion-exchange characteristics, making them acceptable for use as bleaching, solutions in food manufacturing .Because of their excellent adsorption capacity, modified montmorillonite clays are widely utilized as heavy metal scavengers in soil and water remediation (L. Zhang *et al.*,2018).

2-2. Kaolinite

Due to its exceptional qualities, kaolinite considered the most significant clay minerals, has a comprehensive interval of industrial applications. A tetrahedral layer and an octahedral layer with a 1:1 layer arrangement are the fundamental units of kaolinite. The main construction is an asymmetry film with a chemical formula ($Al2Si2O5$ $(OH)4$) Fig(2). Cationic dyes, proteins and heavy metal cations and other contaminants have all been widely explored as adsorbents for kaolinite utilized in contamination elimination (Aytas *et al.*,2009),(Al-asheh *et al.*,2003),(Tian *et al* .,2009),(Lee, S.Y *et al.*,2004),(Zhu, R *et al.*,2009).

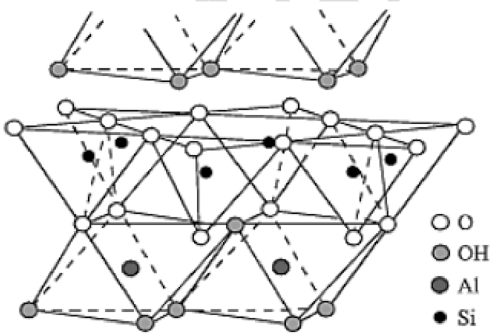


Figure 2. Structure of Kaolinite (P. Leinster *et al.*, 1978)

The clay mineral is mostly used in the production of ceramics and papers. Kaolinite's small white particles have a high water adsorption capacity and a great ability to absorb glaze which is colored, fabricating it ideal for use in ceramics. It's also used as a filling and covered in high-quality paper to give it a smooth white surface and enhance its strength (S. Mukherjee,2013) Micro-fractures are reduced when 20 percent kaolinite is added to Portland cement. Apart from industrial applications, kaolinite, like other clay minerals, may be utilized for ecological cleanup and wastewater processing. Because of the presence of the silicate layer, kaolinite clays help in the decomposition of hydrocarbons when processed oil-seawater emulsions. Furthermore, in acidic settings, the broken borders of the crystalline body may give protons, resulting in the adsorption of heavy metal ions like: (cadmium (II), zinc (II), and lead) from wastewaters (S.M.R. Shaikh *et al.*2017).

2.3. Vermiculite

Vermiculite $(Mg, Fe^{2+}, Fe^{3+})_3(Al, Si)_4O_{10}(OH)_2\ 4(H_2O)$ is a filmed silicate metal having a negative charge ,hydrophilic , filmed crystalline composition as Fig (3). Because cations with reduced valency substitute for their primary cations, like (Al^{+3}) replaced with (Si^{4+}) and (Mg^{2+}) replaced by (Al^{3+}), vermiculite has a high cation exchangeability. In contrast to montmorillonite, mainly cation replacements happen in tetrahedral sheets in vermiculite, limiting the mineral's ability to expand its intermediate region. Because of their high specific surface area and tiny particle sizes, in addition have a large capacity for cation exchange, vermiculite is inexpensive, high-active adsorbent for different pollutants. Vermiculite has also been intensively researched for its ability to eliminate colors from effluents. Crystal violet and methylene-blue and adsorptive interactions on to natural vermiculite in solution were compared (Yu, X *et al*.2015) .Methylene blue's adsorption isotherm appears to be declining and does not fit with the model of Langmuir. The adsorption of crystal violet, moreover, showed a classic Langmuir-isotherm with the same initial concentration. Because of their hydrophilicity, unprocessed clay metals are not appropriate for removing hydrophobic contaminants. To remove persistent organic pollutants such as bisphenol A and tetrabromobisphenol (Liu, S *et al*.,2017) created three new organic vermiculites using various amphoteric surfactants.

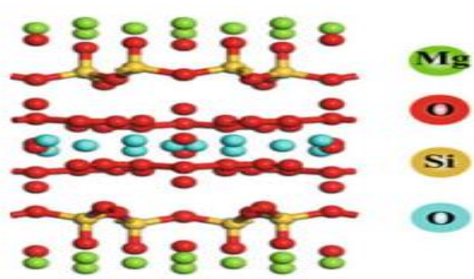


Figure 3: Schematic vermiculite platelet structure (Shaoxian Song and Bowen Li, 2021)

2.4. Mica

Micas can be found in many different types of rocks, including: metamorphic igneous and sedimentary. Their crystal structure allows for the incorporation of a wide range of elements, resulting in a big and diversified mineral group. There are two types of mica: dio-ctahedral and trio-ctahedral micas. Micas are moisture filmed of silicate metals, class of these minerals having a chemical makeup that varies greatly. Their general crystallochemical formula is: $[(Si, Al)_4 O_{10}] (OH, F)_{2–3} (K, Na) (Al, Fe, Mg)_{2–3} [(Si, Al)_4 O_{10} (OH, F)_2$. The crystalline composition is made up of negative charge (2/1) films . Fig (4) is made up of two layers of tetrahedral from silicon oxide sandwiched between one layer of octahedral made up of Al, Mg, or FeO. Its structure allows for a large surface area to be combined with a high ion-exchange capacity, giving such minerals a wide range of possible applications in adsorption disciplines. Its structure allows for a large surface area to be combined with a high ion-exchange capacity, giving such minerals a wide range of possible applications in adsorption disciplines. Furthermore, cleavage produces two reactive planes: basal and edges, each with its own chemical specifications that must be carefully considered because it necessitates separate characterization procedures. In the suspension system containing charged colloidal particles, pH is an inherent characteristic associated with proton activity (ALVAREZ-SILVAand MIRNEZAMI,2010).

Chemical changes to the mineral surface, such as pretreatment/activation or even total synthesis of layered double hydroxides (LDHs), are also investigated in certain ways to boost adsorption efficiency (Ames, 1983) A substantial quantity of waste mica minerals (biotite and muscovite, primarily) has been reported from raw explored mica mines in India's Jharkhand area, which is home to the world's largest mica deposit. Mica is utilized as a potassium source for plants in agriculture, but due to its low potassium content, roughly 75% of the mineral extraction is not used for this purpose and is dumped in the soil. These residues remain on the ground for lengthy periods of time without being treated, causing significant environmental damage to the area's surrounding communities. In that area's community such material could be addressed for study and later usage in adsorption from a more sustainable point of view.

As a result, evaluating the potential use of mica mineral residues in contaminant removal is a challenge, as part of the incentive to promote a circular economy, whose central premise is the valuation of eventually waste materials (mica minerals) that are classified as residues under the linear economy approach. Furthermore, it has been highlighted that only a few research have been conducted to evaluate mineral behavior in the presence of pollutants of varying ionic nature, as well as changes in pH solution during adsorption tests The goal of this research was to develop a comprehensive technique for characterizing the physical, chemical, morphological, and electrostatic surface features of mica minerals (Anna, 2020).

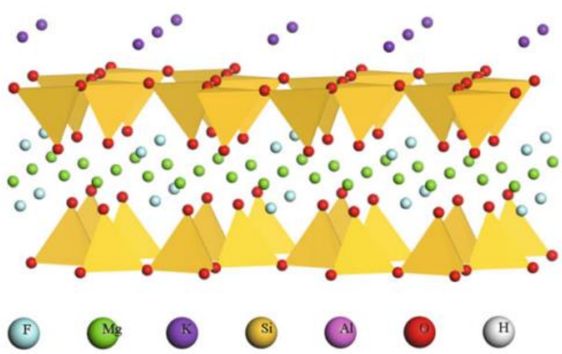


Figure 4: Schematic mica platelet structure (Shaoxian Song and Bowen Li, 2021)

2.5. Diatomite

Diatom is a single-celled alga that is found all over the world and is only ten to dozens of microns in size. Under a high-powered microscope, diatomite deformities such as linear, circular ,disciform and penniform can be seen. The most common mineral compound was (SiO2 H2O), which has a SiO2 concentration of more than 60%. Diatomite is white or gray, but as the impurity (Al2O3, Fe 2O3, CaO, MgO) increases, it turns taupe or sepia (Flower, R.J ,2013). Diatomite is commonly utilized as an adsorbent material for two reasons: a large surface area has a porous structure and a large number of functional groups (Nenadovic *et al*.,2009),(Yurekli,2016) The diatom shell is made up of two layers: an inside layer and an external layer. Puncta, stria, and costa are types of pitted perforation seen on diatomite, according to studies (Selim and Ibrahim,2010) The findings reveal that each of the three sorts is made up of micropores of varying sizes. A wide particle sizes range and permeability allow it to adsorb liquids (1.5–4) times its own content. Diatomite is also chemically stable, being inaccessible in all strong acids and bases except hydrofluoric acid (Round,1961) Metal cations can adsorb on the surface because of the porous structure and negative charge. Diatomite has been widely utilized to treat dye wastewater due to its porous composition ,large area and abundance of surface functional groups(Kim et al.,2016), (Hethnawi et al.,2017), (Darvishi Cheshmeh Soltani *et al*.,2016),(Dang, T.D *et al* 2016). Methylene blue adsorption capacity of cleaned diatomite is around 27.86 mg/g. whereas diatomite mixed with other materials can significantly enhance the capacity of adsorption (Zhang, J *et al*,2013),(Yuan *et al* .,2016),(Zhang, Y *et al*.,2015). Diatomite made with activated carbon, for example, has a methylene blue adsorption capability of (505.1 mg/g) (Liu, D *et al*., 2013).

Table 1. Characteristics of diatomite adsorption for dye degradation and their application in a real-time system

Adsorbate	**dye**	**PH**	**Time (min)**	**Qe (mg /g)**	**Reference**
Raw DE	JGB	6	90	40	(Z. Medjdoubi *et al*.,2019)
Chito sun DE	SY	2.4	30		(Y.Z. Zhang *et al*.,2015)
Demicrosphere	MB		30	15	(S. Yan, W *et al* .,2018)
NaoH-DE	MB			27.8	(J. Zhang, Q *et al* .,2013)
Cu20DE	MB	6	120	30.2	(X. Tao *et al* 2018)
DE-Carbone	CV	2	60	192.3	(Z. Yanzhuo *et al*.,2013)
Diatomite	MB	7	10		(R.A.Shawabkeh *et al* .,2003)
Chito sun DE	MO	5	30	35.1	(P. Zhao *et al.*,2017)
Diatomite	MB	11	2880	376	(M.A. Al-Ghouti *et al*,2009)
Nio-DE	BR46	8	5	98.1	(R.K. Sheshdeh *et al.*,2014)

2.6. Zeolite

A Swedish mineralogist found zeolite in vesicular basalt in 1756, and it acquired its name from the quick hydrolysis of water due to heating. Sodium, calcium, aluminum, potassium, magnesium ions and others acts the main composition of zeolite as shown in Fig. (5). The Si4+ in a tetrahedron can be replaced with Al^{3+}, causing the electric neutrality to be broken and a negative charge to arise. Potassium , Sodium , Calcium , Magnesium, and other ions are frequently adsorbed on the zeolite surface to neutralize this negative charge, giving it the ion-exchange property (van Bekkum *et al* .,1991) Some studies on the adsorption capabilities of different colors on natural zeolites have been discussed last years. The kinetic analysis was performed using a uniform diffusion model with mass - transfer barrier. Two dyes had adsorption capabilities with 55.9 mg/g and 14.9 mg/g respectively on natural zeolite. (Armagan *et al.*, 2003),((Armagan *et al.*, 2004) . investigated the adsorption of three dyes (reactive red (239),reactive black (5)and reactive yellow (176)) on a Turkey clinoptillolite and compared it to a clay sample, sepiolite. Both zeolite and natural sepiolite have restricted adsorption capabilities for active dyes, according to the adsorption data. When the obtained values were matched to the Langmuir- isotherm, the improved zeolite yielded adsorption capability of 111 mg/g for reactive red, 89 (mg/g) for yellow and 61 (mg/g) for black. (Y.E. Benkli *et al.*, 2003) investigated the utilize of HTAB-modified clinoptilolite in a fixed bed for the elimination of reactive azo-dyes such as red (239),reactive black (5) and yellow (176). The results showed that modified zeolite removed dye in the following shape: (black > yellow > red). (D. Karadag *et al* .,2007) investigated the impact of multiple surfactants of cetyltrimethylammonium bromide (CTAB) and hexadecyltrimethylammonium bromide (HTAB) on dye adsorption of raw zeolite and surfactant modified zeolite for the adsorption of main red (BR46) and reactive yellow (RY176). With increasing pH, BR46 adsorption onto natural zeolite raised to a moderate level, whereas pH had no effect on RY176 adsorption. Increased ionic strength resulted in a reduction in BR46 adsorption and a rising in RY176 adsorption. BR46 adsorption on normal zeolite is better than (RY176) adsorption on (CTAB) and (HTAB) improved zeolites(D. Karadag *et al* .,2007) .CTAB developed-natural zeolite was also tested for additional adsorption of reactive dye. Because of the dye molecules' hydrophilicity, Reactive Red 239 has a two-fold higher adsorption capacity than Reactive Blue 5. For the two anionic dyes, the pseudo2nd. order model offered a very excellent fit. With increasing starting dye concentration, the projected maximum adsorption capacity rose.but the relationship is non linear with pH and temperature. (S.K. Alpat.,2008) also employed Turkish clinoptilolite for toluidine blue O adsorption (TBO). According to kinetic investigations, TBO adsorption on clinoptilolite was matched model to the 2nd order of adsorption with a 2 various spread process. At a pH of 11.0, the greatest adsorption capability of clinoptilolite for TBO was 2.1104 (mol/g). Basic dye adsorption was investigated in an Australian natural clinoptiloite (S.B. Wang. *et al* .,2008). At 50°C, the natural zeolite had a maximum adsorption capability of 2.8105 mol/g for RhodamineB and 7.9105 mol/g for methylene blue, respectively. Adsorption with pseudo 2nd.order kinetics could be described as a two-stage diffusion process, according to kinetic studies. It was also shown that zeolites regenerated by high intervals of temperature calcination and Fenton oxidation had the same adsorption capability with the fresh sample, however it was lower. The two regeneration approaches were only able to restore 60% of capacity. (Yu, Y *et al* .,2014) looked into Malachite green and Pb^{2+} ions from an aqueous medium competing for adsorption on natural zeolite from Australia .(S. Wang *et al.*,2007) The adsorption isotherm of malachite green follows the Langmuir model for a single system, and the adsorption capacity is 5105 mol/g. The adsorption of Pb^{2+} and malachite green is minimized to (80-90%) of the single component, respectively. The overall adsorption, on the other hand, is higher. (Kim, S.A *et al* .,2013) investigated the adsorption of methylene blue on a Chinese-natural zeolite in column experiments at various initial concentrations and flow rates. Natural zeolite was found to be attractive for eliminating methylene blue from the solution.

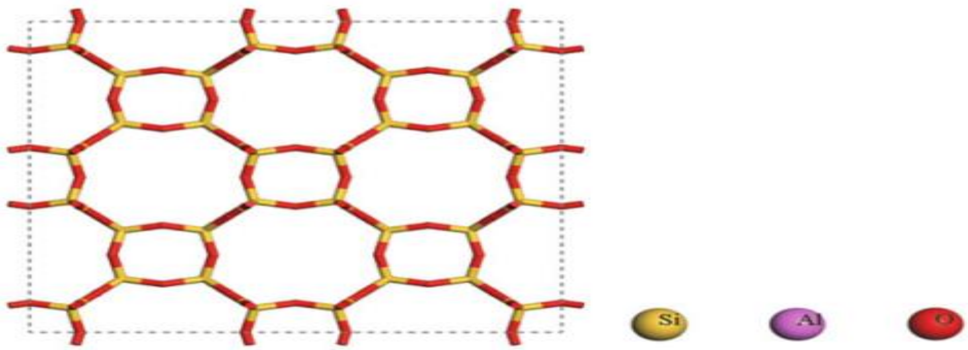


Figure 5 : Schematic structure of zeolite (Shaoxian Song and Bowen Li, 2021).

Table 2: Data of previous studies for zeolite

Ref.	Adsorbent	Adsorbate	Concetraion	Time	PH	Dose	Removal %
(BOlent Armagan *et al* .,2004)	Zeolite (clinoptilolite)natural and modified zeolites	Everzol Black,Everzol Red, Everzol Yellow)	25 mg/L	4 h	7--8		35%, 35% and 25%, respectively.
(Shaobin and Yuelian Peng,2010)	An Australian natural zeolite	(basic dyes, methylene blue and rhodamine B)		24hr	8.5	0.1 g	(higher MB adsorption than RB
(Erol Alver, Aysegül Ü. Metin ,2012)	The natural zeolite was modified	(anionic dyes, namely Reactive Red 239 (RR-239) and Reactive Blue 250 (RB-250))	50 mg/L.		2–10.	0.05–1.0 g	modified > natural zeolite, 93
(Orhan Ozdemira *et al.*,2004) 93	Sepiolite and zeolite, highly porous minerals	(Reactive Black 5, Red 239 and Yellow 176)	25 g/m3	4h	7.5--9		BF and 86.6% for MB.

2.7. Tourmaline

A major area in the space of non-metallic mineralogy is tourmaline's ambient chemical behavior. Tourmaline is a cyclosilicate mineral, which means it is made up of silicate minerals. Its hardness ranges between (7–7.5)and its density ranges lie in intervals of (3.02–3.25) grams per cubic centimeter. The structure of tourmaline, A combination of boron triangles and a six-tetrahedral silicate ring distinguish this material, is linked to its environmental chemical behavior. According to their chemical makeup, tourmaline species can be classified into three groups: (1) Schorl, the most prevalent tourmaline species, is thought to for 95 percent or more of tourmaline found naturally (Lameiras *et al*.,2011).(2) Dravite (NaMg3Al6[Si6O18](BO3)3), a sodium magnesium rich tourmaline endmember (OH4) It's color dark yellow to brownish black. (3) Elbaite (formula Na(Li, Al)3Al6[Si6O18](BO3)3(OH4)). Tourmaline exhibits instantaneous and permanent polarity, which can generate an electrostatic field and a persistent electric dipole, as well as automatically change the pH of a solution (Wang, C.P *et al* .,2011). According to the findings, the

(OH) functional group of (PT) could be the most important surface functional group for the adsorption of dye. After physisorption, a step of reduced molecular diffusion allowed for the active elimination of DR23 by PT (Liu, N., et al 2016)explored photoassisted Fenton degradation of azo-dye methyl-orange with tourmaline particles (Tokumura et al.,2006)As the concentration of dye declined and the concentration of tourmaline grew, the efficiency of discoloration improved (Wang, C *et al* .,2013).

Table 3: Characteristics of tourmaline adsorption for dye degradation and their application in a real-time approach

Adsorbent	**Dye**	**pH**	**Removal efficiency (%)**	**The optimal dose of tourmaline (%)**	**Reference**
Tb/ Tourmaline/ TiO_2)	Methyl- orange	6.5-9.5	98.8	0.5	Huang *et al.*, (2017)
Ce / Tourmaline / TiO_2	Methyl -orange		94.6	0.4	Zhang *et al.*, (2015)
Tourmaline /SiO_2/TiO_2	Methyl -orange		97.22	4	Meng *et al.*, (2006)

3. Kinds of Dyes and their effects

Dyes are mostly derived from food processing, pharmaceutical, printing, and maquillage, textile wastewater among other things. According to reports, the global dye output is about 7–9 million tons per year, with 10–15 percent of these dyes being released into water ecosystems without proper disposal. Dyes progressively, especially in the textile and fabric sectors. According to their chemical structures and qualities, they are categorized as:(sulphur, vat, acid, insoluble azo, dispersion , cation) dyes. Most hues had one or more aromatic rings derived from benzene, naphthalene, anthracene, and other chemicals, indicating chemical stability and severe toxicity. Furthermore, dyes were difficult to remove due to their high concentrations and colors. According to real-world examples, colorful suspended spices concentrations in dye wastewater might reach between100 and 150 mg/L, with chemical-oxygen –demands (COD) ranging from (3000 – 16000) mg/L. Furthermore, substantial amounts of acid and base were utilized in the manufacturing of dyes, resulting in noticeable pH fluctuations in wastewater processing and increasing the cost of processing. As a result, it was obvious almost colors were difficult to biodegrade and that the effluent was rather complex. Some investigations have found the negative impact of dyes on human health in terms of environmental toxicity. Azo dyes acts an example, were widely employed in manufacturing applications such as textile coloring; nevertheless, anilines derived from incompletely degraded azo dyes have been linked to malignant tumors such as: (bladder, spleen, liver) cancer. Days like : (Disperse ,Red 1), (Disperse, Red 13), and (Disperse, Orange 1) exhibited an important reduction in the impact of DNA of (HepG2) cells, according to. (Chang, 2007),(Chang.,2009) discovered a link between anthrax-union dyes like Disperse Blue (180) and cancer incidence among employees in dye facilities. Due to its difficult biodegradation, toxicity affecting, and alachite green, a kind of triphenylmethanedyes, has been classified according to the previous chemical incarcinogenetic test (Hong *et al* .,2008) . As more studies and reports reveal the physiotoxicity of triphenylmethane dyes on living creatures, several nations also areas throughout the world have banned the manufacturing and use of these very hazardous colors. Dyes containing aromatic rings have shown to have substantial ecotoxicity and persistence, therefore establishing effective strategies to minimize dye concentrations in actual water systems is critical. Although the advanced-oxidation process had a high efficiency for dyes degradation, it was nevertheless costly, hard to operate, and resulted in major pollution. Photodegradation, electrocoagulation ,adsorption,membrane,fenton process and flocculation were among the various ways and technologies for wastewater processing. Flocculation is a better method for removing hydrophobic dyes, with a decolorization rate of up to 92%.Nevertheless, the movement efficiency of hydrophilic dyes was quite small. Adsorption outperformed other approaches because of its simple cost, lack of major pollutants, and high elimination efficiency. Despite the fact that adsorption did not remove the aromatic rings of dyes, strong interaction between adsorbents and active groups of dyes allowed the amounts of colors in water to be decreased below the permissible drinking water threshold. However, there are some factors to consider, such as (1) higher adsorption capacity: innovative adsorbents incorporating minerals and nanomaterials must be generated with the advent of nanotechnology to obtain improved adsorption capacity and ability to reuse. (2) Adsorption that is selective: in practice, wastewater contained a variety of contaminants, and adsorbing dyes in particular were critical for the lifespan of adsorbents. (3) The adsorbents' stability: because the water conditions in practice were difficult, thermodynamically stable adsorbents were needed, so these adsorbents that were (acid, alkali) proof, and corrosion resistant were it is acceptable of recycling and displayed good promise in actual dyes processing (Yanbo Zhoua ,2019).

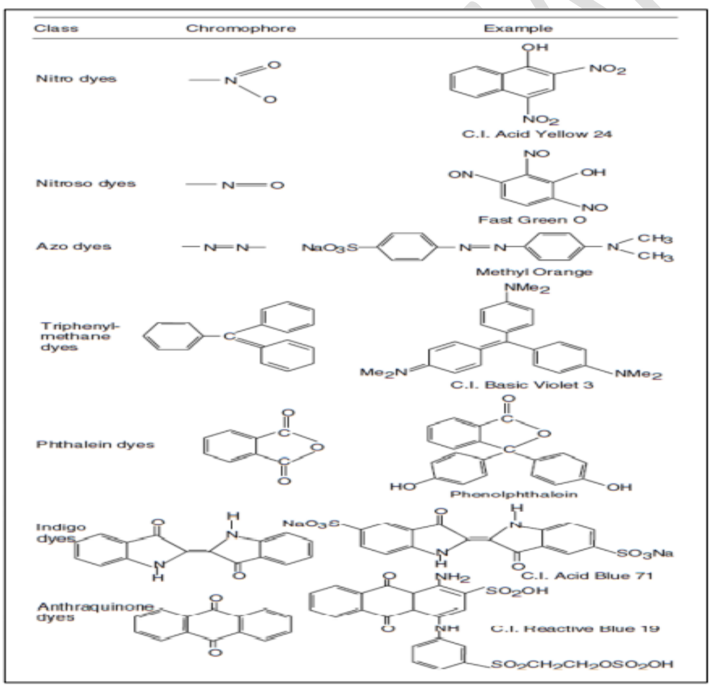


Figure 6. The chemical structures of few synthetic dyes (Iqbal M and Saeed A, 2009)

Table 4: The previous studies of some types of mineral have adsorption capacities to remove varies dyes

Minerals Kinds	**Kind of removed dye**	**Adsorption capacity (mg / g)**	**Reference**
Natural zeolite clinoptilolite	Safranine T dye	0.05513	(Muqing Qiua *et al* .,2009)
Natural zeolite clinoptilolite	Amido Black 10B dye	0.0112	(Muqing Qiua *et al* .,2009)
The natural zeolite was modified	(RR-239)and (RB-250).	33.0,20.6	(Erol Alver, Aysegül Ü. Metin,2012)
Sepiolite	(Reactive-Black -5,Red-239and Yellow-176)	(169.1g/kg, 120.5 g/kg and 108.8g/kg: yellow, black , red).respectively	(OrhanOzdemira *et al.*,2007)
zeolite, highly porous minerals	(Reactive-Black -5,Red-239and Yellow-176)	111.1,88.5,60.6 g/kg : red ,yellow ,black respectively	(OrhanOzdemira *et al.*,2007)
Alkaline treated clinoptilolite	methylene blue	47.3	(Murat Akgül and Abdülkerim Karabakan,2011)
Porous-Clay-Heterostructures with Silica-zirconia (SiZr-PCH)	Acid Blue 25	266	(Aguiar *et al.*, 2017)
Smectite rich natural clays	Basic yellow (28)	77	(Chaari *et al.*, 2019)
Pure kaolin	Methylene blue	15.55	(Dipa Ghosh *et al.*,2002)
NaOH-treated pure kaolin	Methylene blue	20.49	(Dipa Ghosh *et al.*,2002)
Calcined pure kaolin	Methylene blue	8.88	(Dipa Ghosh *et al.*,2002)
Clay mineral	Methylene blue	58.2	(A. Gurses *et al.*,2004)
montmorillonite clay (MC)	methylene blue (MB)	300	(C.A.P. Almeida *et al.*,2009)
mica mineral	Safranin Orange ,Reactive Black 5	2.92,0.17	(Anna Carla Ribeiro *et al* .,2021)
Powdered Tourmaline	diazo direct dye DR23	153	(Na Liua *et al.*,2018)
crystalline zeolite A (FA-ZA)	Methylene blue	43.76	(WANG Chunfeng *et al.*,2009)
Modified–natural-bentonite(166)	Di- azo -dye	7.14	(Toor and Jin, 2012)

Montmorillonite -(K10)	Crystal violet	370.37	(Sarma *et al.*, 2016)
Acid modified-clay-beads	Methylene-blue	223.19	(Auta and Hameed, 2012)
Sepiolite-clay	Direct-Blue	106	(Santos and Boaventura, 2016)
Palygorskite	Methylene-blue	132.72	(Mu and Wang, 2016)
Acid Activated Kaolinite	Congo-Red	12.36	(Hai *et al.*, 2015 Bis-imidazolium)
Modified-bentonite	Telon-dyes	108	(Makhoukhi *et al.*, 2015)
Montmorillonite	Methylene-blue	74	(Zhou *et al.*, 2014)
Montmorillonite	Methylene blue	289.12	(Almeida *et al.* ,2009)
Kaolin (Persia)	Methylene blue	28.95	(Tehrani-Bagha *et al.*,2011)
Natural zeolite	Methylene blue	21.78	(Wang and Zhu ,2006)
b Kaolinite	Methylene blue	102.04	(Krishnan *et al.* ,2015)
Natural clay (Portugal)	Methylene blue	22.2	(Hajjaji *et al.* ,2016)
Zeolites from kaolin (Egypt)	Methylene blue	11.13 *to* 21.41	(AEl-Mekkawi *et al.*,2016)
DE	Methylene blue	11	(M. Hadri *et al.*,2017)
DE	Methylene blue	198	(M.A. Al-Ghouti.,2003)
DE	MG	23.6	(L. Tian *et al.*,2016)
Chitosan-DE	SY	30	(Y.Z. Zhang *et al.*,2015)
Kaolinite ….109	Methylene blue	45.45	(Sarma *et al.* ,2011)
Raw coal-bearing kaolin…..109	Methylene blue	78.1	(W.Gao *et al.*,2016)
Activated-bentonite-(Turkey)	Acid-blue (193)	740.5	(O¨ zcan *et al.* ,2004)

Activated-bentonite-(Spain)	Sella-fast-brown (H)	360.5	(Espantaleon *et al.*,2003)
Clay-(Tunisia)	Basic-blue (9)	300	(Bagane and Guiza ,2000)
Calcined-alunite-(Turkey)	Reactive-yellow (64)	236	(O¨ zacar and Sengil ,2003)
Calcined-alunite-(Turkey)	Acid-blue (40)	212.8	(O¨ zacar and Sengil ,2002)
Diatomit- (Jordan)	Basic-blue (9)	198	(Al-Ghouti *et al*. ,2009)
Calcined alunite (Turkey)	Reactive-blue (114)	170.7	(O¨ zacar and Sengil ,2003) 166
Sepiolite-(Turkey)	Reactive-yellow 176	169.1	(Ozdemir *et al.* ,2004)
Activated-clay	Basic-red (18)	157	(SingaporeHo *et al.*,2001)
Diatomite-(Jordan) 33	Basic-blue (9)	156.6	(Shawabkeh and Tutunji 2003)
Sepiolite (Turkey)	Reactive-black (5)	120.5	(Ozdemir *et al.* ,2004)
Zeolite-(Turkey)	Reactive-red (239)	111.1	(Ozdemir *et al.* ,2004)
Sepiolite -(Turkey))	Reactive -red -239	108.8	(Ozdemir *et al.* ,2004)
Hydrotalcite	Reactive-yellow-208	47.8	(Lazaridis *et al.* ,2003)
Zeolite-(Turkey)	Reactive-yellow-176	88.5	(Ozdemir *et al.* ,2004)
Clay/carbons mixture 111	Acid-blue- 9	64.7	(Ho and Chiang ,2001)
Activated-clay 169	Basic-red-18	157	(Ho, Y.S *et al.*,2001)
Zeolite	Basic-dye	55.86	(Meshko, V.*et al.*,2001)
Modified montmorillonite	Methylene-blue	322.6	(Wibulswas ,2009)
Bentonite	Methylene-blue	151/175	(Hong, S *et al.*,2009)

Charred dolomite	dye (E-4BA)	950	(Walker, G., *et al.*,2003)
Na-Bentonite	Congo-red	35.84	(Vimonses, V., *et al.*,2009)
Kaolin	Congo-red	1.98	(Chen, D., *et al.*,2011)
Modified silica	Acid-blue (25)	45.8	(Phan, T *et al.*,2000)
Montmorilloni.115	Methylene blue	289.1	(Almeida *et al.* ,2009)
Bentonite	Methylene blue	151-175	(Hong *et al.* ,2009)
Diatomite.115	Methylene blue	198	(Al-Ghouti *et al.* ,2003)

4. Adsorption

The process of adsorption is the collection of soluble compounds in a solution on a surface. Adsorption is a separation technique in which one or more molecules of a gas or liquid phase are adsorbed on a solid adsorbent's surface. The components to be separated are selectively retained using a solid-phase with a big surface area in this separation process. Adsorbent (sorbent) is the adsorbing phase, while adsorbate is the substance concentration adsorbed on the phase surface (sorbate). The main advantages of an adsorption treatment for water pollution prevention include lower initial development costs, a simple design, simple operation, and no or little harmful material creation. (Ong S.T *et al.*,2007),(Chakraborty Sourja *et al.*,2006). As the adsorption process continues:

$$Qe=(Co-Ce)V/m \quad (1)$$

Where: Qe: The adsorption amount of the molecules at the equilibrium step (mg/g), V acts the solution volume (mL); m acts is the mass of adsorbent (g); Co and Ce acts the initial and equilibrium adsorbate concentrations (mg/L), respectively. (Pirbazari A *et al*., 2014)

Table 5: Methods used to treat wastewater from dyes (Mahmoud E. K., 2009)

Process	Advantages	Disadvantages
Biodegradation	Rates of elimination by oxidizable materials about 90%	Low biodegradability of dyes
Coagulation-flocculation	Elimination of insoluble dyes	Production of sludge, costs
Adsorption on activated carbon	organic substances and Suspended solids well reduced	Cost of activated carbon
Ozone treatment	Good decolorization	No reduction of COD, additional costs
Electrochemical process	Capacity of adaptation to different volumes and pollution loads	Iron hydroxide sludge
Reverse osmosis	Removal hydrolyzes reactive dyes, all mineral salts and chemical auxiliaries	High pressure
Nanofiltration	Separation of organic compounds of low molecular weight and divalent ions from monovalent salts	----------
Ultrafiltration-microfiltration	Low pressure	Insufficient quality of the treated wastewater

5. Factors affecting adsorption of dye

Numerous factors, like medium pH, temperature, initial dye concentration and adsorbent dose might affect dye adsorption efficiency. Each adsorbent has its own set of ideal operating parameters for dye adsorption. Optimizing these circumstances, on the other hand, will be extremely advantageous to extensive applications and the knowledge of adsorption mechanisms.

5.1. pH

pH variations can impact the surface charge and ionization degree for adsorbents (Nandi, B.K and Goswami, 2009) The removal effectiveness of cationic dyes decreases at lower pH values, whereas the removal percentage of dyes decreases and increases for cation dyes (Mohamad Amran *et al.*,2011). The (pHpzc) point of zero- charge is an important factor for determining the adsorption mechanism's favorability. Because of the presence of (OH-) and (COO-), pHpzc is advantageous for cationic-dye adsorption (Savova, D *et al.*,2003),(Dehghani *et al.*,2013) discussed the impact of pH on chitosan/zeolite composite adsorption of (Reactive-Red -120) and (Reactive-Red -196). They discovered that when pH rose, the removal effectiveness of RR120 and RR196 was reduced. (Takam *et al.* 2017) utilized adsorption to eliminate cationic dye (Azur-II) and anionic dye (Reactive-Red2) from natural cocoa shell husk (CPHN) .The removal effectiveness of cationic dyes decreases at lower pH intervals, whereas the removal ratio of dyes decreases and increases for cation dyes (Mohamad Amran *et al.*,2011).

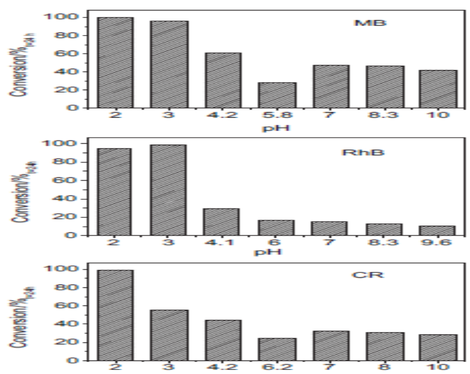


Figure 7 : Influence of pH on the catalyzed declorization of (MB, RhB and CR) in the tourmaline /H2O2 system at 25 ◦C (Cuiping Wang *et al.*, 2013)

5.2. Initial concentration

The connection between the accessible sites on an adsorbent surface and the initial-dye concentration generally determines the elimination effectiveness. Commonly, when the sites of adsorption on the adsorbent's surface are (saturated), the degradation ratio falls as the initial dye concentration increases; however, if the adsorption sites on the adsorbent's surface are (unsaturated), the degradation percentage rises as the initial dye amounts rise due to rising initial dye concentration gives high mass transfer driving- force for adsorption (Eren, Z and Acar, F.N., 2006).

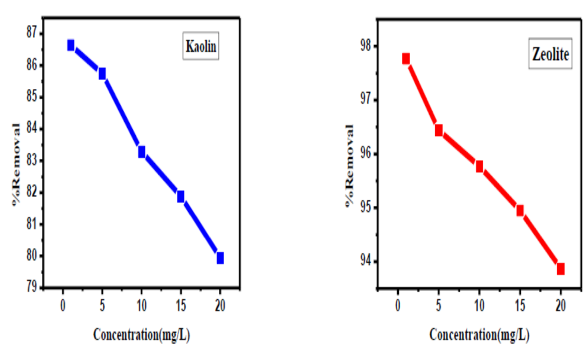


Figure 8 : Influence of initial concentration on the eliminating of methylene blue (MB) by kaolin and ,zeolite-x (zemedkun Mulushewa *et al.*,2021)

5.3. Temperature

Another important aspect that might disclose whether adsorption is exothermic or endothermic is temperature (Argun, M.E *et al*., 2008) Adsorption is an endothermic process where the adsorption ability rises as the temperature rises. This might be attributable to an increase in dye molecule mobility as well as the number of active-sites in adsorb (Senthilkumaar *et al*., 2006). Adsorption, on the other hand, is an exothermic reaction. The explanation for this might be that when the temperature rises, Adsorptive connections among molecules of dye and adsorbent active sites are reduced. (Ofomaja and Ho, Y., 2007)

5.4. Amount of adsorbent

Generally, the removal effectiveness improves when the quantity of adsorbent is increased due to the number of sorption sites rises with increased adsorbent dosage (Ofomaja, A.E., 2008). The connection between adsorption ability and adsorbent dose provides sufficient data for removing a certain quantity of dye with the least amount from the adsorbent, allowing for an economic evaluation of an adsorbent's practical applicability (Mohamad Amran *et al.*,2011)

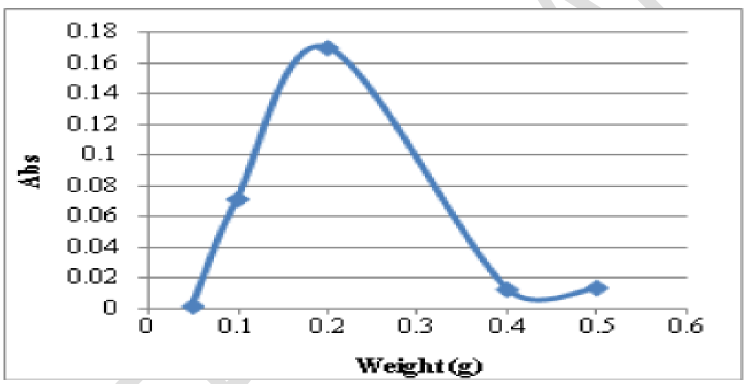


Figure 10. Effect of weight of lime stone on removal of MBGRL dye over lime stone surface (Hussein A. Esmael, 2014)

6. Conclusion

This paper covers the removal of various colors from simulated-wastewater using adsorption technique, especially a focus on clays/zeolites and their composites, the review demonstrates that compounds and developed adsorbents with good distributed pores and large surface areas have a high level adsorption capability. Aside from that, environmental factors involving pH, adsorbent dosage, initial dye concentration and temperature are important elements that have an impact on dye adsorption. So as to achieve the actual wastewater treatment requirements, extra work in the mixed pollutants system should be done. For low-cost long-term running, a better regeneration mechanism is a big obstacle. Researchers should focus on converting more unique adsorbents into classical adsorbents, allowing certain appropriate materials to be employed more often and broadly in dyeing wastewater treatment at a lower cost.

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