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Review article

General overview to understand the adsorption mechanism of textile dyes and heavy metals on the surface of different clay materials

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ABSTRACT

The adsorption process is one of the most cost-effective methods for eliminating various types of pollutants from water. Clay minerals can be converted into biosorbents for environmental remediation. This literature review summarizes the different types of natural clays, their crystal structures, classifications, physical and chemical properties, and industrial applications. Also the main results of recent studies on the process and mechanism of adsorption on natural clay materials to eliminate heavy metals and highly emerging toxic dyes. The Langmuir and Freundlich models are the most commonly used isotherms in most previous studies. In addition, the adsorption kinetics of the majority of dyes and heavy metals using natural clays are based on the pseudo-second-order model. High adsorption capacities of 909.09 mg g^{-1} for synthetic dyes and 179 mg g^{-1} for heavy metals were observed. This review article suggests that clays can be modified by various methods to improve their adsorption efficiencies by increasing their specific surface areas. The clays' low cost and ability to regenerate show that these materials are environmentally friendly and beneficial for industrial ecology.

1. Introduction

Nowadays, it is necessary to preserve water resources to save humanity and make its existence more secure (Thamarai Selvi and Zahir Hussain, 2022). Today, the greatest problem for the environment and ecosystems is water pollution, which is considered an indispensable element of all socio-economic activities, regardless of the degree of development of countries (Doltade et al., 2022). Increasing industrial activity is putting increasing pressure on the world's freshwater reserves (Miyah et al., 2017). Indeed, these activities generate a wide variety of chemicals that are discharged into the water cycle, endangering the fragile natural equilibrium that has allowed life to develop on Earth (Varol, 2020). The existence of these pollutants, even in small amounts, is very threatening, making humans, aquatic organisms, wildlife, and plants vulnerable to various diseases and even death (Miyah et al., 2021). In addition, it is reported that more than 3 billion people in the world live in areas where water is scarce (Diagboya et al., 2020). According to the report of the World Health Organization (WHO), about 844 million people in the world lack access to clean water (Sarkar et al., 2020). Due to limited economic resources or infrastructure, millions of poor people die each year from diseases caused by unsufficient and poor-quality water (Mohapi et al., 2020). Therefore, the absence or inadequacy of treatment systems leads to the non-biodegradable toxic chemicals' accumulation in the water cycle (Benjelloun et al., 2022). The main organic pollutants are pesticides, polycyclic aromatic hydrocarbons, plasticizers,

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Abbreviations: SY, Sunset Yellow; NB, Nile Blue; MB, Methylene Blue; BR46, Basic Red 46; BFBN, Blue Functionalized Boron Nitride; RFRN, Rose-FRN; DR23, Direct Red 23; BY28, Basic Yellow 28; AB75, Acid Brown 75; SLV, Sodium Leuco-Vat; TC, Tetracycline; CV, Crystal Violet; TB, Toluidine Blue; MV, Methyl Violet; BD85, Direct Blue 85; BV 16, Basic Violet 16; RR 120, Reactive Red 120; DO34, Direct Orange 34; CR, Congo Red; SAF, Safranin; MO, Methyl Orange; MR, Methyl Red; MG, Malachite Green; BG, Blue BG; YL, Yellow 7 GLL; BB9, Basic Blue 9; BB41, Basic blue 41; Ph, Phosphate; OTC, Oxytetracycline; OG, Orange G.

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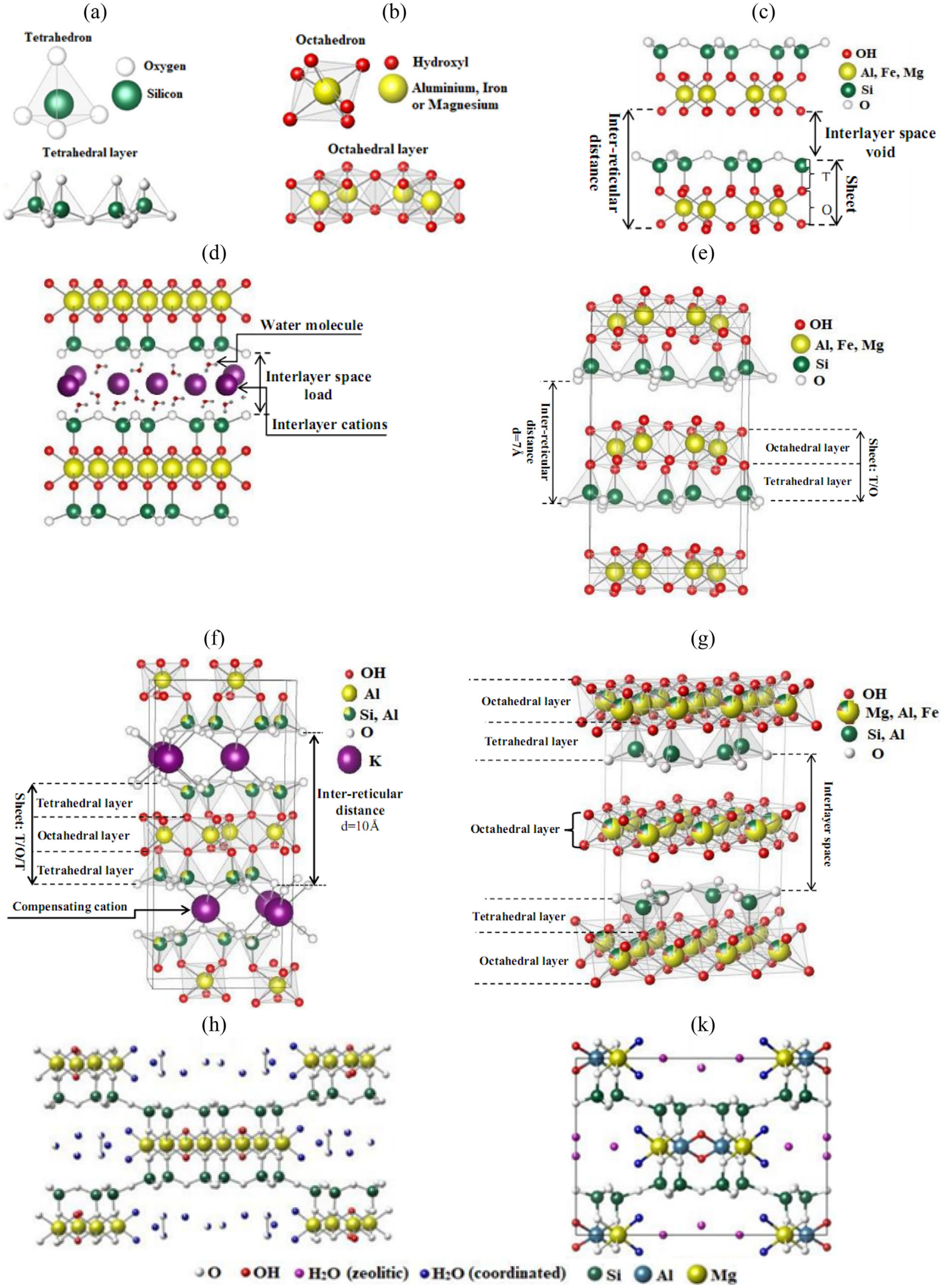


Fig. 1. Schematic representation of various clay minerals: tetrahedral layer (a), octahedral layer (b), not charged (c), charged (d), T/O clay minerals (e.g. kaolinite) (e), clay minerals T/O/T example: muscovite (f), clay minerals T/O/T-O example: chlorite (g), projection on the (001) plane of the structure of fibrous minerals: Sepiolite (h) and Palygorskite (k).

phenols, polybrominated diphenyl ethers, polychlorinated biphenyls, and drug residues, as well as synthetic dyes produced by the textile industry (Buruga et al., 2019). In addition, other very emerging inorganic contaminants are heavy metals such as arsenic, cadmium, cobalt, mercury, lead, chromium, and many other toxic metal ions including nitrates and phosphates. (Abdullahi et al., 2020; Aloulou et al., 2020; Nabbou et al., 2019; Benhiti et al., 2020). Organic textile dyes are responsible for the toxicity, odor, unpleasant taste, and coloration of the water, degrading water quality and causing the loss of aquatic life (Teo et al., 2022). This situation implies the need to treat colored effluents before they are discharged into the environment (Sriram et al., 2022). The tex-

Table 1
Classification of the main groups of clay minerals and their mineral species (X: monovalent interfoliar cation, Y: octahedral cation, Z: tetrahedral cation, and R: divalent or trivalent cation).

Sheet types	Inter-reticular distance (Å)	Interlayer cations	Octahedral layer nature	The electrical charge of the sheet	Groups	Formulas	Mineral Species
TO or 1/1	7	None or H_2O	Dioctahedral	0	Kaolinite	$Al_2Si_2O_5(OH)_4$	Kaolinite, dickite, nacrite, halloysite
			Trioctahedral		Serpentine	$(R^{2+})_6Si_4O_{10}(OH)_8$ R^{2+}=Mg^{2+}, Fe^{2+}, Mn^{2+}or Ni^{2+}	Chrysotile, berthiérine, amesite, antigorite, lizardite
TOT or 2/1	10	Non-hydrated	Dioctahedral	0,9 – 1,0	Micas	$X_2Y_{4\text{-}6}Z_8O_{20}$ (OH, F)$_4$	Muscovite, celadonite, paragonite, phengite
			Trioctahedral				Phlogopite, annite, biotite, lepidolite
			Dioctahedral	2	Micas hard		Margarite, chernykhite
			Trioctahedral				Clintonite, kinoshitslite bityite, anandite
	10 to 15	Hydrated and exchangeable	Dioctahedral	0,6 – 0,9	Vermiculite	$(Si_4)(Al_{4\text{-}p}Mg_p)(Si_{4\text{-}q})O_{20}(OH)_4$	Vermiculite Dioctaédrique
			Trioctahedral				Vermiculite Trioctaédrique
	10 to 18	Hydrated and exchangeable	Dioctahedral	0,2 – 0,6	Smectites	$(Al, Mg, Fe)_4(Si, Al)_8O_{20}(OH)_4 \bullet X_{0.85}nH_2O$	Montmorillonite, beidellite, nontronite, volkonskoite
			Trioctahedral			$(Mg_{6\text{-}z}R^{3+}_z)(Si_{8\text{-}y}Al_y)O_{20}(OH)_4 \bullet X_xnH_2O$	Saponite, hectorite, sauconite
	9	None	Dioctahedral	0	Pyrophyllite	$Al_4(Si_{8\text{-}x}Al_x)O_{20\text{-}x}(OH)_{4+x}$	Pyrophyllite, ferripyrophyllite
			Trioctahedral		Talc	$(Mg_{6\text{-}z\text{-}y}Fe^{2+} Fe^{3+}_y)(Si_{8\text{-}x}Fe^{3+}_x)O_{20+y\text{-}x}(OH)_{4\text{-}y+x}$	Talc, willemseite, kerolite, pimelite
TOT-O or 2/1/1	14	In hydroxide form	Dioctahedral Di, Trioctahedral Trioctahedral	Variable	Chlorites	$[(R^{2+}, R^{3+})_6(Si, Al)_8O_{20}(OH)_4][(R^{2+}R^{3+})_6(OH)_{12}]$	Donbassite Cookeite, sudoite Clinochlore, pennantite, chamosite, nimite
2/1In slats (ribbons)	10	Hydrated and exchangeable	Dioctahedral Trioctahedral	Variable	Palygorskite Sepiolite	$Si_8O_{20}Mg_5(OH)_2(H_2O)_4{\cdot}4H_2O$ $Si_6Mg_4O_{15}(OH)_26H_2O$	Attapulgite Sepiolite
Variable	Variable	Variable	Dioctahedral	Variable	Interstratified minerals	variable	Tosudite (smectite-chlorite)
			Trioctahedral				Kulkeite (chlorite-talc)

Table 2
Main mineral compositions of natural clays.

Iron oxides and hydroxides	Feldspars	Carbonates	Quartz	Organic matter
Hematite (Fe_2O_3) Magnetite (Fe_3O_4) Goethite (FeOOH)	Feldspar type -Potassic (Si_3AlO_8)K -Sodic (Si_3AlO_8) -Calcic ($Si_2Al_2O_8$)Ca	Calcite ($CaCO_3$) Dolomite (Ca, Mg)(CO_3)$_2$ Magnesite ($MgCO_3$)	Free silica	- Living components (microflora, roots, pedofauna) - Plant and animal debris - Molecular organic matter or humus: sugars, amino acids, fatty acids, alcohols, esters, etc. -Humic substances: fulvic acid, humic acids, humin.

tile industry is one of the industries responsible for high water consumption and generates effluents loaded with recalcitrant organic molecules that are difficult to treat by conventional water purification systems (Munjur et al., 2020). The world's production of dyes is estimated at more than 8.10^5 tons per year (de Araújo et al., 2021; El-Gaayda et al., 2021). Furthermore, it is estimated that $1.4.10^5$ tons of textile dyes are released into the environment globally each year (de Araújo et al., 2021; El-Gaayda et al., 2021). All the dyes are toxic for their composition and modes of use (Ambika and Srilekha, 2021). They can cause skin diseases in humans and even skin cancers (Tiwari et al., 2022). Thus, the untreated effluents of these dyes are responsible, after their discharge, for the increasing accumulation of recalcitrant substances difficult to biodegrade in water (Tijani et al., 2021). Similarly, heavy metals have toxic effects on organisms when their concentrations exceed specified levels, which can cause various complica-

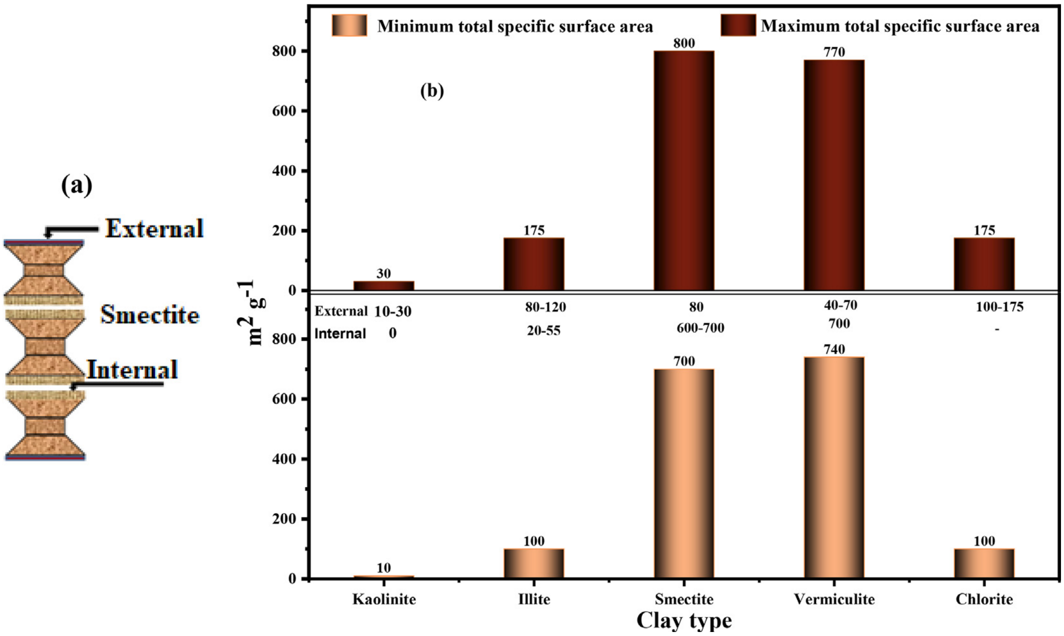


Fig. 2. (a) External and internal clay surfaces (for example, smectite); (b) External, internal, and total specific surfaces of major clay families.

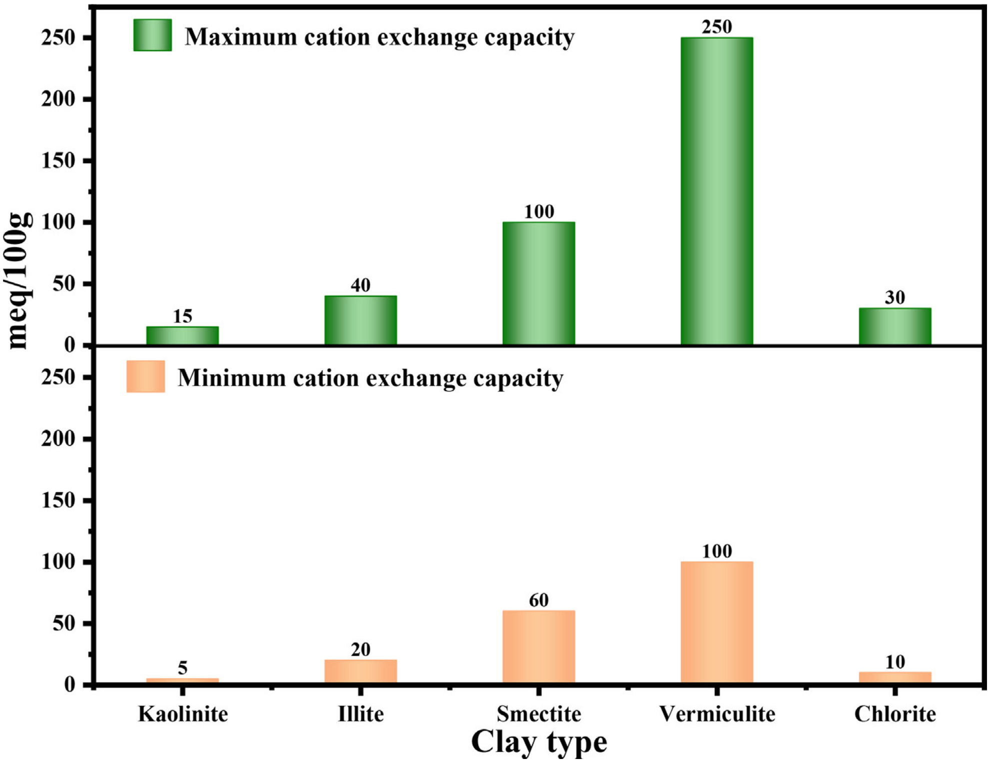


Fig. 3. Cation exchange capacities of the main clay families.

tions in plants and animals. In humans, they cause acute and chronic diseases, such as cancer, Alzheimer's disease, Parkinson's disease, kidney dysfunction, osteoporosis, and heart failure (Rehman et al., 2021; Alengebawy et al., 2021). The situation is aggravated by the absence or insufficiency of an adequate water treatment system capable of reducing the concentration of toxic substances that present chronic chemical risks. (Eswaran et al., 2021). It can be said that poorly treated wastewater inevitably leads to a deterioration of the water sources quality and, consequently, to a lack of drinking water in many countries (Mukhopadhyay et al., 2021).

Several depollution processes have been developed to protect the environment and offer the possibility of reusing wastewater (Sellaoui et al., 2021). They are different from each other and can be cited as examples: adsorption on commercial activated carbon, electrolysis, flotation, chemical precipitation, ion exchange, membrane filtration (ultrafiltration, nanofiltration, and reverse osmosis), photocatalysis, chemical oxidation, etc (Benjelloun et al., 2021; Miyah et al., 2020; Znad et al., 2018; Iaich et al., 2021; Miyah et al., 2022). Most of these technologies are very expensive, especially when applied to high-throughput effluents (Melhaoui et al., 2021). In addition, some of these processes can produce

Table 3
Some uses of clays in the industry.

Areas of use		Application example			**Ref**
Ceramic industry	**Traditional ceramics**	Type	Terracotta	Bricks, tiles, flues, drainage pipes, floor and wall coverings, floor and wall coverings, and pottery	(Martinello et al., 2022; Kieufack et al., 2021)
			Earthenware	Sanitary equipment, dishes, and tiles	(Chalouati et al., 2021; Dondi et al., 2021)
			Sandstone	Floor tiles, pipes, chemical equipment, and sanitary equipment	
			Porcelains	Tableware, chemical devices, and electrical insulators	(Arslan, 2021; Pahari et al., 2021)
	Ceramics for the environment	**Type**	**Filtres**	- Treatment of water intended for consumption Treatment of industrial wastewater from painting	(Akowanou et al., 2016; Grema et al., 2021; Opafola et al., 2021)
			Mineral membranes	Treatment and recovery of textile wastewater	(Ağtaş et al., 2021)
			Heterogeneous catalysts	Degradation of the antibiotic sulfathiazole	(Rojas-Mantilla et al., 2021)
			Adsorbents	Removal of NO_2 and SO_2 gases	(Kinoshita et al., 2022)
	Bioceramics	**Used in the human body** - Orthopedic prostheses - Dental restorations - Hips and bone grafts			(Kenawy and Khalil, 2020)
	Refractory ceramics	Electric furnace, blast furnace, ladle steel, household waste incinerator, glass melting furnace, and rotary cement furnace construction			(Grine et al., 2021)
Water treatment		**Categories**	**Wastewater** **Industrial process water** **Drinking water**	**Removal of pollutants from water by:** Adsorption process Clay ceramic filter	(Olaremu et al., 2021)
Oil industry		Clay was used as a filler and catalyst carrier.			
Food Industry		Bio-nanocomposite films for food packaging, storage, and preservation, effective against food spoilage bacteria			(Jayakumar et al., 2021; Tiwari et al., 2021)
Cosmetic industry		High-quality pyrophyllite is used as a base in various face and body powders.			(Ali et al., 2021)
Pharmaceutical industry		- Halloysite nanotubes can be loaded with various drugs, including anticancer drugs, antibiotics, analgesics, antihypertensives, anti-inflammatories, and nucleic acid therapeutics. Halloysite nanotubes modified with chitosan oligosaccharides show the ability to enhance the therapeutic effect of the anticancer drug doxorubicin. Tissue engineering and regenerative medicine.			(Mobaraki et al., 2021; García-Villén et al., 2021)
Paper industry		Papermaking			
Plastic industry		Pyrophyllite is used as a filler in a variety of applications, such as polyvinyl chloride (PVC), low-density polyethylene (LDPE), and high-density polyethylene (HDPE).			(Ali et al., 2021)
Rubber industry		Low-grade pyrophyllite is used as a dusting agent, lubricating molds and preventing surface sticking during manufacturing.			
Insecticide industry		Pyrophyllite is used as a carrier in insecticides.			
Paint industry		High-quality finely ground pyrophyllite is used in paints as a pigment filler and suspending agent.			
Energy domain		**Solar and chemical energy conversion** Manufacture of clay-based composites for photocatalysis (photocatalysts).			(Zou et al., 2022; Boutaleb et al., 2021; Wan et al., 2022; Yang et al., 2021)
		Energy storage and conversion Synthesis of Si nanostructures derived from silicate minerals and their composites for application in energy-related fields such as rechargeable batteries, and hydrogen evolution. Layered nanoclays and their derivatives as electrodes, electrolyte fillers/additives, separators in rechargeable batteries and superconductors, and catalysts in water splitting, CO_2 reduction, and oxygen reduction.			
Metal casting		Make art objects, ornaments, and objects of daily use.			(Eyankware et al., 2021; Nnamele and Egwuonwu, 2020)

Fig. 4. Uses of natural clays in various fields.

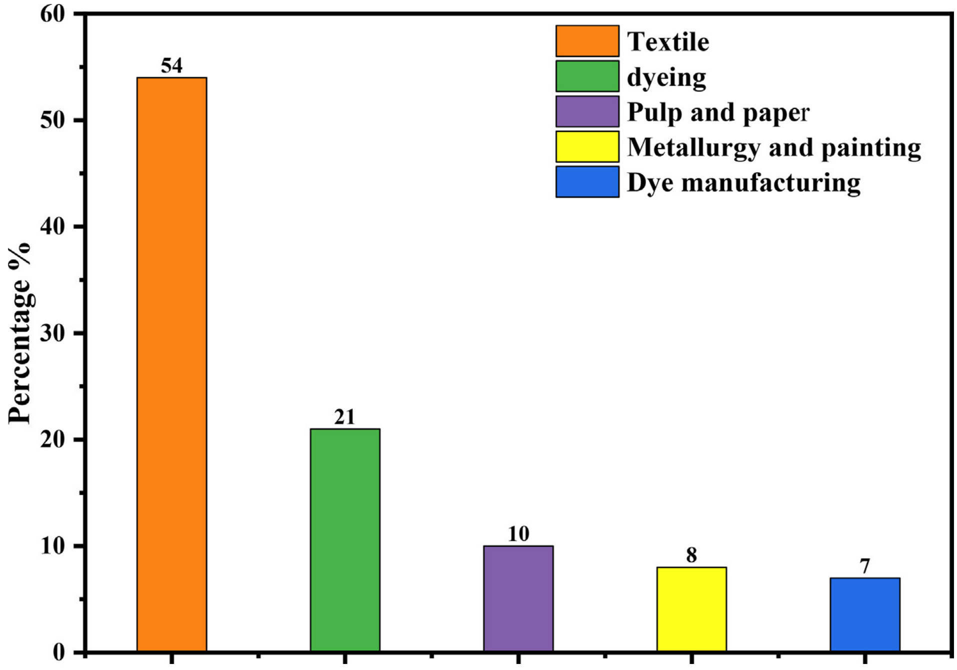


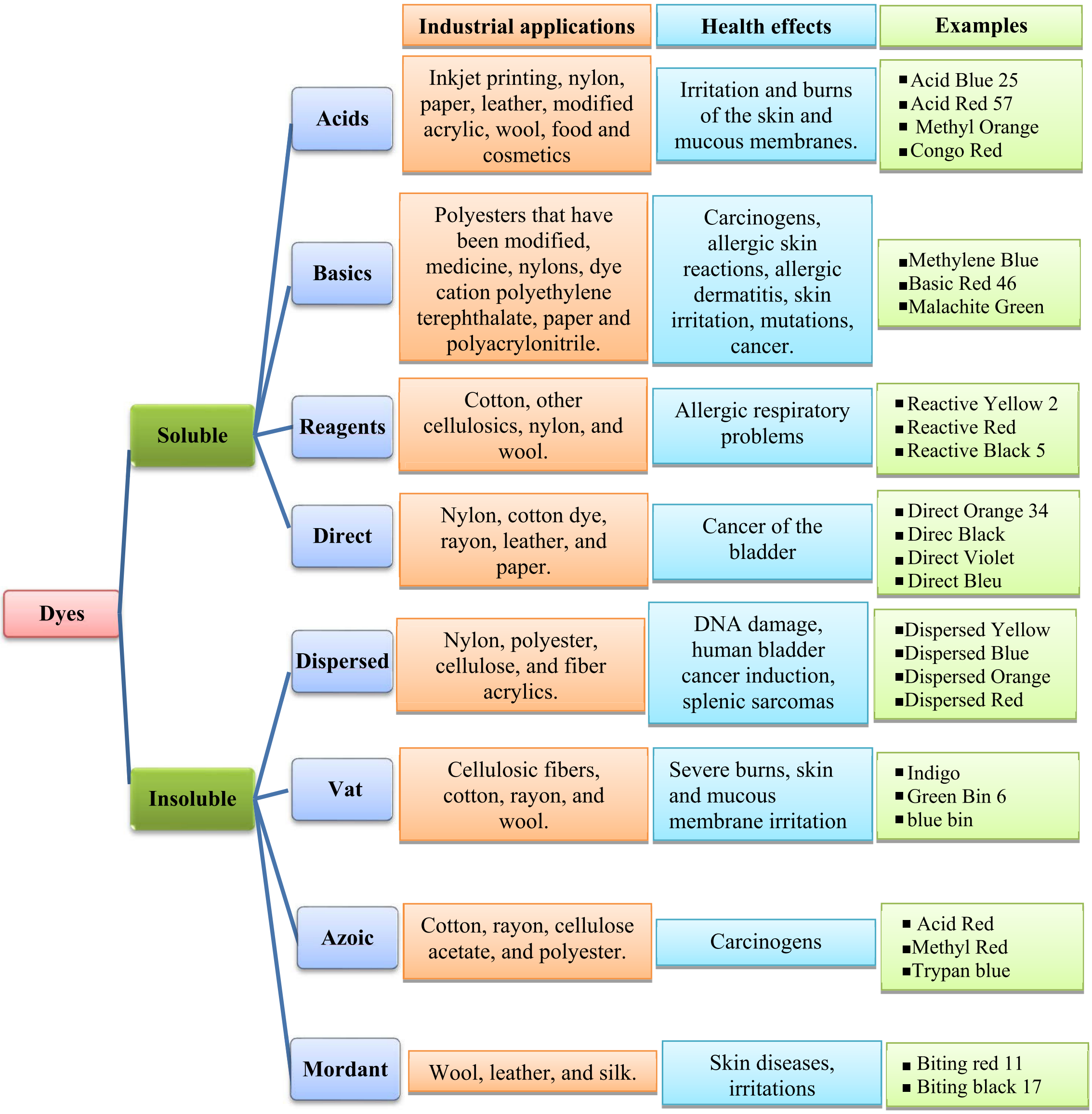
Fig. 5. Percentage of industries responsible for the presence of dye effluents in the environment.

by-products that are more toxic than the original products (Thotagamuge et al., 2021). The adsorption process is one of the most adopted techniques for the removal of contaminants of different natures, such as textile dyes and heavy metals (Saleem et al., 2019).

On the other hand, for low volume discharges, research was then directed towards less expensive and widely available treatment processes, using adsorbents namely clays, zeolites, fly ash, pyrophyllite, eggshells, snail shells, hydroxyapatite, metal oxides, and nanocomposite materials (Miyah et al., 2017); (Saleem et al., 2019; Fabryanty et al., 2017; Awual et al., 2019; Wei et al., 2021; Romdhane et al., 2020) However, most of these adsorbents are microparticles, and the small contact area requires considerable time to achieve maximum pollutant removal (Cao et al., 2020). As most industries need a fast removal rate to cope with increasing pollutant capacities, there is an urgent need to develop adsorbents that are durable, economical, and offer both high removal rates and high adsorption capacities (Yönten et al., 2020). With the latest trends in environmental sustainability, scientists are focusing on the use of low-cost natural materials to effectively remove harmful substances from wastewater (Miyah et al., 2021; Dabagh et al., 2022). Clay is a natural, non-toxic, abundant, durable, and high-surface area material used in the adsorption process (Jawad and Abdulhameed, 2020). Clay has long been used in crafts such as pottery and various ceramic products used in building construction, such as bricks and tiles (Antonelli et al., 2020). Due to its ability to exchange ions, swell and transform, clay has a wide range of uses in wastewater treatment, the paper industry, paint, cosmetics, pharmaceuticals, and the ceramic industry (Sulyman et al., 2021; Luty-Błocho et al., 2021; Kubendiran et al., 2021). Since the rise of the oil refining and petrochemical industries, clay has been used as a catalyst (Vieira et al., 2022).

In addition, the clay can be modified to improve its efficiency and adsorption capacities using various treatments, such as thermal treatments (calcination), chemical treatments (acid and basic activation), cationic exchange, grafting of organic compounds (surfactant), or polymer activation, etc (Vieira et al., 2016; Hradil et al., 2020; Gamoudi and Srasra, 2018).

This literature review is devoted to recent research on the use of natural and modified clay materials as effective adsorbents for the treatment of polluted water and highlights the structure, classification, and physicochemical properties of clays and their use in the



	Industrial applications	Health effects	Examples
Acids	Inkjet printing, nylon, paper, leather, modified acrylic, wool, food and cosmetics	Irritation and burns of the skin and mucous membranes.	▪Acid Blue 25 ▪Acid Red 57 ▪ Methyl Orange ▪Congo Red
Basics	Polyesters that have been modified, medicine, nylons, dye cation polyethylene terephthalate, paper and polyacrylonitrile.	Carcinogens, allergic skin reactions, allergic dermatitis, skin irritation, mutations, cancer.	▪Methylene Blue ▪Basic Red 46 ▪Malachite Green
Reagents	Cotton, other cellulosics, nylon, and wool.	Allergic respiratory problems	▪Reactive Yellow 2 ▪Reactive Red ▪Reactive Black 5
Direct	Nylon, cotton dye, rayon, leather, and paper.	Cancer of the bladder	▪Direct Orange 34 ▪Direc Black ▪Direct Violet ▪Direct Bleu
Dispersed	Nylon, polyester, cellulose, and fiber acrylics.	DNA damage, human bladder cancer induction, splenic sarcomas	▪Dispersed Yellow ▪Dispersed Blue ▪Dispersed Orange ▪Dispersed Red
Vat	Cellulosic fibers, cotton, rayon, and wool.	Severe burns, skin and mucous membrane irritation	▪Indigo ▪Green Bin 6 ▪blue bin
Azoic	Cotton, rayon, cellulose acetate, and polyester.	Carcinogens	▪ Acid Red ▪Methyl Red ▪Trypan blue
Mordant	Wool, leather, and silk.	Skin diseases, irritations	▪ Biting red 11 ▪ Biting black 17

Fig. 6. Different classes of dyes and their industrial applications and health effects.

Table 4
Adsorption experiments on natural clays as adsorbent materials for dye removal from water.

Adsorbent	Adsorbate	Types of dyes	Adsorption capacity	Kinetic model	Adsorption isotherm	Specific surface area (m^2/g)	Ref
Iranian natural clay Bushehr	SY NB	Cationic Anionic	67.82 mg g^{-1} 72.25 mg g^{-1}	Pseudo-second order	Langmuir	12.85	(Esvandi et al., 2020)
Colombian natural bentonite clay	BR 46	Cationic	594 mg g^{-1}	Pseudo-second order	Langmuir	47	(Paredes-Quevedo et al., 2021)
Iranian natural clay Isfahan	CV	Cationic	9.37 mg g^{-1}	–	–	40	(Najafi et al., 2021)
Moroccan clay Na-Montmorillonite	TB CV	Cationic Cationic	5.80 mmol g^{-1} 5.40 mmol g^{-1}	Pseudo-second order	Langmuir	77	(El Haouti et al., 2019)
Iraqi red kaolin clay	MB	Cationic	240.4 mg g^{-1}	Pseudo-second order	Langmuir and Freundlich	35.6	(A. H. Jawad A. S. Abdulhameed, , 2020)
Turkey's raw Sepiolite clay from Eskişehir	DR 23 MB	Anionic Cationic	649.37 mg g^{-1} 125 mg g^{-1}	Pseudo-second order	Langmuir	329.7	(Largo et al., 2020)
Tunisian natural clay from Jebel Romana	BY 28	Cationic	76.92 mg g^{-1}	–	Langmuir	71	(Chaari et al., 2019)
Tunisian natural clay from Khledia	AB 75	Anionic	8.33 mg g^{-1}	–		52.2	
Tunisian natural clay from Jebel Stah	SLV	Anionic	12.5 mg g^{-1}	–	Langmuir	85	(Chaari et al., 2021)
Chinese natural red clay from Gansu Province	MB TC	Cationic	112.39 mg g^{-1} 109.35 mg g^{-1}	Pseudo-second order	Langmuir	57.34	(Wang et al., 2021)
Chinese natural red clay from Inner Mongolia	MB TC	Cationic	85.79 mg g^{-1} 93.19 mg g^{-1}	Pseudo-second order	Langmuir	58.96	
Moroccan red clay from the Tetouan region	MB	Cationic	18.7 mg g^{-1}	Pseudo-second order	Langmuir	22.4	(Bentahar et al., 2019)
Moroccan rhassoul clay from the east of the Middle Atlas			166.7 mg g^{-1}			119	
Natural bentonite	BV16	Cationic	434.78 mg g^{-1}	Pseudo-second order	Langmuir	43.35	(Khalilzadeh Shirazi et al., 2020)
Tunisian natural clay from Tabarka	RR 120	Anionic	1.2 mg g^{-1}	Pseudo-second order	Langmuir	47	(Abidi et al., 2019)
Tunisian natural clay from Fouchana			0.8 mg g^{-1}			80	
Illitic clay	MB CV	Cationic Cationic	62.5 mg g^{-1} 330.0 mg g^{-1}	–	Langmuir Freundlich	128	(Sakin Omer et al., 2018)
Tunisian raw haloysitic clay from the Nefza region	DO34	Anionic	9.48 mg g^{-1}	Pseudo-second order	Freundlich	20	(Chaari et al., 2015)
Algerian natural bentonite from Maghnia	MB CR	Cationic Anionic	345.82 mg g^{-1} 315 mg g^{-1}	Pseudo-second order	Langmuir	84	(Oussalah et al., 2019)
Moroccan natural Safiot Clay	MB SAF	Cationic Cationic	68.49 mg g^{-1} 45.45 mg g^{-1}	Pseudo-second order	Langmuir	-	(El Kassimi et al., 2021)
Turkey's natural clay from Erzurum Province	MB	Cationic	113.63 mg g^{-1}	Pseudo-second order	Langmuir	-	(Bingül, 2022)
Iranian natural clay K from Azarshahr	MB	Cationic	123.5 mg g^{-1}	Pseudo-second order	Langmuir	34.66	(H. Aghdasinia H. R. Asiabi, Environ, , 2018)
Iranian natural clay D from Azarshahr			909.09 mg g^{-1}			43.78	
Iranian natural clay G (purchased from Tabriz)			833.33 mg g^{-1}			52.85	
Moroccan natural clay from the Jorf Arfoud region	MO MB	Anionic Cationic	13.71 mg g^{-1} 15.82 mg g^{-1}	Pseudo-second order	Freundlich Langmuir	-	(Assimeddine et al., 2020)
Tunisian raw clay from Jebel Louka	MR	Anionic	397 mg g^{-1}	Pseudo-second order	Langmuir	37.7	(Romdhane et al., 2020)
Turkey's natural red clay from Oltu/Erzurum region	MG	Cationic	84.75 mg g^{-1}	Pseudo-second order	Freundlich	41.87	(Sevim et al., 2021)
Tunisian Smectite Clay	CV	Cationic	86.54 mg g^{-1} (Sono-assisted adsorption)	Pseudo-second order	Langmuir-Freundlich and Toth	74	(Hamza et al., 2018)
Moroccan natural clay from the Agadir region	MB CV CR	Cationic Cationic Anionic	279.95 mg g^{-1} 231.74 mg g^{-1} 61.12 mg g^{-1}	Pseudo-second order	Langmuir	76.971	(Bentahar et al., 2017)

Table 4 (*continued*)

Adsorbent	Adsorbate	Types of dyes	Adsorption capacity	Kinetic model	Adsorption isotherm	Specific surface area (m^2/g)	Ref
Moroccan natural clay from Fez city	BG YL	Cationic Cationic	101 mg g^{-1} 127 mg g^{-1}	Pseudo-second order	Langmuir	28	(Hicham et al., 2019)
Brazilian bentonite	MO MB	Anionic Cationic	2.2 mg g^{-1} 100 mg g^{-1}	Pseudo-second order	Sips	-	(Fernandes et al., 2020)
Tunisian natural clay from Djebel Aïdoudi	MB	Cationic	241.96 mg g^{-1}	–	Langmuir	69.00	(Amari et al., 2018)
Saudi natural red clay from the southern region	MB	Cationic	50.25 mg g^{-1}	Pseudo-second order	Langmuir	63.15	(Khan, 2020)
Moroccan natural Safiot clay from the Safi region	BB9 BY28	Cationic Cationic	58.45 mg g^{-1} 58.89 mg g^{-1}	Pseudo-second order	Langmuir	-	(El Kassimi et al., 2021)
Pakistani bentonite clay	MG	Cationic	223 mg g^{-1}	pseudo-first-order	Langmuir	115.99	(Ullah et al., 2021)
Bentonite purchased from Alfa Aesar			149 mg g^{-1}			38.306	
Turkey’s red mud clay			125 mg g^{-1}			16.796	
Moroccan natural Muscovite clay from the Khemisset region	MB	Cationic	59.828 mg g^{-1}	Pseudo-second order	–	-	(Amrhar et al., 2021)
Moroccan natural Safiot clay from Safi city	BB9 BB41 BY28	Cationic Cationic Cationic	68.49 mg g^{-1} 128.2 mg g^{-1} 166.67 mg g^{-1}	–	Langmuir	-	(El Kassimi et al., 2020)
Iraqi natural clay from Topkhana	MB	Cationic	128.8 mg g^{-1}	Pseudo-second order	Langmuir	53.5	(Salh et al., 2020)
Algerian natural bentonite from Maghnia	MV	Cationic	480.79 mg g^{-1}	Pseudo-second order	Langmuir	-	(Mahammedi, 2021)
Palygorskite cay	SAF	Cationic	195 mmol kg^{-1}	Pseudo-second order	Langmuir	173	(Sieren et al., 2020)
Sepiolite clay			45 mmol kg^{-1}			250	
Kaolin clay	MB	Cationic	83 mg g^{-1}	–	–	-	(Ethaib et al., 2020)
Moroccan bentonite clay from the Nador region	MB	Cationic	60 mg g^{-1}	–	Freundlich	271.81	(Hmeid et al., 2021)
Sepiolite clay	BR46	Cationic	110 mg g^{-1}	Pseudo-second order	Freundlich and Langmuir	108	(Santos and Boaventura, 2016)
	DB85	Anionic	232 mg g^{-1}	pseudo-first-order	Langmuir		

ceramic industry. In addition, we provide a general overview of the selectivity and sensitivity of interactions between different fillers to understand the adsorption mechanisms of textile dyes and heavy metals on the surface of raw clays or clays subjected to various treatments and modifications, while studying their beneficial effects on adsorption performance, regeneration capacity, cost analysis, and industrial scale applications.

2. Clay minerals: Structure and classification

2.1. Crystal structure of clay minerals

Clays consist of minerals whose particles are essentially lamellar phyllosilicates and stacks of silicate two-dimensional sheets. The lamellar crystal structure is based on two important entities (Fig. 1) (Orta et al., 2020).

- The siliceous tetrahedral layers SiO_4 (T) are arranged in a two-dimensional hexagonal lattice, in which a Si^{4+} cation is surrounded by four oxygen atoms as shown in Fig. 1a.
- Alumina (Al), iron (Fe), or magnesium (Mg) octahedron layers are located in the center of the octahedron and are surrounded by six hydroxyl groups or oxygen atoms as shown in Fig. 1b.

The structural organization of phyllosilicates is based on a framework of oxygen and hydroxyl ions that occupy the tops of octahedral ($O^{2-}$and OH^-) and tetrahedral (O^{2-}) assemblies. In the cavities of these elementary structural units, cations of variable sizes (Si^{4+}, Al^{3+}, Fe^{3+}, Fe^{2+}, Mg^{2+}) are in tetrahedral or octahedral positions (Wal et al., 2021).

These elements are organized along a plane to form octahedral and tetrahedral layers, the number of which determines the thickness of the sheet. The space between two successive parallel sheets is called interlayer space (Fig. 1). This latter can be empty and the sheets are neutral and then linked directly to each other by hydrogen bonds, such as kaolinite (Fig. 1c), or by Van Der Waals bonds, such as talc or pyrophyllite (Lucas, 1962). Where filled by various cations, which can be either dry or hydrated, the most frequent are Ca^{2+}, Mg^{2+}, K^+, Na^+, and Li^+, which form “bridges” from one sheet to the other (Fig. 1d) (Tchieno Melataguia, 2016; Zaid, 2020).

When two cavities out of three of the octahedral layer are occupied by Al^{3+} or by another trivalent metal ion, the structure is called di-octahedral. When all the octahedral cavities are occupied by bivalent metal ions, the structure is called tri-octahedral (Thiebault, 2020).

2.2. Classification of clays

There are different classifications of clay; the most classical is based on the structure and thickness of the sheet (Table 1). We distinguish three main groups:

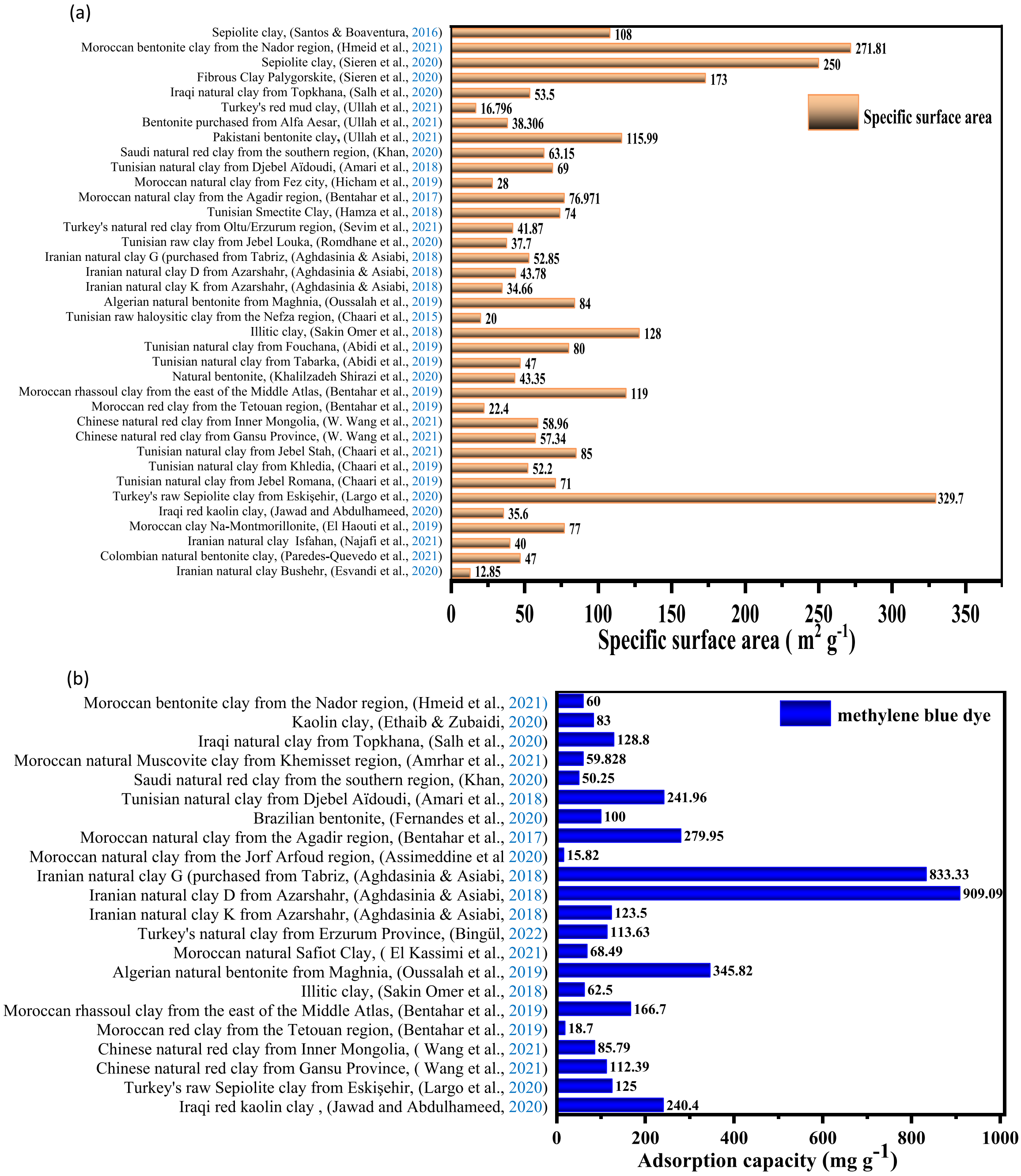


Fig. 7. Comparison of: (a) specific surface values, (b) the adsorption capacities of MB cationic dye, (c) the adsorption capacities of some cationic dyes, (d) the adsorption capacities of some anionic dyes by various natural clays.

2.2.1. Phyllite minerals

Phyllite minerals, or phyllosilicates, are minerals of the group of silicates with sheet structures built by the stacking of tetrahedral layers (T) being connected to an octahedral layer (O) by common oxygen atoms or hydroxyl groups. The number of associations of these layers determines the thickness of their structural units, the interfoliar (interlayer space) charge, and the composition of interfoliar elements. The minerals of this type of structure can be classified into subgroups of the type T/O or 1/1, type T/O/T or 2/1, and type T/O/T-O or 2/1/1 (Olaremu, 2021; Han et al., 2019).

2.2.2. Minerals of type 1/1 or 1 T/1O

The sheet consists of a tetrahedral layer and an octahedral layer. The inter-reticular distance is about 7 Å (Fig. 1e). This type corresponds to the kaolinite group.

2.2.3. Minerals of type 2/1 or 2 T/1O

The current classification of clay minerals as 2/1 is based on their crystallochemical composition. Since Stokholm (AIPEA, 1963), the first criterion is a global resultant of this composition, expressed by the interfoliar charge, followed by the di or trioctahedral character. The origin of the charge (tetrahedral or octahedral substitution), and even the nature of the cation saturating the charge K in micas (Robert and Agronomic Annals, 1975). In their classification project, Méring and Pédro (1969) even make use of finer characteristics, which are the order or the disorder in the isomorphic substitutions or the distribution of the compensating cations (Méring and Pédro, 1969).

The sheet consists of an octahedral layer sandwiched between two tetrahedral layers. The characteristic equidistance varies from 9.4 to 15 Å according to the content of the interleaf. Smectites, ver-

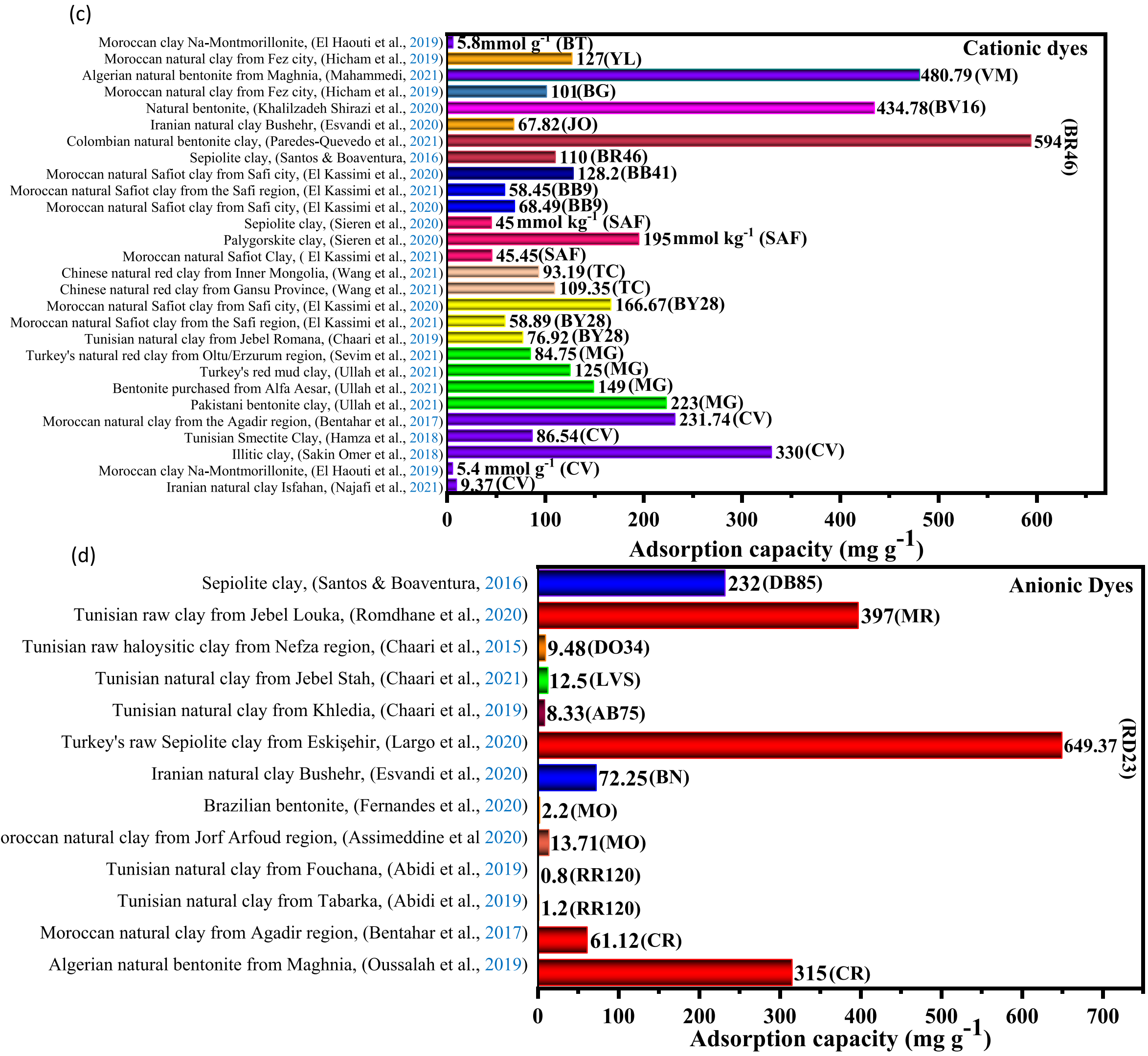


Fig. 7 (*continued*)

miculites, and micas are examples of this type (Michel, 1971). Muscovite is a mineral with this structure, belonging to the mica family (Fig. 1f).

2.2.4. Minerals of type 2/1/1 or (2 T/1O)1O

The clay minerals of type 2/1/1 (T/O/T-O) have a crystalline structure identical to the 2/1 except that the interfoliar space is not occupied by compensating cations as in the preceding case (Fig. 1f), but by an octahedral layer, of brucitic nature ($Mg(OH)_2$) or gibbsitic ($Al(OH)_3$) (Delavernhe, 2012). The characteristic equidistance is then about 14 Å. The chlorite groups correspond to this type (Fig. 1g).

2.2.5. Fibrous minerals

Fibrous minerals are characterized by discontinuous clayey sheets (Fig. 1). They are distinguished by their particular structure in pseudo-sheets constituted by continuous planes of oxygen atoms separated between them by two planes containing a compact assembly of oxygen atoms and hydroxyl groups. The stacking of the two discontinuous planes forms entangled octahedrons, creating a ribbon. It is the width of this ribbon that characterizes each family. The oxygens of the continuous plane form the base of the tetrahedron, whose point is constituted by the oxygen of the ribbon. These tetrahedra are occupied at their centers by Si^{4+} ions. Mg^{2+} or Al^{3+} ions occupy the octahedral gaps (Aoun, 2016). The ribbons are terminated by bonds between these cations and water molecules. We distinguish two main families among these fibrous minerals: the sepiolites, which correspond to a ribbon with 8 octahedrons and which comprise essentially Mg as an exchangeable cation, rarely Na (Fig. 1h), and the palygorskites (also called attapulgite) (Fig. 1k), which are constituted of a ribbon with 5 octahedrons and richer in Al than the sepiolite.

2.2.6. Inter-layered minerals

There are, of course, inter-stratified minerals, formed by the regular stacking [(2 T/1O)/ (2 T/1O)] or irregular [(1 T/1O)/ (2 T/1O)] of sheets of two different types. The most common is the case of illite–smectite (I/S), kaolinite-smectite (K/S), and chlorite-vermiculite (Ch/V) (Caner, 2011; Abidi, 2015).

Table 1 below gives the classification of the main groups of clay minerals (Wal et al., 2021; Tchieno Melataguia, 2016; Boucheta, 2017; Clauer, 2005).

2.2.7. Associated minerals

The clay minerals are linked to other non-phyllite compounds. The main ones are grouped in Table 2 (Tankpinou Kiki, 2016; Bouzidi, 2012).

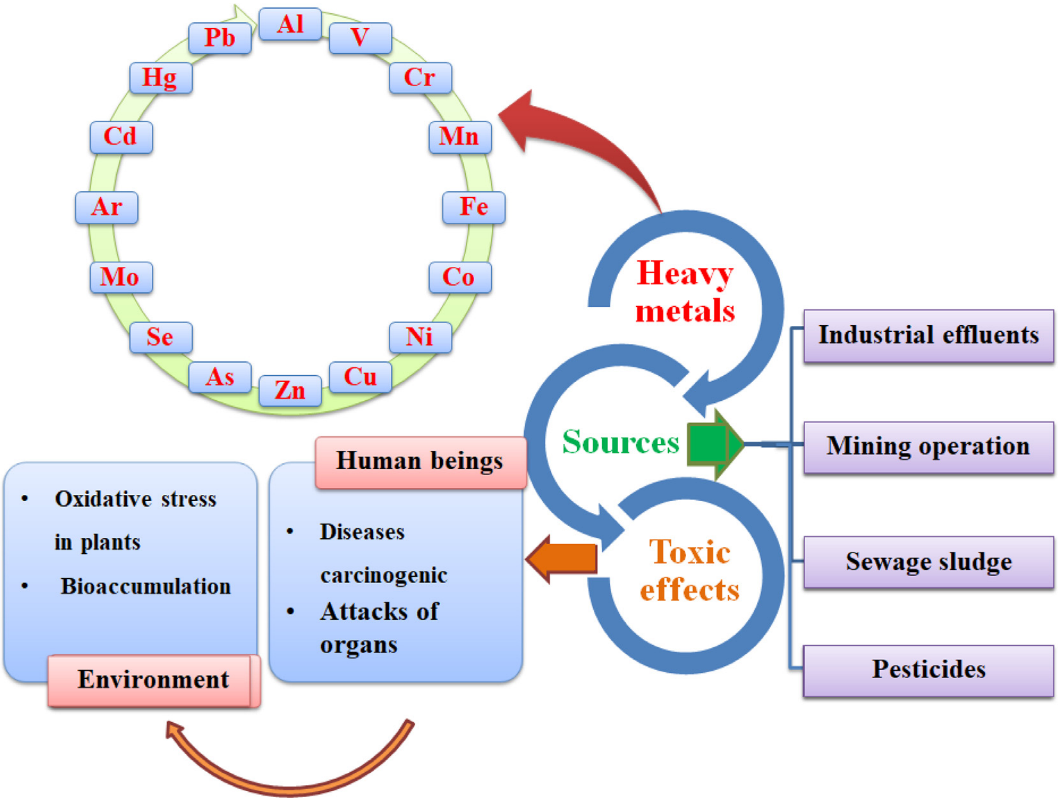


Fig. 8. Some sources and toxic effects of common heavy metals.

3. Physico-chemical properties of clays

Clay minerals are characterized by several properties that are related to their chemical composition, their structure and morphology, and also to the physical and chemical conditions in which they are found (Meziti, 2016). These properties can be physical or chemical, they are numerous and widely used for the characterization of clay minerals. The most fundamental important properties in the adsorption processes are the specific surface and the cationic exchange capacity (CEC) (Anouar et al., 2019; Zhang et al., 2021).

3.1. Clay surfaces charges

The majority of clay minerals are characterized mainly by a non-neutral electrical surface, which is due to both isomorphic substitutions and the environment, leading to two types of charges (Kouadri, 2018; Li et al., 2021).

- A permanent negative charge on the surface is related to ion substitution in the sheet. This is because the metal cation is replaced by another low-valence metal (Al^{3+} by Si^{4+} in the tetrahedral layer, Mg^{2+} or Fe^{2+} by Al^{3+} in the octahedral layer). These substitutions lead to a charge deficit which is compensated for outside the sheet by compensating cations such as Li^{+}, Na^{+}, Ca^{2+}, K^{+}, or Mg^{2+}.
- A variable charge depends on the pH of the medium. It can be positive or negative and is located at the edge of the sheets. In an acidic medium, positively charged species predominate, while in a basic medium, negatively charged species predominate.

3.2. Specific surface area

Clays and clay minerals have a small particle size and a complex porous structure with a large specific surface area relative to the volume of the particles, which allows strong physical and chemical interactions with dissolved species. These interactions are due to electrostatic repulsion, crystallinity, and specific adsorption or cation exchange reactions. The highly porous surface that has an attractive force suggests that the binding power will also be high (Uddin, 2017). The surface area of clays is greater than that of minerals of the same size but in different shapes, in addition to the relative surface area increasing with decreasing diameter (Velde, 1995).

The total surface includes the external surface, included between the clay particles, and the internal surface corresponding to the interfoliar space, except for the kaolinite group, which has only an external surface (Fig. 2a) (Mbuyi, 2012). The typical values of the surfaces of the main clay families are provided in Fig. 2b (Berthonneau, 2013).

3.3. Cation exchange capacity

One of the most important properties of clay minerals is their cation exchange capacity (CEC). Because of its negative structural charge, clay can reversibly fix some cations in aqueous solutions (Qlihaa et al., 2016). Substitutions of cations of different electrical charges then cause a loss of the electrical neutrality of the sheet. The stability of the crystal structure is then ensured by the presence of compensating cations in the interfoliar space. These ions adsorbed on the surface can be called “ions in exchangeable position”. They can be differentiated into two categories: those strongly bound to the surface like K^{+} ions and those easily exchangeable with the ions of the solution. The sum in milliequivalent per 100 g of clay of all the cations adsorbed on the surface of the clay is called: Cationic Exchange Capacity (CEC in meq/100 g). The CEC is then a measure of the capacity of the clay to exchange compensating cations, the most common (Li^{+}, Na^{+}, Ca^{2+}, K^{+}, or Mg^{2+}) (Bernard, 2022; Muhammed et al., 2021). The CEC is gener-

Table 5
Main characteristics and adsorption capacities of various natural clay adsorbents for the removal of heavy metals from wastewater.

Adsorbent	Heavy metals	pH	Dose	Concentration of M(II)	Time (min)	Equilibrium temperature	Adsorption capacity	Kinetic model	Adsorption isotherm	Specific surface area (m^2/g)	Ref
Moroccan natural clay from the Tangier - Tetouan - Al Hoceima region	Cd(II)	5.6	3 g/ 60 mL	100 mg/L	60	–	92 %	–	Langmuir and Freundlich	-	(Es-sahbany et al., 2021)
Moroccan natural clay from Chaouia	Cu(II)	5	0.02 g/ 40 mL	100 mg/L	90	Room temperature	48.24 mg g^{-1}	Pseudo-second order	Langmuir	-	(Barrak et al., 2021)
Pakistani silty clay from Baluchistan	Ni (II)	5	0.6 g	50 µg/L	60	318 K	3.603 mg g^{-1}	Pseudo-second order	Langmuir	-	(Samad et al., 2020)
	Cd (II)	7	0.4 g	50 µg/L	60	318 K	5.480 mg g^{-1}				
Moroccan natural clay from Sale	Cu (II)	8.5	–	100 ppm	85	–	86 %	–	Langmuir and Freundlich	-	(Es-sahbany et al., 2021)
	Co(II)	8			84		85.5%				
	Ni (II)	8			85		84 %				
	Pb (II)	8.5			83		85%				
Moroccan natural clay from the northern region	Ni(II)	4	6 g/L	140 mg/L	100	338 K	1.407 mg g^{-1}	Pseudo-second order	Freundlich	-	(Loutfi et al., 2021)
Tunisian natural clay from Jebel Chakir	Cr(III)	5	1 g/L	200 mg/L	120	(22 ± 3 °C)	179 mg g^{-1}	–	–	48.95	(Ghorbel-Abid and Trabelsi-Ayadi, 2015)
Moroccan natural clay from the river “Abu Burq”	Cd (II)	–	2 g/L	200 mg/L	10	(25 ± 2 °C)	5.65 mg g^{-1}	Pseudo-second order	–	-	(Es-said et al., 2021)
Ukrainian chamotte clay	Pb (II)	6	1 g	500 mg/L	24 h	Room temperature	11 mg g^{-1}	–	Langmuir	-	(Rakhym et al., 2020)
Moroccan natural clay from the Ouezzane region	Ni(II)	7	3.5 g	100 ppm	2 h	25 °C	2.4 mg g^{-1} (70–75%)	–	Freundlich and Langmuir	-	(Es-sahbany et al., 2019)
Romanian natural clay from Vladiceni	Pb(II)	7	4.0 g/L	0.40 mmol/L	10	(20 ± 2 °C)	0.098 mmol/g (97 %)	Pseudo-second order	Freundlich	-	(Azamfire et al., 2020)
	Hg(II)	2	4.0 g/L	0.40 mmol/L	10	(20 ± 2 °C)	0.059 mmol/g (55 %)				
Iraqi natural clay from Tagaran	Cd (II)	6	0.1 g	100 mg/L	100	20 °C	11.5 mg g^{-1}	Pseudo-second order	Langmuir and Freundlich	51.4	(Aziz et al., 2020)
Bentonite clay	Cr(III)	6	1 g/L	10 mg/L	90	25 °C	151,5 mg/g (95.21%)	Pseudo-second order	Freundlich	15.646	(Ahmadi et al., 2020)
	Cr(VI)	3					161.3 mg g^{-1} (95.74%)				
Algerian kaolin clay from Bordj Bou Arreridj region	Cu(II)	7	0.2 g	25 et 50 mg/L 100 mg/L	10 30	25 °C	52.63 mg g^{-1} (97.5%)	Pseudo-second order	Temkin	7.5	(Bahah et al., 2020)
	Pb(II)	7	0.2 g	25, 50 et 100 mg/L.	First minute at all concentrations	25 °C	57.30 mg g^{-1} (99.95%)				
Tunisian natural clay from Jebel El Aidoudi	Cd(II)	6	1 g/L	–	3 h	20 °C	21.93 mg g-1	–	Langmuir	86	(Khalfa et al., 2020)
	Zn(II)						20.86 mg g-1				
	Pb(II)						29.11 mg g-1				
	Cu(II)						22.30 mg g-1				
Algerian natural clay from El Menia	Pb(II)	5–6	1 g	10 mg/L	40	25° C	15.5 mg g-1	Pseudo-second order	Temkin	79.46	(Athman et al., 2020)
	Zn(II)						2.10 mg g-1		Langmuir		
	Cu(II)						7.35 mg g-1		Freundlich		
	Ni(II)				60		9.80 mg g-1		Freundlich		
Nigerian bentonite clay from Afuze	Fe(III)	6	0.05 g	88.52 mg/L	150	303 K	4.2 mg g-1	Pseudo-second	Langmuir	-	(Abdullahi et al., 2020)
	Zn(II)			3.276 mg/L			2.9 mg g-1				

(continued on next page)

Table 5 (*continued*)

Adsorbent	Heavy metals	pH	Dose	Concentration of M(II)	Time (min)	Equilibrium temperature	Adsorption capacity	Kinetic model	Adsorption isotherm	Specific surface area (m^2/g)	Ref
								order			
Commercial bentonite clay	Cr(VI)	2	0.04 g	58 ppm	60	25 °C	11.076 mg g^{-1}	–	Scatchard	-	(Altun, 2020)
Egyptian natural clay near the city of Minia	Cr(VI)	5	0.5 g/L	30 mg/L	90	298 K	7.0 mg g^{-1}	Pseudo-second order	Freundlich	34	(E. A. Ashour M. A. Tony, SN, , 2020)
Natural clay bentonite	Cu(II) Zn(II) Ni(II)	4.6	60 g/L	80 mg/L 13 mg/L 1 mg/L	–	27 ± 1 °C	99.9% 89.2% 99.9%	–	–	-	(Esmaeili et al., 2019)
Montmorillonite (MMT)	Ni(II) Cu(II)	2.4	0.1 g/L	100 mg/L	180	25 °C	12.89 mg g^{-1} 7.62 mg g-1	Pseudo-second order	Langmuir	699	(Gafoor Dhanasekar et al., 2021)
Egyptian natural clay from El-Hammam	Fe(II) Ni(II) Zn(II)	1.5	0.1 g	50 mg/L	60	25 ± 1 °C	5.74 mg g^{-1} 1.17 mg g^{-1} 4.33 mg g^{-1}	Pseudo-second order	Langmuir	-	(El-Maghrabi and Mikhail, 2014)
Saudi natural clay	Pb(II)	6.2	1 g/L	20 mg/L	1 h	–	166 mg g^{-1}	Pseudo-second order	Langmuir	28	(Abdel Ghafar et al., 2020)
Moroccan natural clay from the Marrakech region	Cd(II)	–	0.8 g	200 mg/L	120	–	5.25 mg g^{-1}	Pseudo-second order	Langmuir	23.07	(Abbou et al., 2021)

ally given only for a neutral pH. In addition, the CEC value can be determined by a simple test known as the methylene blue (MB) test (Yukselen and Kaya, 2008). Fig. 3 gives the CEC values for some clay families (Muhammed et al., 2021).

4. Industrial uses of clays

Clays and clay minerals are more and more used daily nowadays and are reasonably replacing metals in various fields as cheaper, more efficient, and more environmentally friendly alternatives (A. G. Olaremu, Chemistry Research Journal. 6, 157-168, 2021). Clay has a wide range of industrial uses (Table 3), high geological availability, and large reserves and production facilities. However, the ceramic industry is the main consumer of this raw material (Comin et al., 2021).

Clay materials are characterized by the presence of a significant proportion of fine phyllosilicate particles smaller than 2 µm (Barakan and Aghazadeh, 2021). Due to the sheet structure of these particles, clays are different from other powders used in ceramics. The high specific surface of these minerals and their platelet structure allow clays to form gels, colloidal suspensions, and especially plastic pasted with water (Zaccaron et al., 2021).

The production of silicate ceramics is largely based on this characteristic in that it facilitates the preparation of suspensions (homogeneous and stable) suitable for the casting of malleable pastes (easy to shape), as well as raw parts with good mechanical resistance (Sabatino et al., 2021).

Clays can be modified by different methods summarized in Fig. 10. The synthesis of natural clay-based composites improved electrochemical properties for applications in the field of energy storage and conversion (Lan et al., 2021). Fig. 4 and Table 3 present some uses of clays.

5. Removing organic and inorganic pollutants by raw clay

5.1. Removal of dyes with natural clays

Dyes are organic compounds, an assembly of chromophore groups (NR_2, NHR, NH_2, COOH, and OH), auxochromes (N_2, NO, and NO_2), and conjugated aromatic structures (benzene rings, anthracene, perylene, etc.) (Sakin Omer et al., 2018; Bouazza, 2019). Dyes can be divided into three categories according to their core structure: anionic dyes (acidic, reactive, and direct), non-ionic dyes (disperse), and cationic dyes (basic) (Sakin Omer et al., 2018; Elgarahy et al., 2021; Sharma et al., 2021). Fig. 6 shows the main dyes classified according to their application methods on different substrates (Jency et al., 2021; Benkhaya and rabet, 2020). They are widely used in various industries, such as printing, food, cosmetics, leather, paper, and textile industries. (Jency et al., 2021; Jiang et al., 2021; Wang et al., 2021). This industry will lead to excessive wastewater discharges of organic dyes, which are potentially toxic and cause serious pollution to the environment and human health (Sivakumar and Lee, 2022; Qin et al., 2021). The industries responsible for the presence of dye effluents in the environment are presented in Fig. 5 (Boukarma et al., 2021). During the weaving process, approximately 10–15% of the dye is released into the receiving aquatic environment, resulting in highly colored pollutants that are aesthetically unfavorable to the environment (Velusamy et al., 2021). However, most organic dyes are difficult to degrade under natural conditions due to their structural stability and high solubility (Benjelloun et al., 2021; Nath et al., 2018). Therefore, from an ecological and environmental point of view, it is very necessary to eliminate or minimize the concentration of these dyes in wastewater before discharging them into water bodies (Bisaria et al., 2021).

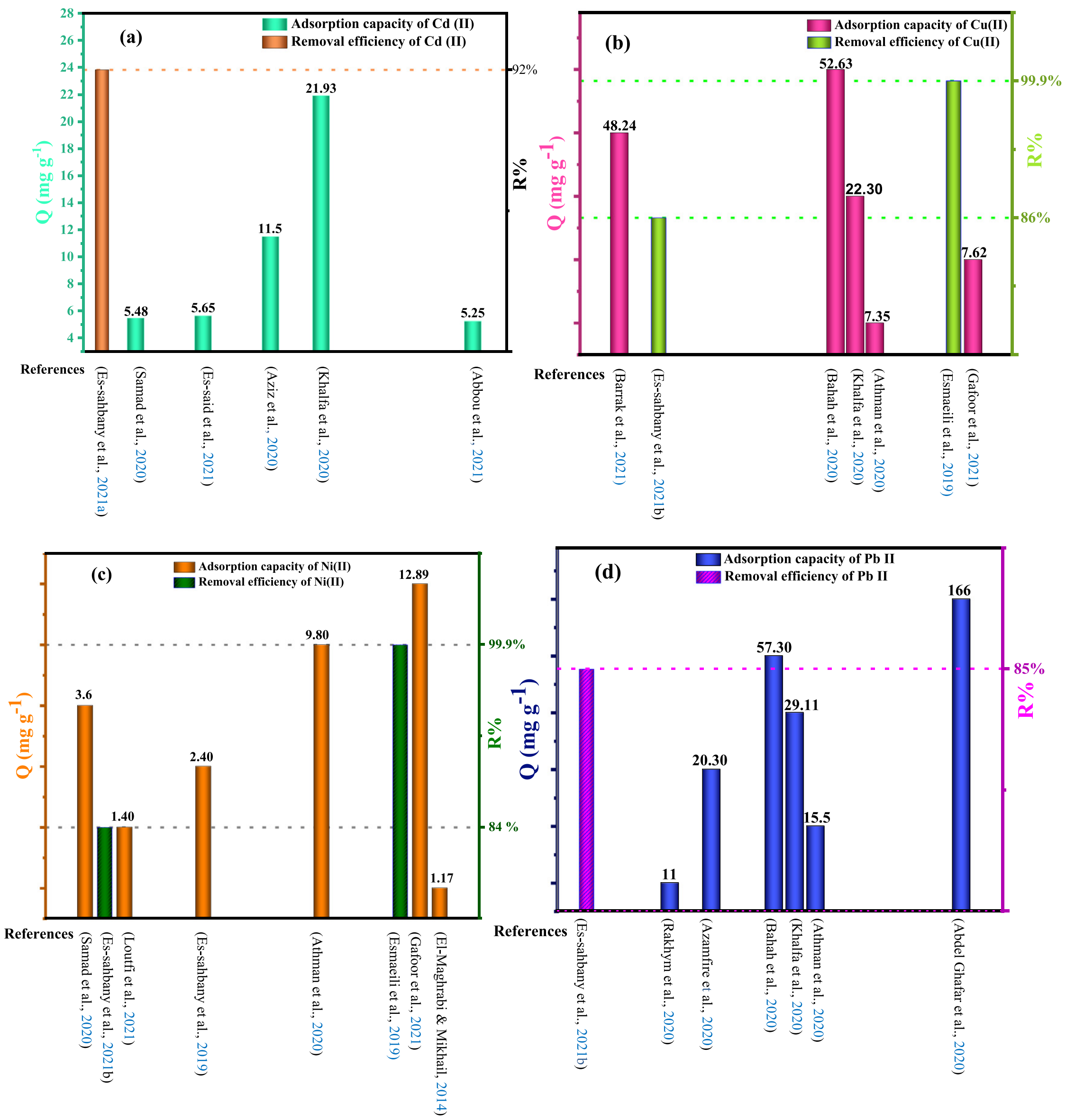


Fig. 9. Comparison of some natural clays for the removal of heavy metals, (a) Cadmium (Cd(II)), (b) Copper (Cu(II)), (c) Nickel (Ni(II)), (d) Lead (Pb(II)), (e) Zinc (Zn(II)), (f) Chromium (Cr(III) and Cr(VI)), (g) Iron ((II), Fe(III)), Mercury (Hg(II)) and Cobalt (Co(II)).

Currently, recent studies (Table 4) show that natural clay materials have some advantages in the adsorption of cationic and anionic dyes. The main characteristics and adsorption capacity of some natural clay adsorbents to remove different dyes in water at a laboratory scale are presented in Table 4.

The analysis of the studies reported in this review allowed us to note that the evaluation of the adsorption capacity of the natural clays for the elimination of the dyes must take into account several variables; the properties of the natural clay (specific surface, the capacity of cationic exchange CEC, the mineralogical composition, etc.). The size, shape, and type of the targeted dyes as well as the experimental conditions such as the pH, the dose of adsorbent, the initial concentration of adsorbate, the temperature, the contact time, etc. From the results of the table below, we can see that most of the studies concerned the removal of methylene blue dye (BM), one of the most abundant pollutants in the aquatic environment (Wang et al.,2021).

Fig. 7a summarizes the specific surface area values for natural clays, while Fig. 7b, Fig. 7c, and Fig. 7d show the adsorption capacities of BM and some cationic and anionic dyes, respectively.

Fig. 7b summarizes a comparison of the removal of the cationic dye BM by various natural clays. It is observed that Iranian natural clay studied by H. Aghdasi et al (Goswami et al., 2021) is characterized by the highest adsorption capacity of BM dye of 909.09 mg g^{-1}. M. Assimeddine et al (Aghdasinia and Asiabi, 2018) obtained the lowest adsorption capacity of 15.82 mg g^{-1} using natural Moroccan clay. Due to its large specific surface area and high affinity for MB, natural clay is a good adsorbent for MB removal (Assimeddine et al., 2020). In addition, some clays have a net negative charge, which gives them strong cationic adsorption properties (Rafatullah et al., 2010).

The highest specific surface area of the natural Turkish sepiolite clay is about 329.7 m^2/g with adsorption capacities of 649.37 mg g^{-1} for the anionic dye RD23 and 125 mg g^{-1} for the cationic dye BM (Guaya et al., 2021), while the lowest value of Iranian natural clay is about 12.85 m^2/g, and the adsorption capacities of JO cationic dye and BN anionic dye are 67.82 mg g^{-1} and 72.25 mg g^{-1}, respectively (Largo et al., 2020).

Furthermore, the results indicate that the most appropriate model for the adsorption kinetics of the majority of dyes (cationic

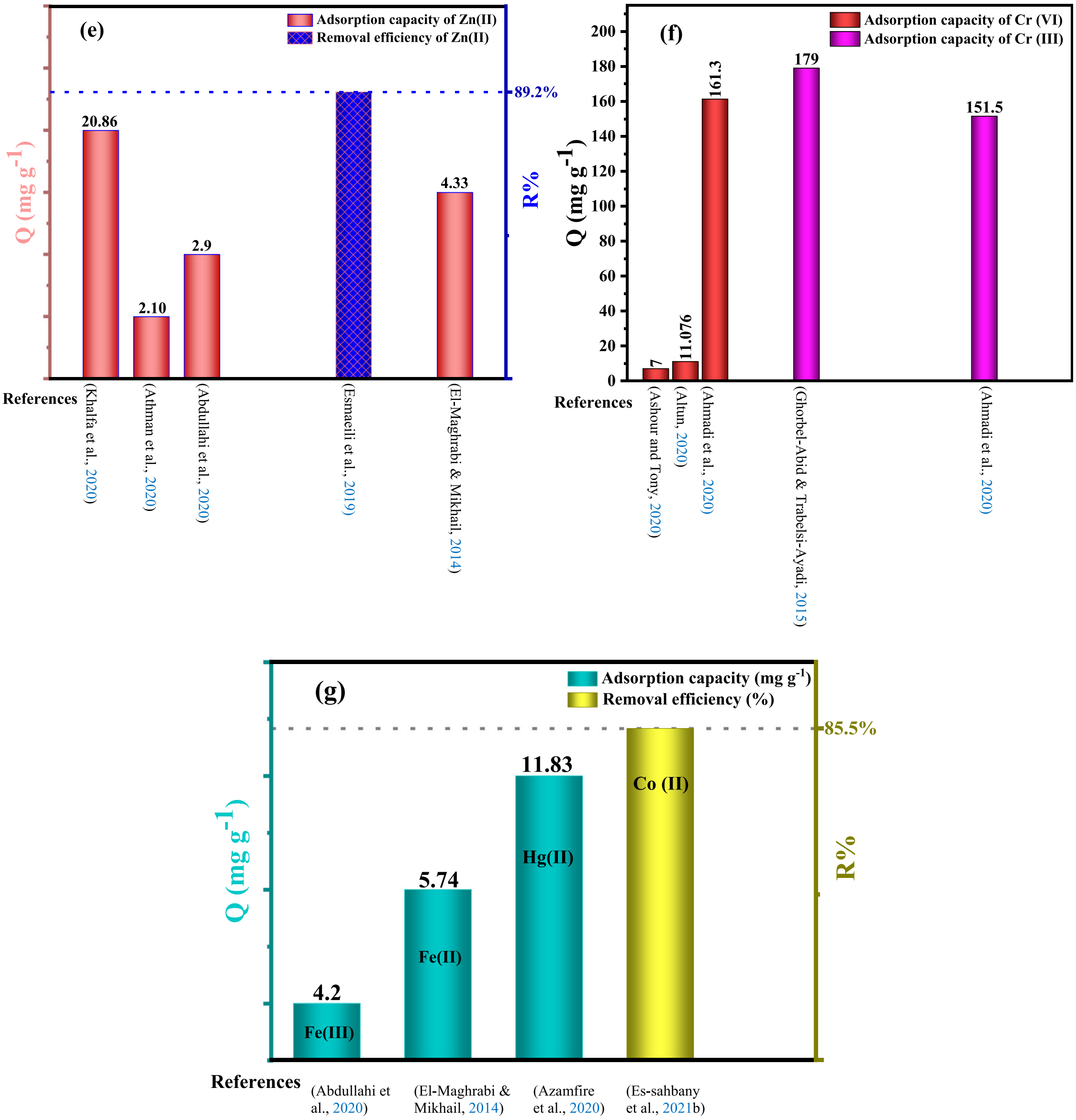


Fig. 9 (*continued*)

or anionic) is the pseudo-second-order model. Furthermore, the authors reported that the adsorption process follows the Langmuir isotherm (Table 4).

5.2. Heavy metals removal

Heavy metals are metallic elements that occur naturally and have a density greater than 5 g cm^{-3} (Briffa et al., 2020). The most common heavy metals are shown in Fig. 8 below and are widely recognized as bioaccumulative elements from various sources that hurt the environment and human health (Fig. 8) (Izydorczyk et al.,2021; Saravanan et al., 2021; Ait Ichou et al., 2020). The most toxic are chromium (Cr), manganese (Mn), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), mercury (Hg) and lead (Pb) (Saravanan et al., 2021). Some low concentrations of heavy metals play a very important role in the human body: The US Food and Drug Administration (FDA) recommends 0.9 mg day^{-1} of Cu, 0.5 mg day^{-1} of Ni, 0.05 to 0.2 mg day^{-1} of Cr, 8 to 11 mg day^{-1} of Zn, and 8 to 18 mg day^{-1} of Fe (U.s., 2001). Recent studies are grouped in Table 5 on the removal of heavy metals by adsorption using natural clay as an adsorbent.

From the recent research results summarized in Table 5 below, it can be seen that natural clay is capable of removing heavy metals to a great extent. Due to their strong tendency to form covalent bonds, clay minerals have a better affinity for heavy metals than alkali and alkaline earth cations (Gahlot et al., 2020). This power also depends on several parameters, namely the specific surface, the cationic exchange capacity (CEC) and the environmental conditions (pH of the solution, contact time, ionic strength, coexisting ions, dose of clay, initial concentration of heavy metals and temperature) (Mao and Gao, 2021). According to the results found, as shown in Table 5, the removal rates of Hg (II) ions by natural Romanian clay at pH = 4.6 and Ni (II) ions by natural bentonite at pH = 2 are 55% and 99.9%, respectively. Table 5 shows that the model best suited to the kinetics of heavy metal adsorption by natural clays is the pseudo-second-order model. Furthermore, the majority of heavy metals also obey the Langmuir isotherm.

Fig. 9 (a-g) shows the adsorption capacity (mg/g) or removal rate (%) of heavy metals listed in Table 6 by various natural clays.

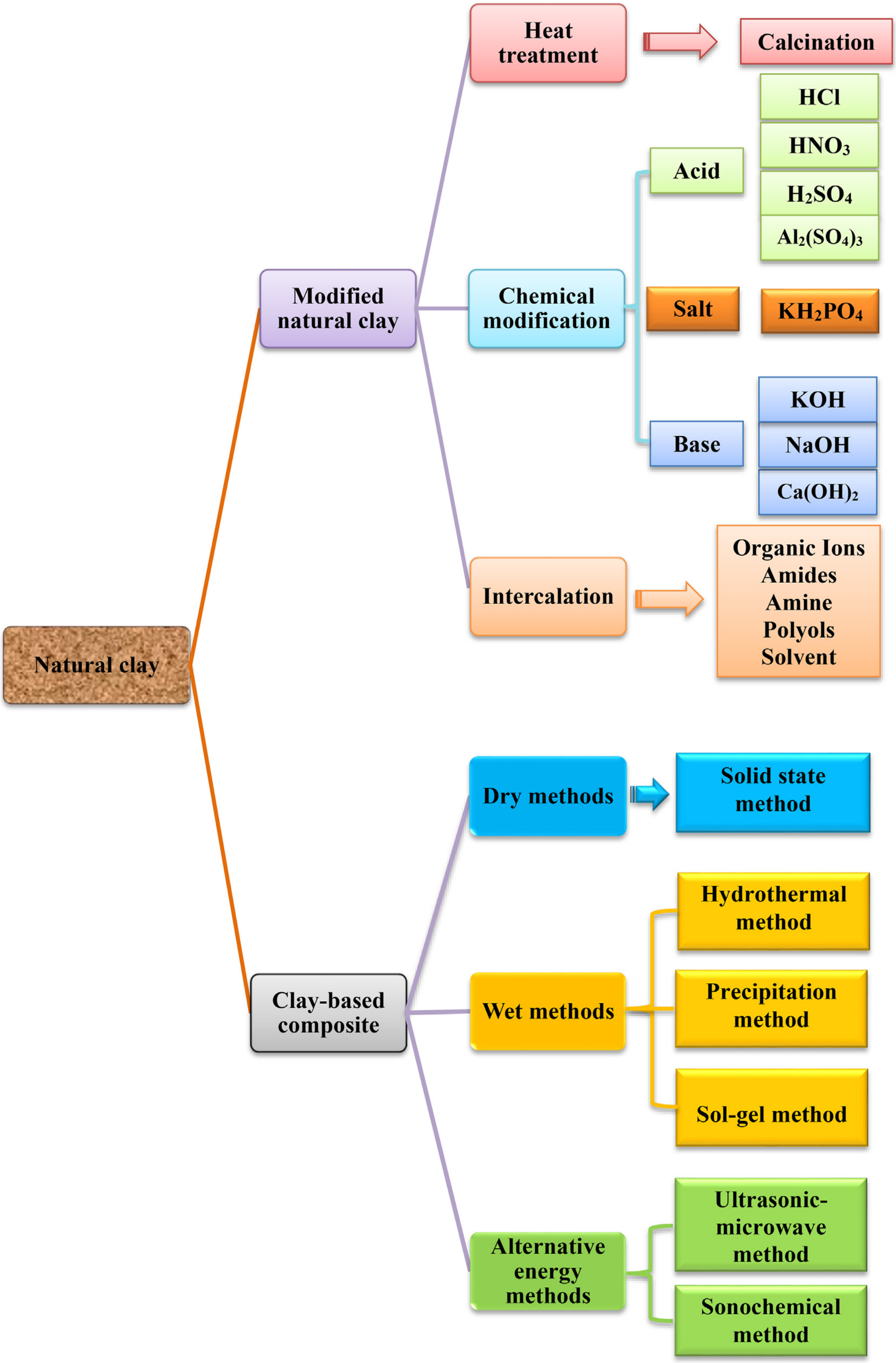


Fig. 10. Summary of different techniques for modifying natural clays.

6. Clay modification methods

Many researchers have demonstrated that natural clays have an exceptional ability to remove various toxic organic and inorganic pollutants (Table 4 and Table 5). However, to achieve better results, current research is directed towards the development of clay-based adsorbents with a high removal potential of various contaminants and a low cost. Recent experimental studies available in

Table 6
An overview of clay modification methods reported by various works of literature.

Natural Clay	**S_{BET} Clay Natural (m^2/g)**	**Adsorbate**	**Adsorption capacity/ efficiency (mg/g) (before Modification)**	**Modification/ methodes**	**S_{BET} Clay modifier (m^2/g)**	**Characterization**	**Adsorption capacity/ efficiency (mg/g) (after Modification)**	**Ref**
Chinese natural red clay from Gansu Province	57.34	MB TC	112.39 109.35	Hydrothermal reconstitution	353.63	XRD, SEM, FTIR, BET and XPS	215.68 209.6	(Wang et al., 2021)
Chinese natural red clay from Inner Mongolia	58.96	MB TC	85.79 93.19		348.13		226.40 230.2	
Iranian natural clay from Dashtestan, Bushehr province	–	Cr(VI)	63.69	Chitosan/Clay composite	–	FTIR, AFM, SEM, VSM, TEM and XRD	80.30	(Foroutan et al., 2020)
				Chemical deposition method Clay/Fe_3O_4	–		97.08	
				Chemical precipitation technique Chitosan /Clay/Fe_3O_4	–		117.64	
Clay industry Best Way Cement Hattar (Pakistan)	8.41	BFBN RFRN	25.05 15.90	Biocomposite of sodium-alginate with acidified clay	–	SEM, XRD, BET and TGA	25.41 18.97	(Kausar et al., 2020)
Moroccan natural clay from Agouraï city	51.4154	Phenol	10.01	Acidified clay (**Chemical activation**)	74.4397	XRF, XRD, SEM, BET and FTIR	15.11	(Dehmani et al., 2020)
Algerian halloysite from Eastern Region	64	CV	–	Halloysite was processed at 600 °C and then by acid leaching with HCl solutions of different concentrations H600-0 N	60.5	BET, FTIR, XRD, ICP-AES and BXFM	104.3	(Belkassa et al., 2021)
				H600-0.5 N	115.4		194.5	(Mellouk et al., 2009)
				H600-3 N	434.0		158.4	
				H600-5 N	503.3		145.5	
Moroccan natural clay from Chaouia (CH)	–	Cu(II)	48.24	Composite beads(CH@AL) (Sodium alginate solution + Clay solution) and stirred until hydrogel was obtained. Then was poured dropwise into 500 mL of 0.1 M $CaCl_2$ using a 50 mL syringe to form spherical beads, then left to harden in $CaCl_2$ solution, and finally washed three times and air dried.	–	XRD, SEM-EDX and TGA	92.44	(Barrak et al., 2021)
Tunisian natural clay	85	SLV	12.5	Acidified clay H_2SO_4-clay (6 h) (**Chemical activation**)	110	XRD, FTIR and SSA	15.45	(Chaari et al., 2021)
Raw clayKaolinite (KT)Montmorillonite (MT) Vermiculite (VT)	- - -	Ph	0–0.24	Zr-modified clay Zr2.48-KT Zr2.48-MT Zr2.48-VT incorporation of hydroxy complexes of zirconium (**dehydroxylation**)	- - -	XRD, SEM and zeta potential	9.58 15.50 9.74	(Huo et al., 2021)
Kaolinite	14	OTC	24	**Intercalation procedure** Methoxy-modified kaolinite Interlayer methoxy grafting of kaolinite was carried out through a reflux procedure.	14.75	XRD, FTIR, and XPS	36	(Ashiq et al., 2021)
Natural montmorillonite (Mt)	77	OG		**CTAB@Mt**	52	XRD, FTIR, BET, TGA/DTA, and SEM -EDS	169.6	(Ouachtak et al., 2021)

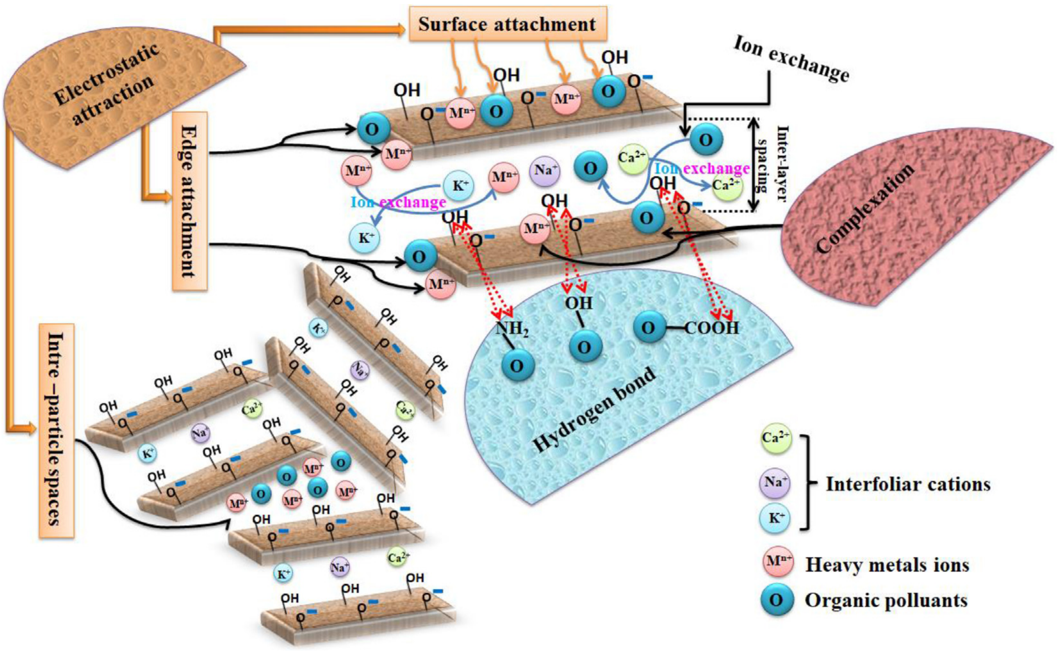


Fig. 11. Adsorption mechanism of dyes and heavy metals at different locations on the surface of the clay.

Table 7
Cost comparison of selected adsorbents.

Adsorbant	Total estimated cost of raw materials used for adsorption	Ref
Treated oil shale ash (TOSA)	$2.15\ (\$\ L^{-1})$	(Miyah et al., 2021)
Walnut shells (TWS)	$0.6968\ (\$\ L^{-1})$	(Benjelloun et al., 2022)
Peanut shells (TPS)	$0.6965\ (\$\ L^{-1})$ for [MB] = 1 kg/L	
Biocomposite hydrogel beads Alginate/Glutaraldehyde/Red Cabbage Extract	$3.17\ (\$\ kg^{-1})$	(Andreas et al., 2021)
Bentonite clays	$0.5–2.2\ (\$\ kg^{-1})$	
Graphene oxide (GO)	$3.31\ (\$\ g^{-1})$	(Rathour and Bhattacharya, 2018)
Crab Carapace Modified (CCM)	$0.561\ (\$\ kg^{-1})$ CCM	(Pap et al., 2020)
Biochar	$0.35–1.2\ \$\ kg^{-1}$	(Han et al., 2019)
Natural clays (montmorillonite, bentonite, etc)	$0.04\ \$\ kg^{-1}$	
Charbon actif	$1.8–2.1\ \$\ kg^{-1}$	
Phosphate natural	$0.078\ \$\ kg^{-1}$	(Hafdi et al., 2020)
Phosphate natural doped with nickel oxide (NP/NiO)	$5.988\ \$\ kg^{-1}$	
Chitosan	$16\ \$\ kg^{-1}$	(Momina et al., 2018)
Chitin	$10\ \$\ kg^{-1}$	

Table 6 below show that the adsorption capacity of natural clay can be improved after specific modifications, which consequently increase more adsorption sites and functional groups to adsorb different environmental pollutants (Barakan and Aghazadeh, 2021). The modification of natural clay is achieved by the use of acids, calcination, polymers or surfactants. These methods give a relatively high adsorption capacity compared to natural clay. For example, clay can be activated by sulfuric acid to increase its specific surface and pore volume. As shown by several authors, the specific surface can be increased from 16.29 m^2/g to 24.68 m^2/g and the pore volume from 0.056 $cm^3\ g^{-1}$ to 0.064 $cm^3\ g^{-1}$, which also leads to an increase in the adsorption capacity (Jedli et al., 2018). However, we have noticed that the texture of the modified clay does not change, because in the case of methoxy-modified kaolinite, the specific surface remains almost unchanged kaolinite and methoxy-modified kaolinite, respectively, 14.2 m^2/g and 14.75 m^2/g, but the pore volume and pore radius vary considerably (Ashiq et al., 2021; Yu et al., 2016).

Fig. 10 below summarizes some methods of activation and modification of natural clays, and Table 6 shows the effect of this modification on the adsorption capacity of various pollutants, as well as the characterization techniques used for raw and activated/modified clays.

7. Dye and heavy metal adsorption mechanisms on clay

The adsorption process is generally due to several physicochemical forces occurring at the adsorbent-adsorbate interface. The high adsorption performance of dyes and heavy metals obtained by clays could be explained by several adsorption mechanisms, such as electrostatic forces, van der Waals forces, hydrophobic interactions, hydrogen bonding, ion exchange, and pore filling. The predominant mechanisms controlling the adsorption of various pollutants by natural and active/modified clays are presented in Fig. 11 (Zhang et al., 2021; Han et al., 2019).

Based on the EDX and FTIR studies, Alorabi et al. (Alorabi et al., 2021) showed that the mechanism by which the cationic crystal violet dye CV was removed by two adsorbents (Saudi natural micro and nanoclays) was of the ion exchange type. Since they observed a

Table 8
Some methods of regeneration of natural or modified clays and recovery of dyes and heavy metals.

Adsorbent		Adsorbates (dyes and heavy metals)	Regeneration method and recovery	Ref
Moroccan muscovite clay		MB	- Thermal regeneration at 500 °C for 3 h, 86.92% recovery after 5 cycles	(Ssouni et al., 2023)
		CV	- Thermal regeneration at 500 °C for 3 h, 80.95% recovery after 5 cycles	
Tunisian Smectite Clay		CV	- With N_2 flow, 79.1% recovery after 5 cycles - With O_2/UV, 75.8% recovery after 5 cycles	(Hamza et al., 2018)
Moroccan natural clay		MB	Thermal regeneration at 500 °C for 3 h, about 60% recovery after 5 cycles	(El-Habacha et al., 2023)
Saudi natural red clay		MB	more than 95% recovery after 4 cycles	(Khan, 2020)
Moroccan natural Safiot clay		BB9	35% recovery after 8 cycles	(El Kassimi et al., 2020)
		BB41	28% recovery after 8 cycles	
Nigerian kaolinite clay	Treated with hydrochloric acid	Fe(III)	0.1 N HCl solution, 42.43 % recovery after 4 cycles	(Dim et al., 2021)
		Cr(VI)	0.1 N HCl solution, 48.54 % recovery after 4 cycles	
	Treated with acetic acid	Fe(III)	0.1 N HCl solution, 39.89 % recovery after 4 cycles	
		Cr(VI)	0.1 N HCl solution, 40.45 % recovery after 4 cycles	

decrease of K^+ and Ca^{2+} in both adsorbents, new peaks of N and C appeared in the EDX analytical spectra, and the positions of some peaks in the FTIR spectra were shifted after the adsorption of the CV dye. This confirmed the exchange of K^+ and Ca^{2+} cations by the CV molecules on the surface of the nanoclay. The OH bond peak also shifted to a lower frequency, indicating the formation of hydrogen bonds between the CV dye and the surfaces of both adsorbents.

Es-sahbany et al (Es-sahbany et al., 2022) explained the removal of many bivalent M^{2+} heavy metal ions (Cu^{2+}, Co^{2+}, Pb^{2+}, and Ni^{2+}) by two adsorption mechanisms: electrostatic attraction and ion exchange. The first one depends on the pH of the aqueous solution, so at low pH, the aqueous solution is rich in hydrogen ions H^+, which compete with metal ions M^{2+} for adsorption sites, limiting the removal of metal ions. Under high pH conditions, OH-adsorbed hydroxyl ions on the clay surface can combine with M^{2+} ions to improve removal efficiency, supporting the electrostatic attraction mechanism. The second relies on naturally occurring cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) in the clay structure, which are exchangeable and can be replaced by M^{2+} heavy metal ions.

Khan et al (Khan et al., 2021) prepared a nanocomposite (chitosan/alginate/modified clay) as an adsorbent for the removal of cationic (methylene blue, BM) and anionic dyes (acid black 172, AN-172) and Cr (VI). They showed that the adsorption of dyes and metal ions on the nanocomposite occurred rapidly, mainly through electrostatic interaction between the adsorbent and the adsorbate, which they confirmed by FTIR analysis before and after the adsorption process, where the peaks of the adsorbent are shifted after the adsorption of Cr (VI). The C-N peaks of the BM adsorbate and the COO peak of the adsorbent were weakened after adsorption due to the charge neutralization between the N^+ group of BM and the COO group of the adsorbent. Similarly, they explained the electrostatic interaction between the sulfonate group of AB-172 and the amino group of the adsorbent by the charge neutralization in which the peaks of the amino and sulfonate groups were weakened, and the appearance of a new peak was responsible for the formation of SO^{3-} and NH^{3+} by the ionization of the moieties (amino and sulfonate) in water.

8. Clay adsorbent cost comparison

Finding the best low-cost adsorbents capable of removing certain pollutants from water is the subject of many researchers. Many factors control the cost of different adsorbents, such as availability, source, synthesis method, processing conditions, recycling, and stability. Inexpensive adsorbents (mainly natural clays and waste materials) can be modified to increase their adsorption capacity. Efforts can be made to perform a risk assessment, a comparative analysis of the costs associated with the removal of contaminants from water by adsorption. Table 7 below summarizes the comparative cost of different adsorbents.

A comparison of cost estimates for a number of adsorbents compared with natural clays used in recent studies, as shown in Table 7, shows that natural clays are less expensive and also represent a remarkable potential for remove organic and inorganic pollutants.

9. Regeneration

Regeneration is an important parameter in evaluating the efficiency of an adsorbent suitable for practical applications. It is defined as the recycling or recovery of the sorbent and is crucial in terms of economic sustainability. In addition, the removal of the pollutant-laden adsorbent becomes a secondary pollution problem. Several methods of adsorbent regeneration have been used, including thermal regeneration, chemical regeneration, steam regeneration, pressure swing regeneration, vacuum regeneration, microwave regeneration, ultrasonic regeneration, gamma irradiation, electrochemical and biological regeneration. The regeneration process depends on several parameters such as pH, temperature, time, and cycles required for the treatment. These must be taken into account for the efficient regeneration of the adsorbent. The regeneration of clays is essential in the fight against organic and inorganic pollution, the cost being an important parameter for the development of new adsorbents (Jain et al., 2021). In the case of clays, chemical treatment is widely used because of its low cost and speed of the process, despite its disadvantages of destroying the surface properties of the adsorbent and producing oxidized sludge (Abdullah et al., 2019). Table 8 summarizes some recent studies on the regeneration of clay adsorbents.

10. Conclusion

Clays are hydrated aluminosilicates of lamellar structure. In nature, clay minerals are often associated with other non-clay substances that can be crystallized (carbonates, quartz, sulfates, organic matter, etc.) or amorphous (amorphous iron hydroxides, silica gels). Due to their physicochemical properties of a high specific surface, swelling, and cation exchange capacity (CEC), clay minerals have very important properties and are widely used in many industrial sectors. In the field of water pollution control, according to various studies reported in this review, different types of natural clay are very effective as adsorbents to remove various types of dyes and heavy metals. According to several studies the illustrated results show that, activated or modified clays have a higher adsorption capacity than raw clays. Therefore, improving the performance of natural clay adsorbents by different modification methods is essential for industrial applications. However, the cost is indeed an important parameter for the comparison and selection of adsorbents. The evaluation of the adsorption capacity of natural clays for the removal of dyes and heavy metals must take into account the properties of the natural clay, the size, nature and shape of the targeted pollutants, the surface defrents modifications performed, as well as the experimental operating conditions. The adsorption mechanism of dyes and heavy metals is mainly related to the specific surface area, ion exchange capacity, electrostatic interactions, hydrogen bonds, and Van Der Waals forces. Raw clays or activated/modified can be regenerated and reused for the adsorption of dyes and heavy metals. For all these points, natural clays, raw or modified, can be considered as good potential adsorbents, less costly and efficient for the elimination of pollutants in wastewater.

CRediT authorship contribution statement

Mohamed El-Habacha: Writing – original draft, review and editing, **Youssef Miyah:** Review and editing and revision, **Salek Lagdali:** Review and editing, **Guellaa Mahmoudy:** Review and editing, **Abdelkader Dabagh:** Review and editing, **Mohamed Chiban:** Review and editing, **Fouad Sinan:** Critical feedback and revision, **Soulaiman Iaich:** Co-supervision, Writing – original draft, **Mohamed Zerbet:** Supervision, Writing – original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

Abbou, B., Lebkiri, I., Ouaddarı, H., Elkhattabi, O., Habsaouı, A., Lebkırı, A., Rıfı, E.H., 2021. Journal of the Turkish Chemical Society Section A: Chemistry. 8, 677–692 10.18596/jotcsa.882016.

Abdel Ghafar, H.H., Radwan, E.K., El-Wakeel, S.T., 2020. ACS Omega 5, 6834–6845. https://doi.org/10.1021/acsomega.0c00166.

Abdullah, N.H., Shameli, K., Abdullah, E.C., Abdullah, L.C., 2019. Compos. B Eng. 162, 538–568. https://doi.org/10.1016/j.compositesb.2018.12.075.

Abdullahi, A., Ighalo, J., Ajala, O., AyiKa, S., 2020. Chemical Society Section A: Chemistry., 727–744 https://doi.org/10.18596/jotcsa.703913.

Abidi, N., Duplay, J., Jada, A., Errais, E., Ghazi, M., Semhi, K., Trabelsi-Ayadi, M., 2019. C. R. Chim. 22, 113–125. https://doi.org/10.1016/j.crci.2018.10.006.

Abidi, N. 2015. PhD Thesis. https://tel.archives-ouvertes.fr/tel-01222041.

Aghdasinia, H., Asiabi, H.R., 2018. Environ. Earth Sci. 77, 218. https://doi.org/10.1007/s12665-018-7342-5.

Ağtaş, M., Dilaver, M., Koyuncu, İ., 2021. Water Sci. Technol. 84, 1059–1078. https://doi.org/10.2166/wst.2021.290.

Ahmadi, A., Foroutan, R., Esmaeili, H., Tamjidi, S., 2020. Environ. Sci. Pollut. Res. 27, 14044–14057. https://doi.org/10.1007/s11356-020-07756-x.

Ait Ichou, A., Benhiti, R., Abali, M., Dabagh, A., Chiban, M., Zerbet, M., Carja, G., Sinan, F., 2020. Desalin. Water Treat. 178, 193–202. https://doi.org/10.5004/dwt.2020.24952.

Akowanou, A. V. O., Aïna, M. P., Groendijk, L., Yao, K. B., 2016. HAL. 72. https://hal.archives-ouvertes.fr/hal-03160019.

Alengebawy, A., Abdelkhalek, S.T., Qureshi, S.R., Wang, M.Q., 2021. Toxics. 9, 42 10.3390/toxics9030042.

Ali, M.A., Ahmed, H.A.M., Ahmed, H.M., Hefni, M., 2021. Appl. Sci. 11, 11357. https://doi.org/10.3390/app112311357.

Alorabi, A.Q., Hassan, M.S., Alam, M.M., Zabin, S.A., Alsenani, N.I., Baghdadi, N.E., 2021. Nanomaterials 11, 2789. https://doi.org/10.3390/nano11112789.

Aloulou, W., Aloulou, H., Khemakhem, M., Duplay, J., Daramola, M.O., Ben Amar, R., 2020. Environ. Technol. Innov. 18, 10.1016/j.eti.2020.100794 100794.

Altun, T., 2020. J. Chil. Chem. Soc. 65, 4790–4797. https://doi.org/10.4067/S0717-97072020000204790.

Amari, A., Gannouni, H., Khan, M., Almesfer, M., Elkhaleefa, A., Gannouni, A., 2018. Appl. Sci. 8, 2302. https://doi.org/10.3390/app8112302.

Ambika, S., Srilekha, V., 2021. Environmental Advances. 4,. https://doi.org/10.1016/j.envadv.2021.100072 100072.

Amrhar, O., Berisha, A., El Gana, L., Nassali, H., Elyoubi, M.S., 2021. Int. J. Environ. Anal. Chem. 1–26. https://doi.org/10.1080/03067319.2021.1897119.

Andreas, A., Winata, Z.G., Santoso, S.P., Angkawijaya, A.E., Yuliana, M., Edi Soetaredjo, F., Ismadji, S., Yi Hsu, H., Woo Go, A., Ju, Y.H., 2021. J. Mol. Liq. 329,. https://doi.org/10.1016/j.molliq.2021.115579 115579.

Anouar, F., Elmchaouri, A., Taoufik, N., Rakhila, Y., 2019. J. Environ. Chem. Eng. 7,. https://doi.org/10.1016/j.jece.2019.103404 103404.

Antonelli, R., Malpass, G.R.P., da Silva, M.G.C., Vieira, M.G.A., 2020. J. Environ. Chem. Eng. 8,. https://doi.org/10.1016/j.jece.2020.104553 104553.

Aoun, M. 2016. PhD thesis, University of the Mentouri brothers of Constantine.

Arslan, V., 2021. Physicochem. Probl. Miner. Process. 57, 97–111 10.37190/ppmp/135749.

Ashiq, A., Walpita, J., Vithanage, M., 2021. Chemosphere 276,. https://doi.org/10.1016/j.chemosphere.2021.130079 130079.

Ashour, E.A., Tony, M.A., 2020. SN Appl. Sci. 2, 2042. https://doi.org/10.1007/s42452-020-03873-x.

Assimeddine, M., Abdennouri, M., Barka, N., Rifi, E., Sadiq, M., 2020. J. Environ. Treat. Tech. 8, 1258–1267 10.47277/JETT/8(3)1267.

Athman, S., Sdiri, A., Boufatit, M., 2020. Int J Environ Res. 14, 1–14. https://doi.org/10.1007/s41742-019-00232-6.

Awual, M.R., Hasan, M.M., Islam, A., Rahman, M.M., Asiri, A.M., Khaleque, M.A., Sheikh, M.C., 2019. J. Clean. Prod. 228, 778–785. https://doi.org/10.1016/j.jclepro.2019.04.280.

Azamfire, B., Bulgariu, D., Bulgariu, L., 2020. Rev. Chim. 71, 37–47 10.37358/RC.20.7.8223.

Aziz, B.K., Shwan, D.M.S., Kaufhold, S., 2020. Environ. Sci. Pollut. Res. 27, 38384–38396. https://doi.org/10.1007/s11356-019-06995-x.

Bahah, S., Nacef, S., Chebli, D., Bouguettoucha, A., Djellouli, B., New, A., 2020. Arab. J. Sci. Eng. 45, 205–218. https://doi.org/10.1007/s13369-019-03985-6.

Barakan, S., Aghazadeh, V., 2021. Environ. Sci. Pollut. Res. 28, 2572–2599. https://doi.org/10.1007/s11356-020-10985-9.

Barrak, I., Ayouch, I., Kassab, Z., El Achaby, M., Barhoun, A., Draoui, K., 2021. Mater. Today:. Proc. https://doi.org/10.1016/j.matpr.2021.07.392.

Belkassa, K., Khelifa, M., Batonneau-Gener, I., Marouf-Khelifa, K., Khelifa, A., 2021. J. Hazard. Mater. 415,. https://doi.org/10.1016/j.jhazmat.2021.125656 125656.

Benhiti, R., Ait Ichou, A., Zaghloul, A., Aziam, R., Carja, G., Zerbet, M., Sinan, F., Chiban, M., 2020. Synthesis, Environ Sci Pollut Res. 27, 45767–45774. https://doi.org/10.1007/s11356-020-10444-5.

Benjelloun, M., Miyah, Y., Akdemir Evrendilek, G., Zerrouq, F., Lairini, S., 2021. Arab. J. Chem. 14,. https://doi.org/10.1016/j.arabjc.2021.103031 103031.

Benjelloun, M., Miyah, Y., Bouslamti, R., Nahali, L., Mejbar, F., Lairini, S., 2022. Chemistry Africa. 375–393. https://doi.org/10.1007/s42250-022-00328-1.

Benkhaya, S., M' rabet, S., El Harfi, A., 2020. Inorg. Chem. Commun. 115,. https://doi.org/10.1016/j.inoche.2020.107891 107891.

Bentahar, S., Dbik, A., Khomri, M.E., Messaoudi, N.E., Lacherai, A., 2017. J. Environ. Chem. Eng. 5, 5921–5932. https://doi.org/10.1016/j.jece.2017.11.003.

Bentahar, Y., Draoui, K., Hurel, C., Ajouyed, O., Khairoun, S., Marmier, N., 2019. J. Afr. Earth Sc. 154, 80–88. https://doi.org/10.1016/j.jafrearsci.2019.03.017.

Bernard, E., 2022. RILEM Technical Letters. 7, 47–57 10.21809/rilemtechlett.2022.162.

Berthonneau, J. 2013. PhD thesis, University of Aix-Marseille. https://tel.archives-ouvertes.fr/tel-00958572.

Bingül, Z., 2022. J. Mol. Struct. 1250,. https://doi.org/10.1016/j.molstruc.2021.131729 131729.

Bisaria, K., Sinha, S., Singh, R., Iqbal, H.M.N., 2021. Chemosphere 284,. https://doi.org/10.1016/j.chemosphere.2021.131263 131263.

Bouazza, F., 2019. Abou-Bekr Belkaid - Tlemcen. PhD thesis.

Boucheta, A. 2017. PhD Thesis, University Djillali Liabes, Faculty of Sciences Sidi Bel Abbes.

Boukarma, L., Aziam, R., Baroud, S., Eddaoudi, E., Sinan, F., Sadki, I., Tahrouch, S., Chiban, M., 2021. E3S Web Conf. 240, 02004. https://doi.org/10.1051/e3sconf/202124002004.

Boutaleb, N., Chouli, F., Benyoucef, A., Zeggai, F.Z., Bachari, K., 2021. Polym. Compos. 42, 1648–1658. https://doi.org/10.1002/pc.25941.

Bouzidi, N. 2012. PhD thesis, Ecole Nationale Supérieure des Mines de Saint-Etienne. https://tel.archives-ouvertes.fr/tel-00847400.

Briffa, J., Sinagra, E., Blundell, R., 2020. Heliyon. 6, e04691.

Buruga, K., Song, H., Shang, J., Bolan, N., Jagannathan, T.K., Kim, K.-H., 2019. J. Hazard. Mater. 379,. https://doi.org/10.1016/j.jhazmat.2019.04.067 120584.

Caner, L. 2011. PhD thesis, University of Poitiers. (2011). https://tel.archives-ouvertes.fr/tel-00605819.

Cao, G., Gao, M., Shen, T., Guo, S., Zhao, B., Zhao, Q., 2020. Colloids Surf A Physicochem Eng Asp 596,. https://doi.org/10.1016/j.colsurfa.2020.124735 124735.

Chaari, I., Moussi, B., Jamoussi, F., 2015. J. Alloy. Compd. 647, 720–727. https://doi.org/10.1016/j.jallcom.2015.06.142.

Chaari, I., Fakhfakh, E., Medhioub, M., Jamoussi, F., 2019. J. Mol. Struct. 1179, 672–677. https://doi.org/10.1016/j.molstruc.2018.11.039.

Chaari, I., Medhioub, M., Jamoussi, F., Hamzaoui, A.H., 2021. J. Mol. Struct. 1223,. https://doi.org/10.1016/j.molstruc.2020.128944 128944.

Chalouati, Y., Mannai, F., Bennour, A., Srasra, E., 2021. Int. J. Appl. Ceram. Technol. 18, 2323–2335. https://doi.org/10.1111/ijac.13713.

Clauer, N., 2005. Chemical news. 285–86, 93–98.

Comin, A.B., Zaccaron, A., Nandi, V. de S., Inocente, J.M., Muller, T.G., Peterson, M., 2021. Int. J. Appl. Ceram. Technol. 18, 1814–1824. https://doi.org/10.1111/ijac.13749.

Dabagh, A., Abali, M., Ait Ichou, A., Benhiti, R., Sinan, F., Zerbet, M., 2022. J. Dispers. Sci. Technol. 1–10. https://doi.org/10.1080/01932691.2022.2093215.

de Araújo, T.P., Tavares, F. de O., Vareschini, D.T., Barros, M.A.S.D., 2021. Environ. Technol. 42, 2925–2940 10.1080/09593330.2020.1718217.

Dehmani, Y., Sellaoui, L., Alghamdi, Y., Lainé, J., Badawi, M., Amhoud, A., Bonilla-Petriciolet, A., Lamhasni, T., Abouarnadasse, S., 2020. J. Mol. Liq. 312,. https://doi.org/10.1016/j.molliq.2020.113383 113383.

Delavernhe, L. 2012. PhD thesis, University of Nantes. https://tel.archives-ouvertes.fr/tel-00671340.

Diagboya, P.N., Olu-Owolabi, B.I., Mtunzi, F.M., Adebowale, K.O., 2020. Surf. Interfaces 19,. https://doi.org/10.1016/j.surfin.2020.100506 100506.

Dim, P.E., Mustapha, L.S., Termtanun, M., Okafor, J.O., 2021. Arab. J. Chem. 4,. https://doi.org/10.1016/j.arabjc.2021.103064 103064.

Doltade, S.B., Yadav, Y.J., Jadhav, N.L., 2022. South African Journal of Chem. Eng. 40, 100–106. https://doi.org/10.1016/j.sajce.2022.02.004.

Dondi, M., García-Ten, J., Rambaldi, E., Zanelli, C., Vicent-Cabedo, M., 2021. Resour. Conserv. Recycl. 168,. https://doi.org/10.1016/j.resconrec.2020.105271 105271.

El Haouti, R., Ouachtak, H., El Guerdaoui, A., Amedlous, A., Amaterz, E., Haounati, R., Ait Addi, A., Akbal, F., El Alem, N., Labd Taha, M., 2019. J. Mol. Liq. 290,. https://doi.org/10.1016/j.molliq.2019.111139 111139.

El Kassimi, A., Boutouil, A., El Himri, M., Rachid Laamari, M., El Haddad, M., 2020. J. Saudi Chem. Soc. 24, 527–544. https://doi.org/10.1016/j.jscs.2020.05.005.

El Kassimi, A., Achour, Y., El Himri, M., Laamari, R., El Haddad, M., 2021. Int. J. Environ. Anal. Chem. 1–22. https://doi.org/10.1080/03067319.2021.1873306.

El Kassimi, A., Achour, Y., El Himri, M., Laamari, M.R., El Haddad, M., 2021. Biointerface Res Appl Chem. 11, 12717–12731 10.33263/BRIAC115.1271712731.

El-Gaayda, J., Titchou, F.E., Oukhrib, R., Yap, P.S., Liu, T., Hamdani, M., Akbour, R.A., 2021. J. Environ. Chem. Eng. 9,. https://doi.org/10.1016/j.jece.2021.106060 106060.

Elgarahy, A.M., Elwakeel, K.Z., Mohammad, S.H., Elshoubaky, G.A., 2021. Cleaner Engineering and Technology. 4,. https://doi.org/10.1016/j.clet.2021.100209 100209.

El-Habacha, M., Dabagh, A., Lagdali, S., Miyah, Y., Mahmoudy, G., Sinan, F., Chiban, M., Iaich, S., Zerbet, M., 2023. Environ. Sci. Pollut. Res. 101007/s11356-023-27413-3.

El-Maghrabi, H.H., Mikhail, S., 2014. J. Environ. Earth Sci. 4, 38–46.

Esmaeili, A., Mobini, M., Eslami, H., 2019. Appl Water Sci 9, 97. https://doi.org/10.1007/s13201-019-0977-x.

Es-sahbany, H., Berradi, M., Nkhili, S., Hsissou, R., Allaoui, M., Loutfi, M., Bassir, D., Belfaquir, M., El Youbi, M.S., 2019. Mater. Today:. Proc. 13, 866–875. https://doi.org/10.1016/j.matpr.2019.04.050.

Es-sahbany, H., El Hachimi, M.L., Hsissou, R., Belfaquir, M., Es-sahbany, K., Nkhili, S., Loutfi, M., Elyoubi, M.S., 2021. Mater. Today:. Proc. 45, 7299–7305. https://doi.org/10.1016/j.matpr.2020.12.1102.

Es-sahbany, H., Hsissou, R., El Hachimi, M.L., Allaoui, M., Nkhili, S., Elyoubi, M.S., 2021. Mater. Today:. Proc. 45, 7290–7298. https://doi.org/10.1016/j.matpr.2020.12.1100.

Es-sahbany, H., El Yacoubi, A., El Hachimi, M.L., Boulouiz, A., Chafik El Idrissi, B., El Youbi, M.S., 2022. Materials Today: Materials Today: Proceedings. 58, 1162–1168. https://doi.org/10.1016/j.matpr.2022.01.301.

Es-said, A., Nafai, H., Lamzougui, G., Bouhaouss, A., Bchitou, R., 2021. Scientific African. 13, e00960.

Esvandi, Z., Foroutan, R., Peighambardoust, S.J., Akbari, A., Ramavandi, B., 2020. Surf. Interfaces 21,. https://doi.org/10.1016/j.surfin.2020.100754 100754.

Eswaran, S.G., Narayan, H., Vasimalai, N., 2021. Biocatal. Agric. Biotechnol. 36,. https://doi.org/10.1016/j.bcab.2021.102140 102140.

Ethaib, S., Zubaidi, S.L., 2020. IOP Conf. Ser.: Mater. Sci. Eng. 928,. https://doi.org/10.1088/1757-899X/928/2/022030 022030.

Eyankware, M.O., Ogwah, C., Ike, J.C., 2021. RE. 3 10.30564/re.v3i2.3057.

Fabryanty, R., Valencia, C., Soetaredjo, F.E., Putro, J.N., Santoso, S.P., Kurniawan, A., Ju, Y.H., Ismadji, S., 2017. Journal of Environmental Chemical Engineering. 5, 5677–5687. https://doi.org/10.1016/j.jece.2017.10.057.

Fernandes, J.V., Rodrigues, A.M., Menezes, R.R., Neves, G. de A., 2020. Materials. 13, 3600. https://doi.org/10.3390/ma13163600.

Foroutan, R., Peighambardoust, S.J., Mohammadi, R., Omidvar, M., Sorial, G.A., Ramavandi, B., 2020. Int. J. Biol. Macromol. 151, 355–365. https://doi.org/10.1016/j.ijbiomac.2020.02.202.

Gafoor Dhanasekar, A., Sathees Kumar, Sankaran, Sivaranjani, Sabeena Begum, Zunaithur Rahman, 2021. Materials Today: Proceedings. 37, 2033 2040. https://doi.org/10.1016/j.matpr.2020.07.500.

Gahlot, R., Taki, K., Kumar, M., 2020. Environmental Nanotechnology Monitoring & Management. 14,. https://doi.org/10.1016/j.enmm.2020.100339 100339.

Gamoudi, S., Srasra, E., 2018. Appl. Clay Sci. 165, 17–21. https://doi.org/10.1016/j.clay.2018.07.042.

García-Villén, F., Ruiz-Alonso, S., Lafuente-Merchan, M., Gallego, I., Sainz-Ramo, M., Saenz-del-Burgo, L., Pedraz, J.L., 2021. Pharmaceutics. 13, 1806. https://doi.org/10.3390/pharmaceutics13111806.

Ghorbel-Abid, I., Trabelsi-Ayadi, M., 2015. Arab. J. Chem. 8, 25–31. https://doi.org/10.1016/j.arabjc.2011.02.030.

Goswami, B., Das, C., Mahanta, D., 2021. J. Storage Mater. 44. https://doi.org/10.1016/j.est.2021.103429.

Grema, A.S., Idriss, I.M., Alkali, A.N., Ahmed, M.M., Iyodo, M.H., 2021. European Journal of Engineering and Technology Research. 6 10.24018/ejeng.2021.6.7.2623.

Grine, O., Moussi, B., Hajjaji, W., Pilate, P., Yans, J., Jamoussi, F., 2021. Arab. J. Geosci. 14, 1595. https://doi.org/10.1007/s12517-021-08099-8.

Guaya, D., Jiménez, R., Sarango, J., Valderrama, C., Cortina, J.L., 2021. J. Water Process Eng. 43,. https://doi.org/10.1016/j.jwpe.2021.102274 102274.

Hafdi, H., Joudi, M., Mouldar, J., Hatimi, B., Nasrellah, H., El Mhammedi, M.A., Bakasse, M., 2020. Environ. Res. 184,. https://doi.org/10.1016/j.envres.2020.109322 109322.

Hamza, W., Dammak, N., Hadjltaief, H.B., Eloussaief, M., Benzina, M., 2018. Ecotoxicol. Environ. Saf. 163, 365–371. https://doi.org/10.1016/j.ecoenv.2018.07.021.

Han, H., Rafiq, M.K., Zhou, T., Xu, R., Mašek, O., Li, X., 2019. J. Hazard. Mater. 369, 780–796. https://doi.org/10.1016/j.jhazmat.2019.02.003.

Hicham, Z., Bencheqroun, Z., El Mrabet, I., Kachabi, M., Nawdali, M., Neves, I., 2019. Mediterr. J. Chem. 8, 158–167 10.13171/mjc8319050803hz.

Hmeid, H.A., Akodad, M., Baghour, M., Moumen, A., Skalli, A., Azizi, G., Anjjar, A., Aalaoul, M., Daoudi, I., 2021. Mor. J. Chem 9, 416–433 10.48317/IMIST.PRSM/morjchem-v9i3.23303.

Hradil, D., Hradilová, J., Lanterna, G., Galeotti, M., Holcová, K., Jaques, V., Bezdička, P., 2020. Appl. Clay Sci. 185,. https://doi.org/10.1016/j.clay.2019.105412 105412.

Huo, J., Min, X., Wang, Y., 2021. Z, Environ. Res. 194,. https://doi.org/10.1016/j.envres.2020.110685 110685.

Iaich, S., Miyah, Y., Elazhar, F., Lagdali, S., El-Habacha, M., 2021. Desalin. Water Treat. 235, 251–271 10.5004/dwt.2021.27618.

Izydorczyk, G., Mikula, K., Skrzypczak, D., Moustakas, K., Witek-Krowiak, A., Chojnacka, K., 2021. Environ. Res. 197,. https://doi.org/10.1016/j.envres.2021.111050 111050.

Jain, A., Kumari, S., Agarwal, S., Khan, S., 2021. Process Saf. Environ. Prot. 152, 441–454. https://doi.org/10.1016/j.psep.2021.06.031.

Jawad, A.H., Abdulhameed, A.S., 2020. Surf. Interfaces 18,. https://doi.org/10.1016/j.surfin.2019.100422 100422.

Jayakumar, A., Radoor, S., Nair, I.C., Siengchin, S., Parameswaranpillai, J., 2021. R. E.k, Food Packaging and Shelf Life. 30,. https://doi.org/10.1016/j.fpsl.2021.100727 100727.

Jedli, H., Brahmi, J., Hedfi, H., Mbarek, M., Bouzgarrou, S., Slimi, K., 2018. J. Pet. Sci. Eng. 166, 476–481. https://doi.org/10.1016/j.petrol.2018.03.064.

Jency, M., Gowrisankar, L., Krishnaveni, J., Renugadevi, N., 2021. Journal of Environmental Treatment Techniques. 9, 218–223 10.47277/JETT/9(1)223.

Jiang, Q., Han, Z., Yu, X., Yuan, Y., Ren, Y., Li, J., Zhao, C., Cheng, Z., 2021. J. Environ. Chem. Eng. 9,. https://doi.org/10.1016/j.jece.2021.106636 106636.

Kausar, A., Sher, F., Hazafa, A., Javed, A., Sillanpää, M., Iqbal, M., 2020. Int. J. Biol. Macromol. 161, 1272–1285. https://doi.org/10.1016/j.ijbiomac.2020.05.266.

Kenawy, S.H., Khalil, A.M., 2020. Biointerface Res Appl Chem. 10, 5747–5754 10.33263/BRIAC104.747754.

Khalfa, L., Sdiri, A., Bagane, M., Cervera, M.L., 2020. Int. J. Environ. Sci. Technol. 17, 2123–2140. https://doi.org/10.1007/s13762-019-02614-x.

Khalilzadeh Shirazi, E., Metzger, J.W., Fischer, K., Hassani, A.H., 2020. Colloids Surf A Physicochem Eng Asp 598,. https://doi.org/10.1016/j.colsurfa.2020.124807 124807.

Khan, M.I., 2020. Mater. Res. Express 7,. https://doi.org/10.1088/2053-1591/ab903c 055507.

Khan, M.N., Chowdhury, M., Rahman, M.M., 2021. Materials Today Sustainability. 13,. https://doi.org/10.1016/j.mtsust.2021.100077 100077.

Kieufack, G., Bomeni, I.Y., Ngapgue, F., Tchamba, A.B., Mbog, M.B., Kouonang, S.T., Wouatong, A.S.L., 2021. SN Appl. Sci. 3, 856. https://doi.org/10.1007/s42452-021-04837-5.

Kinoshita, H., Yasui, K., Hamasuna, T., Yuji, T., Misawa, N., Haraguchi, T., Sasaki, K., Mungkung, N., 2022. Polymers 14, 164. https://doi.org/10.3390/polym14010164.

Kouadri, H. 2018. Elaboration, Ph.D. Thesis, University Ferhat Abbas Setif-1. http://dspace.univ-setif.dz:8888/jspui/handle/123456789/3110.

Kubendiran, H., Hui, D., Pulimi, M., Chandrasekaran, N., Murthy, P.S., Mukherjee, A., 2021. Monitoring & Management. 16,. https://doi.org/10.1016/j.enmm.2021.100561 100561.

Lan, Y., Liu, Y., Li, J., Chen, D., He, G., Parkin, I.P., 2021. Adv. Sci. 8, 2004036. https://doi.org/10.1002/advs.202004036.

Largo, F., Haounati, R., Akhouairi, S., Ouachtak, H., El Haouti, R., El Guerdaoui, A., Hafid, N., Santos, D.M.F., Akbal, F., Kuleyin, A., Jada, A., Ait Addi, A., 2020. J. Mol. Liq. 318,. https://doi.org/10.1016/j.molliq.2020.114247 114247.

Li, S., Mu, B., Wang, X., Wang, A., 2021. Dyes Pigm. 190,. https://doi.org/10.1016/j.dyepig.2021.109322 109322.

Loutfi, M., Mariouch, R., Belfaquir, M., Elyoubi, M.S., 2021. Mater. Today:. Proc. 45, 7457–7467. https://doi.org/10.1016/j.matpr.2021.02.018.

Lucas, J. 1962. bulletins and briefs. 23. https://www.persee.fr/doc/sgeol_0080-9020_1962_mon_23_1.

Luty-Błocho, M., Podborska, A., Musielak, B., Hessel, V., 2021. J. Mol. Liq. 340,. https://doi.org/10.1016/j.molliq.2021.116884 116884.

Mahammedi, F., 2021. Arabian Journal of Chemical and Environmental Research. 8, 83–96.

Mao, S., Gao, M., 2021. J. Mol. Liq. 334,. https://doi.org/10.1016/j.molliq.2021.116143 116143.

Martinello, K., Hower, J.C., Pinto, D., Schnorr, C.E., Dotto, G.L., Leandro, M., Oliveira, S., Ramos, C.G., 2022. Geosci. Front. 13,. https://doi.org/10.1016/j.gsf.2021.101151 101151.

Mbuyi, J.S., 2012. Presses univ. de Louvain. 400.

Melhaoui, R., Miyah, Y., Kodad, S., Houmy, N., Addi, M., Abid, M., Mihamou, A., Serghini-Caid, H., Lairini, S., Tijani, N., Hano, C., Elamrani, A., 2021. Scientific World Journal 2021, e6659902.

Mellouk, S., Cherifi, S., Sassi, M., Marouf-Khelifa, K., Bengueddach, A., Schott, J., Khelifa, A., 2009. Appl. Clay Sci. 44, 230–236. https://doi.org/10.1016/j.clay.2009.02.008.

Méring, J., Pédro, G., 1969. Bulletin of the French Clay Group 21, 1–30.

Meziti, C. 2016. PhD thesis, University A.Mira-Bejaia, Faculty of Technology.

Michel, R. 1971. Bulletin of the French Clay Group. 23, 1 1.

Miyah, Y., Lahrichi, A., Idrissi, M., Boujraf, S., Taouda, H., Zerrouq, F., 2017. Journal of the Association of Arab Universities for Basic and Applied Sciences. 23, 20–28. https://doi.org/10.1016/j.jaubas.2016.06.001.

Miyah, Y., Lahrichi, A., Kachkoul, R., El Mouhri, G., Idrissi, M., Iaich, S., Zerrouq, F., 2020. Arab Journal of Basic and Applied Sciences. 27, 248–258. https://doi.org/10.1080/25765299.2020.1776008.

Miyah, Y., Benjelloun, M., Lahrichi, A., Mejbar, F., Iaich, S., El Mouhri, G., Kachkoul, R., Zerrouq, F., 2021. J. Environ. Chem. Eng. 9,. https://doi.org/10.1016/j.jece.2021.106694 106694.

Miyah, Y., Benjelloun, M., Salim, R., Nahali, L., Mejbar, F., Lahrichi, A., Iaich, S., Zerrouq, F., 2022. J. Mol. Liq. 362,. https://doi.org/10.1016/j.molliq.2022.119739 119739.

Mobaraki, M., Karnik, S., Li, Y., Mills, D.K., 2021. Appl. Sci. 12, 87. https://doi.org/10.3390/app12010087.

Mohapi, M., Sefadi, J.S., Mochane, M.J., Magagula, S.I., Lebelo, K., 2020. Crystals 10, 957. https://doi.org/10.3390/cryst10110957.

Momina, M., Shahadat, M., Isamil, S., 2018. RSC Adv. 8, 24571–24587. https://doi.org/10.1039/C8RA04290J.

Muhammed, N.S., Olayiwola, T., Elkatatny, S., 2021. J. Pet. Sci. Eng. 206,. https://doi.org/10.1016/j.petrol.2021.109043 109043.

Mukhopadhyay, A., Tripathy, B.K., Debnath, A., Kumar, M., 2021. Surf. Interfaces 26,. https://doi.org/10.1016/j.surfin.2021.101412 101412.

Munjur, H.M., Hasan, M.N., Awual, M.R., Islam, M.M., Shenashen, M.A., Iqbal, J., 2020. J. Mol. Liq. 319, 10.1016/j.molliq.2020.114356 114356.

Nabbou, N., Belhachemi, M., Boumelik, M., Merzougui, T., Lahcene, D., Harek, Y., Zorpas, A.A., Jeguirim, M., 2019. C. R. Chim. 22, 105–112 10.1016/j.crci.2018.09.010.

Najafi, H., Asasian-Kolur, N., Sharifian, S., 2021. J. Mol. Liq. 344,. https://doi.org/10.1016/j.molliq.2021.117822 117822.

Nath, I., Chakraborty, J., Heynderickx, P.M., Verpoort, F., 2018. Appl Catal B 227, 102–113. https://doi.org/10.1016/j.apcatb.2018.01.032.

Nnamele, C.N., Egwuonwu, C.A., 2020. Awka Journal of Fine and Applied. 7, 117–130.

Olaremu, A.G., 2021. Chemistry Research Journal. 6, 157–168 http://chemrj.org›chemrj-2021-06-02-157-168.

Opafola, O.T., David, A.O., Ajibade, F.O., Adeyemi, H.O., Solana, O.I., Odugbose, B.D., 2021. SN Appl. Sci. 3, 415. https://doi.org/10.1007/s42452-021-04405-x.

Orta, M. del M., Martín, J., Santos, J.L., Aparicio, I., Medina-Carrasco, S., Alonso, E., 2020. Appl. Clay Sci. 198,. https://doi.org/10.1016/j.clay.2020.105838 105838.

Ouachtak, H., El, A., Guerdaoui, R., Haounati, S., Akhouairi, R.E., Haouti, N., Hafid, A. A., Addi, B., Šljukić, D.M.F., Santos, M.L., Taha, 2021. J. Mol. Liq. 335,. https://doi.org/10.1016/j.molliq.2021.116560 116560.

Oussalah, A., Boukerroui, A., Aichour, A., Djellouli, B., 2019. Int. J. Biol. Macromol. 124, 854–862. https://doi.org/10.1016/j.ijbiomac.2018.11.197.

Pahari, G., Gupta, P., Sarkar, U.K., Ray, D., Garai, S., Mondal, A., 2021. J. Indian Chem. Soc. 98,. https://doi.org/10.1016/j.jics.2021.100036 100036.

Pap, S., Kirk, C., Bremner, B., Sekulic, M.T., Shearer, L., Gibb, S.W., Taggart, M.A., 2020. Water Res. 173,. https://doi.org/10.1016/j.watres.2020.115573 115573.

Paredes-Quevedo, L.C., González-Caicedo, C., Torres-Luna, J.A., Carriazo, J.G., 2021. Water Air Soil Pollut. 232, 4. https://doi.org/10.1007/s11270-020-04968-2.

Qin, L., Pan, Y., Xie, F., Yu, L., Huai, R., Yang, L., Zhang, D., Zhou, Z., 2021. Inorg. Chem. Commun. 133,. https://doi.org/10.1016/j.inoche.2021.108988 108988.

Qlihaa, A., Dhimni, S., Melrhaka, F., Hajjaji, N., Srhiri, A., 2016. J. Mater. Environ. Sci. 7, 1741–1750.

Rafatullah, M., Sulaiman, O., Hashim, R., Ahmad, A., 2010. J. Hazard. Mater. 177, 70–80. https://doi.org/10.1016/j.jhazmat.2009.12.047.

Rakhym, A.B., Seilkhanova, G.A., Kurmanbayeva, T.S., 2020. Mater. Today:. Proc. 31, 482–485. https://doi.org/10.1016/j.matpr.2020.05.672.

Rathour, R.K.S., Bhattacharya, J., 2018. Appl. Surf. Sci. 437, 41–50. https://doi.org/10.1016/j.apsusc.2017.12.139.

Rehman, A.U., Nazir, S., Irshad, R., Tahir, K., Rehman, K., UlIslam, R., Wahab, Z., 2021. J. Mol. Liq. 321,. https://doi.org/10.1016/j.molliq.2020.114455 114455.

M. Robert, Agronomic Annals, INRA. 26, 363-399 (1975). https://hal.inrae.fr/hal-02730762.

Rojas-Mantilla, H.D., Ayala-Duran, S.C., Pupo Nogueira, R.F., 2021. Chemosphere 291,. https://doi.org/10.1016/j.chemosphere.2021.132966 132966.

Romdhane, D.F., Satlaoui, Y., Nasraoui, R., Charef, A., Azouzi, R., 2020. J. Chem. 2020, 1–17. https://doi.org/10.1155/2020/4376173.

Romdhane, D.F., Satlaoui, Y., Nasraoui, R., Charef, A., Azouzi, R., 2020. Adsorption, Journal of Chemistry. 2020, e4376173.

Sabatino, G., Franzone, M., Martinelli, M.C., Rondinella, M.T., Italiano, F., Caccamo, M.T., Mezzatesta, F., Magazù, S., Tripodo, A., Di Bella, M., 2021. Atti Accad. Pelorit. Pericol. Cl. Sci. Fis. Mat. Nat. 99. https://doi.org/10.1478/AAPP.99S1A43. A43-1-A43-19.

Sakin Omer, O., Hussein, M.A., Hussein, B.H.M., Mgaidi, A., 2018. Arab. J. Chem. 11, 615–623. https://doi.org/10.1016/j.arabjc.2017.10.007.

Saleem, J., Shahid, U.B., Hijab, M., Mackey, H., McKay, G., 2019. Biomass Conv. Bioref. 9, 775–802. https://doi.org/10.1007/s13399-019-00473-7.

Salh, D.M., Aziz, B.K., Kaufhold, S., 2020. SILICON 12, 87–99. https://doi.org/10.1007/s12633-019-00100-0.

Samad, A., Din, M.I., Ahmed, M., 2020. Chin. J. Chem. Eng. 28, 1171–1176. https://doi.org/10.1016/j.cjche.2019.12.016.

Santos, S.C.R., Boaventura, R.A.R., 2016. J. Environ. Chem. Eng. 4, 1473–1483. https://doi.org/10.1016/j.jece.2016.02.009.

Saravanan, A., Senthil Kumar, P., Jeevanantham, S., Karishma, S., Tajsabreen, B., Yaashikaa, P.R., Reshma, B., 2021. Chemosphere 280,. https://doi.org/10.1016/j.chemosphere.2021.130595 130595.

Sarkar, S., Ponce, N.T., Banerjee, A., Bandopadhyay, R., Rajendran, S., Lichtfouse, E., 2020. Environ. Chem. Lett. 18, 1569–1580. https://doi.org/10.1007/s10311-020-01021-w.

Sellaoui, L., Dhaouadi, F., Li, Z., Jr, T.R.S.C., Igansi, A.V., Pinto, L.A.A., Dotto, G.L., Petriciolet, A.B., Pinto, D., Chen, Z., 2021. J. Environ. Chem. Eng. 9 (105516). https://doi.org/10.1016/j.jece.2021.105516.

Sevim, F., Lacin, O., Ediz, E.F., Demir, F., 2021. Environ. Prog. Sustain. Energy 40, e13471.

Sharma, J., Sharma, S., Soni, V., 2021. Reg. Stud. Mar. Sci. 45,. https://doi.org/10.1016/j.rsma.2021.101802 101802.

Sieren, B., Baker, J., Wang, X., Rozzoni, S.J., Carlson, K., McBain, A., Kerstan, D., Allen, L., Liao, L., Li, Z., 2020. Adv. Mater. Sci. Eng. 2020, 1–12. https://doi.org/10.1155/2020/8845366.

Sivakumar, R., Lee, N.Y., 2022. Chemosphere 286,. https://doi.org/10.1016/j.chemosphere.2021.131890 131890.

Sriram, G., Bendre, A., Mariappan, E., Altalhi, T., Kigga, M., Ching, Y.C., Jung, H.Y., Bhaduri, B., Kurkuri, M., 2022. Sustainable Materials and Technologies 31, https://doi: 10.1016/j.susmat.2021.e00378 e00378.

Ssouni, S., Miyah, Y., Benjelloun, M., Mejbar, F., El-Habacha, M., Iaich, S., Ait Addi, A., Lahrichi, A., 2023. Case Studies in Chemical and Environmental Engineering. 8,. https://doi.org/10.1016/j.cscee.2023.100456 100456.

Sulyman, M., Kucinska-Lipka, J., Sienkiewicz, M., Gierak, A., 2021. Arab. J. Chem. 14,. https://doi.org/10.1016/j.arabjc.2021.103115 103115.

Tankpinou Kiki, Y. S. 2016. PhD thesis, University of Bordeaux and University of Abomey-Calavi (Benin). https://tel.archives-ouvertes.fr/tel-01476079.

Tchieno Melataguia, F.M., 2016. viz. mangiferin and quercetin. University of Dschang. Thesis.

Teo, S.H., Ng, C.H., Islam, A., A-Alsultan, G., Joseph, C.G., Janaun, J., Taufiq-Yap, Y.H., Khandaker, S., Islam, G.J., Znad, H., Awual, Md. R., 2022. J. Clean. Prod. 332, 10.1016/j.jclepro.2021.130039 130039.

Thamarai Selvi, M., Zahir Hussain, A., 2022. Mater. Today:. Proc. 59, 1349–1356. https://doi.org/10.1016/j.matpr.2021.12.005.

Thiebault, T., 2020. Crit. Rev. Environ. Sci. Technol. 50, 1451–1514. https://doi.org/10.1080/10643389.2019.1663065.

Thotagamuge, R., Raziq, M., Kooh, R., Mahadi, A.H., Lim, C.M., Abu, M., Jan, A., Hanipah, A.H.A., Khiong, Y.Y., Shofry, A., 2021. Environ. Nanotechnol. Monit. Manage. 16,. https://doi.org/10.1016/j.enmm.2021.100562 100562.

Tijani, J.O., Abdullahi, M.N., Bankole, M.T., Mustapha, S., Egbosiuba, T.C., Ndamitso, M.M., Abdulkareem, A.S., Muzenda, E., 2021. J. Water Process Eng. 44,. https://doi.org/10.1016/j.jwpe.2021.102376 102376.

Tiwari, A., Joshi, M., Salvi, N., Gupta, D., Gandhi, S., Rajpoot, K., Tekade, R.K., 2022. Pharmacokinetics and Toxicokinetic Considerations. 2, 569–603. https://doi.org/10.1016/B978-0-323-98367-9.00004-4.

Tiwari, K., Singh, R., Negi, P., Dani, R., Rawat, A., 2021. Mater. Today:. Proc. 46, 10652–10655. https://doi.org/10.1016/j.matpr.2021.01.385.

U.S. Food and Drug Administration, Vanadium, and Zinc, National Academies Press. (2001). https://doi.org/10.17226/10026.

Uddin, M.K., 2017. Chem. Eng. J. 308, 438–462. https://doi.org/10.1016/j.cej.2016.09.029.

Ullah, S., Ur Rahman, A., Ullah, F., Rashid, A., Arshad, T., Viglašová, E., Galamboš, M., Mahmoodi, N.M., Ullah, H., 2021. Water. 13, 965. https://doi.org/10.3390/w13070965.

Varol, M., 2020. Environ. Pollut. 266,. https://doi.org/10.1016/j.envpol.2020.115417 115417.

Velde, B., 1995. Origin and Mineralogy of Clays: Clays and the Environment. 8–42. https://doi.org/10.1007/978-3-662-12648-6_2.

Velusamy, S., Roy, A., Sundaram, S., Kumar Mallick, T., 2021. Chem. Rec. 21, 1570–1610. https://doi.org/10.1002/tcr.202000153.

Vieira, Y., Netto, M.S., Lima, É.C., Anastopoulos, I., Oliveira, M.L.S., Dotto, G.L., 2022. Geosci. Front. 13,. https://doi.org/10.1016/j.gsf.2021.101150 101150.
Vieira, C.M.F., Pinheiro, R.M., Rodriguez, R.J.S., Candido, V.S., Monteiro, S.N., 2016. Appl. Clay Sci. 132–133, 753–759. https://doi.org/10.1016/j.clay.2016.07.001.
Wal, K., Rutkowski, P., Stawiński, W., 2021. Appl. Clay Sci. 215,. https://doi.org/10.1016/j.clay.2021.106323 106323.
Wan, H., Ma, W., Zhou, K., Cao, Y., Liu, X., Ma, R., 2022. Green. Energy Environ. 7, 205–220. https://doi.org/10.1016/j.gee.2021.04.001.
Wang, S., Chen, W., Zhang, C., Pan, H., 2021. Chem. Phys. Lett. 784,. https://doi.org/10.1016/j.cplett.2021.139104 139104.
Wang, W., Zhao, W., Zhang, H., Xu, J., Zong, L., Kang, Y., Wang, A., 2021. Powder Technol. 390, 303–314. https://doi.org/10.1016/j.powtec.2021.05.090.
Wei, W., Li, J., Han, X., Yao, Y., Zhao, W., Han, R., Li, S., Zhang, Y., Zheng, C., 2021. Sci. Total Environ. 778,. https://doi.org/10.1016/j.scitotenv.2021.146189 146189.
Yang, C., Gao, R., Yang, H., 2021. Energy Chem. 3,. https://doi.org/10.1016/j.enchem.2021.100062 100062.
Yönten, V., Sanyürek, N.K., Kivanç, M.R., 2020. Surf. Interfaces 20,. https://doi.org/10.1016/j.surfin.2020.100529 100529.
Yu, C.Y., Chow, J.K., Wang, Y.-H., 2016. Eng. Geol. 202, 122–131. https://doi.org/10.1016/j.enggeo.2016.01.007.
Yukselen, Y., Kaya, A., 2008. Eng. Geol. 102, 38–45. https://doi.org/10.1016/j.enggeo.2008.07.002.
Zaccaron, A., de Souza Nandi, V., Bernardin, A.M., 2021. Journal of Building Engineering 33,. https://doi.org/10.1016/j.jobe.2020.101877 101877.
Zaid, H. 2020. Thesis, University of Mostaganem, http://e-biblio.univ-mosta.dz/handle/123456789/15427.
Zhang, L., Gadd, G.M., Li, Z., 2021. Adv. Appl. Microbiol. 114, 111–139. https://doi.org/10.1016/bs.aambs.2020.07.002.
Zhang, T., Wang, W., Zhao, Y., Bai, H., Wen, T., Kang, S., Song, G., Song, S., Komarneni, S., 2021. Chem. Eng. J. 420,. https://doi.org/10.1016/j.cej.2020.127574 127574.
Znad, H., Abbas, K., Hena, S., Awual, M.R., 2018. Journal of Environmental Chemical Engineering. 6, 218–227. https://doi.org/10.1016/j.jece.2017.11.077.
Zou, Y., Hu, Y., Shen, Z., Yao, L., Tang, D., Zhang, S., Wang, S., Hu, B., Zhao, G., Wang, X., 2022. J. Environ. Sci. 115, 190–214. https://doi.org/10.1016/j.jes.2021.07.015.