King Saud University

Arabian Journal of Chemistry

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REVIEW ARTICLE

Recent Advances in Adsorption Kinetic Models: Their Application to Dye Types

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Abstract   The increased environmental awareness and tighter regulatory standards have prompted various industries to seek appropriate wastewater treatment technologies, in particular, for colored wastewater. This review provides detailed information on dyes, their classification, the environmental impact of water pollution on the national (Morocco) and international scales. Recent studies about the adsorption treatment process for the removal of dyes from the aqueous solution with different adsorbents recognized as a sustainable solution in terms of minimization, recovery, and reuse were evaluated. It is also aimed to synthesize the current literature data concerning low-cost adsorbents by systematically highlighting both their characteristics and capacities. Moreover, the applicability of various kinetic adsorption and isothermal models to the removal of dyes by a wide range of adsorbents is reported in addition to information regarding continuous system adsorption.

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1. Introduction

The complexity of industrial effluents is a major issue that influences the quality of drinking water due to the presence of organic pollutants such as synthetic dyes (Crini et al., 2019; Yaseen and Scholz, 2019). Synthetic dyes are one of the main sources of water pollution due to the dyeing of textile fibers, papers, leathers, plastics, elastomers, and pharmaceuticals (Carvalho et al., 2018; Islam et al., 2019; Mejbar et al., 2019; Uddin et al., 2017; Wang et al., 2019). The annual global production of dyes has reached nearly 700 000 tons and led to the availability of 100 000 dyes in commerce (Mani et al., 2019). The textile industries generate highly polluted effluents

due to the large quantities of water used in the dyeing processes (Tarkwa et al., 2019). About 10 to 15 % of the dyes are released into the receiving aquatic environment during the textile process, creating highly colored contaminants that are aesthetically undesirable to the environment (Ratna and Padhi, 2012). Consequently, the presence of these colored effluents in natural water bodies reduces the penetration of light; delays photosynthetic activity; inhibits the growth of biota; and forms bonds between different metal ions which induce micro-toxicity. These, in turn, adversely affect aquatic organisms and humans due to the interconnected food webs. The water pollution-related health issues include kidney, reproductive, liver, brain, and central nervous system dysfunc-

Table 1 Low-cost adsorbents in the field of separation sciences.

Type of adsorbent	Type of adsorbate	Aim of the study	References
Plant-based magnetite nanoparticles: fig leaves and Azolla	Dyes: Crystal Violet and Methylene Blue	Adsorption of Crystal Violet and Methylene Blue as cationic dyes on the surface of magnetite nanoparticles charged with fig leaves and Azolla-charged magnetite nanoparticles as low-cost natural adsorbents.	(Alizadeh, 2017)
Agrifood waste: Almond shell	Dyes: Eriochrome Black T and Malachite Green	Use of almond shell, a food waste, used as a biosorbent for Eriochrome Black T and Malachite Green from aqueous solutions.	(Ben Arfi et al., 2017)
Sawdust	Dye: Malachite Green	Assessment of the adsorption properties of Malachite Green on a sawdust compound of pine, oak, hornbeam, and fir.	(Deniz, 2017)
Plant: Saw palmetto	Dye: Methylene Blue	Evaluation of the saw palmetto as an economical adsorbent for Methylene Blue in an aqueous solution.	(Papegowda and Syed, 2017)
Agrifood waste: Avocado nuts	Dye: Basic Blue 41	Evaluation of the adsorption of the Basic Blue 41 dye on activated charcoal-based on *Persea americana* nuts with activation using phosphoric acid.	(Regti et al., 2017)
Plant: *Rhizopus arrhizus*	Dyes: Metanil yellow and fast red	Assessment of the biosorbent capacity of Metanil Yellow and Fast Red by the spent biomass of *Rhizopus arrhizus*	(Salvi and Chattopadhyay, 2017)
Agrifood waste: Cocoa shell	Dyes: Azur II and Reactive Red II	Evaluation of the effect of the treatment of the cocoa shell (*Théobroma cacao*) by sliding arc plasma on the adsorption of the cationic dye Azur II and the anionic dye Reactive Red II which coexist in aqueous media.	(Takam et al., 2017)
Agrifood waste: Coconut shells, Golden pods, and Orange Peels	Dye: Methylene Green 5	Comparison of the adsorption capacity of Methylene Green 5 on different hydrochars: based on golden pods, the shell of the coconut, orange peels with the commercial hydrochar based on glucose.	(Tran et al., 2017)
Bagasse of natural sugar cane and Bagasse of sugarcane modified by amine compounds.	Dye: Congo Red	Removal of Congo Red by adsorption by taking into account the chain length of amine compounds by the comparison between unmodified sugar cane bagasse, ethylene modified cane bagasse diamine, diethylene triamine, triethylene tetramine, and tetrathylene pentamine.	(Yu et al., 2017)
Natural zeolites	Dye: Safranin T	The use of heulandite, clinoptilolite, and phillipsite zeolitic minerals in the removal of Safranin T from water.	(Abukhadra and Mohamed, 2019)
Agrifood Waste: Avocado shell modified with nitric/sulfuric acid	Dye: Procyon Red	Removal of the Procyon Red dye by avocado shells modified with sulfuric acid and nitric acid by adsorption.	(Georgin et al., 2018)
Psyllium seeds	Dye: Reactive Orange 16	Effectiveness of psyllium seed powder in removing Reactive Orange dye 16.	(Malakootian and Heidari, 2018)
Organometallic nanomaterials from the Lavoisier Institute	Dyes: Basic Red 46, Basic Blue 41, and Methylene Blue.	Use of organometallic nanomaterials synthesized from 1, 4-benzene dicarboxylate and 2-amino-1, 4-benzene dicarboxylate as organic linkers and tetra isopropyl ortho titanate as a source of metal for the elimination of dyes: Basic Red 46, Basic Blue 41, and Methylene Blue.	(Oveisi et al., 2018)
Biological and Chemical Iron Nanoparticles.	Dye: Crystal Violet	Comparison between chemical and biological iron nanoparticles (based on *Ferula Persica*) to remove Crystal Violet from aqueous media.	(Nasiri et al., 2019)
Animal Waste: Goat Polishing Dust.	Heavy metal: Mercury IIDyes: Safranine and Brilliant Cresyl Blue	Goat polishing dust is in the form of a bio-composite based on collagen rubber and cross-linked styrene-butadiene. The goal of this work is to optimize the synthesis of this biocomposite which will be used for the elimination of Safranine, Brilliant Cresyl Blue, and Mercury II.	(Roy et al., 2019)
Resin-based on 3,5-diacrylamido benzoic acid	Dyes: Rhodamine B and Congo Red	Assessment of the potential of a hyper-crosslinked 3, 5-diacrylamidobenzoic acid resin to adsorb Congo Red and Rhodamine B from an aqueous solution.	(Waheed et al., 2019)
Organo-Vermiculites (vermiculite-surfactant combination)	Dye: Rhodamine B	Effects of the type and location of the functional group (imino, hydroxy, phenyl, pyridile) in vermiculite on the adsorption process of Rhodamine B.	(Wang et al., 2019)

Table 1 (*continued*)

Type of adsorbent	Type of adsorbate	Aim of the study	References
Magnetic chitosan microparticles	Dyes:Tartrazine and Food Yellow 3.	Fabrication of modified magnetic chitosan microparticles and their usage to remove Food Yellow 3 and Tartrazine from an aqueous solution	(Zheng et al., 2019)
Chemically modified masau stones	Heavy metal: Hexavalent Chromium oxanionsDye: Orange II	Removal of hexavalent chromium oxyanions and Orange II from single aqueous solutions, from multicomponent systems, and consecutive biosorption onto chemically modified masau stones.	(Albadarin et al., 2017)
Micro-organism: *Saccharomyces cerevisiae* (yeast biomass)	Metal: Manganese	The use of microorganisms as bio-adsorbents in the removal of toxic metals in water.	(Fadel et al., 2017)
Bacterial strains: *Bacillus catenulatus* (isolated from soils and polluted pond)	Heavy metal: CadmiumDye: Cationic Basic Blue 3	Assessment of the adsorption of Cationic Basic Blue 3 dye and cadmium on the surface of bacterial strains.	(Kim et al., 2015)
Chemically modified Phosphoric acid-activated *Chrysopogon zizanioides* roots Activated Carbon	Dye: Malachite GreenHeavy Metals: Copper (II) and Nickel (II) ions	Methylene Green dye and Copper (II) and Nickel (II) heavy metals removal from wastewater effluents by the adsorption on the phosphoric acid modified vetiver plant roots activated carbon.	(Thanarasu et al., 2020)

tions, mutagenesis, chromosomal fractures, respiratory toxicity, skin and dermatitis irritations, production of eczema and ulceration, itching, watery eyes, and asthma symptoms (Basaleh et al., 2019; Dissanayake Herath et al., 2019; Kumar et al., 2019; Maria et al., 2020; Sharma et al., 2019). Textile effluents, for example, are very concentrated in dyes and carry a large number of other substances added during the coloring process. Due to its high color intensity and great variability in composition, it becomes very difficult to treat textile wastewater (Singh and Arora, 2011). The water quality has been observed mostly by its color, which makes the elimination of colors much more important than the elimination of colorless soluble organic substances from wastewater (Khan and Malik, 2014). Due to their high thermal resistance and photo-stability, dyes can remain in the environment for an extended period in sewers and rivers because they are designed to have high solubility in water (Ratna and Padhi, 2012). Azo dyes are toxic due to the presence of toxic amines in the effluents (Singh and Arora, 2011). Furthermore, anthraquinone dyes remain colored for a long time in textile rejects because of their high resistance against degradation (Carvalho et al., 2018; Singh and Arora, 2011). To preserve public health and aquatic life, several elementary water treatment processes based on physicochemical engineering may be applicable such as coagulation-flocculation, solid-liquid separation by physicochemical decantation and filtration, oxidation, ozonation, and photocatalysis (El Mouhri et al., 2020; EL Mouhri et al., 2019; Fegousse et al., 2019; Idrissi et al., 2016; Miyah et al., 2020, 2017, 2016). The latter are the most common methods to treat such wastewater before being discharged into the environment (Boudissa et al., 2019; Dotto et al., 2019; Louati et al., 2020; Ozbey Unal et al., 2019; Payra et al., 2019; Saratale et al., 2020). Most of these techniques have drawbacks such as the incomplete elimination of dyes, the high requirements for reagents and energy, the low selectivity, the high investment, and operating costs, and the generation of secondary waste difficult to eliminate (Chowdhary et al., 2018; Pavithra et al., 2019). The high performance of the adsorption method was proven thanks to its low cost, high efficiency, minimization of chemical or biological sludge, and regeneration of adsor-

bents. However, the bioaccumulation of pollutants without destruction leads to the death of biomass that adsorbs the pollutants which must be managed before being released into the environment (Crini et al., 2018; Lellis et al., 2019; Miyah et al., 2018; Sulyman et al., 2017). Activated carbon is the best adsorbent and the most common one but it is costly, difficult to regenerate, non-selective, and ineffective for the adsorption of dispersed and vat dyes (Kyzas et al., 2013; Uddin et al., 2017). Low-cost adsorbents for the adsorption of the direct blue-86 dye from an aqueous solution on activated carbon encapsulated in alginate prepared from used peanut shells (Garg et al., 2019), the biosorption of the reactive blue dye BF-5G by the bagasse of malt from the brewing process (Juchen et al., 2018), used banana (*Musa acuminata*) and potato peels (*Solanum tuberosum*) to adsorb the emerald green dye ecologically (Rehman et al., 2019) was developed as a low-cost alternative adsorbent. Studies focused on low-cost adsorbents in recent years due to their economic use and environmentally friendly nature (Table 1). Moreover, the use of biosorbents has a double impact thanks to their low cost and waste-stream reduction (Bello and Raman, 2019). The choice of adsorbents depends on their physicochemical characteristics such as specific surface (m^2/g), particle size, porosity, physicochemical characteristics of adsorbate (e.g., concentration in the solution, solubility, size, functions of chemicals present, competition between different molecules, etc.), and/or physicochemical characteristics of sorption medium (e.g., ionic strength, pH, temperature, agitation, hydrodynamic characteristics). To well understand the mechanism of dyes adsorption, it was important to emphatically discuss the assumptions of adsorption kinetic models such as pseudo-first-order,pseudo-second-order, Avrami, and Elovich, that were tested in the equilibrium kinetic datas of the methylene blue dye adsorption onto lemongrass leaf in the study of Admad et al.(2021) (Ahmad et al., 2021), Bangham kinetic's model was applied and investigated by Zambrano-Intriago et al. (2020) in the equilibrium kinetic datas of the blue dye 19 adsorptions onto rice husk ash (Zambrano-Intriago et al., 2020), Boyd and Intraparticle Diffusion were investigated by Hafdi et al. (2020) in the equilibrium kinetic results of the reactive red

141 azo dye adsorption on natural phosphate doped by nickel-oxide-nanoparticles (Hafdi et al., 2020), and isotherm models such as Langmuir, Freundlich, and Temkin, that were developed to explain the interaction between ordered mesoporous carbon materials and Anionic Acid Violet 90 presented in the research article of Eslek Koyuncu and Okur (2021) (Eslek Koyuncu and Okur, 2021), Bohart Adams and Yoon Nelson that was used to understand in a continuous batch system the adsorption of cationic methylene blue and anionic methyl orange dyes onto the mucilage of *Plantago Psyllium* and the eggshell membrane in the research paper of Mirzaei and Javanbakht (2019) (Mirzaei and Javanbakht, 2019), Brunauer Emmett Teller that was performed by Ferrarini et al. (2016) to see whether the adsorption of Congo red dye onto halloysite-magnetite-based composite is monolayer or multi-layer (Ferrarini et al., 2016), Dubinin Radushkevich that was elucidate to the adsorption of Reactive Blue 4 on the surface of chitosan B in the article paper of Karmaker et al.(2020) (Karmaker et al., 2020) , Flory Huggins which was explained in the Haque et al.(2020) article paper on the adsorption of Anionic Acid Blue 25 on the surface of chitosan-modified cotton gin trash film(Haque et al., 2020), Frenkel-Halsey-Hill, Khan, Koble Corrigan, Mac Millan Teller, Redlich Peterson, Sips, Toth, Harkin Jura, Halsey, and Elovich Larionov, that were applied for the adsorption of methylene blue dye onto Lignin-chitosan blend in the manuscript of Rezakazemi and Shirazian (2019) (Rezakazemi and Shirazian, 2019) , and Wolborska that was performed by Djelloul and Hamdaoui (2014) for modeling the removal of methylene blue using melon peel adsorbent in a fixed bed column (Djelloul and Hamdaoui, 2014) .Information regards continuum systems of adsorption were provided. Breakthrough examples and models were presented and discussed as well as scale-up procedures, and Information like mass zone transference and scale-up were mentioned.

This scientific review has a two-fold objective: First of all, a review of recent studies on the adsorption of different dyes by describing their classes, environmental impact on Morocco and the world, main sources, and the conventional processes for their elimination; and then the interpretation and description of the adsorption results by the materials of different natures and the main kinetic models used.

2. Dyes classification

Currently, the concept of dyes is present in almost all the spheres of our daily life. Their classification is based on the source of the materials (natural or synthetic dyes) and the chemical nature (according to the auxochrome versus the chromophore).

2.1. Classification based on the source of materials

There are two main families of dyes: natural dyes (extracts of mineral or organic matter) and those from chemical synthesis.

2.1.1. Natural Dyes

Dyes have been used by humans for thousands of years. At first, they were made from animals and plants by simple processes like heating or grinding. Among all these dyes, there are two categories: mordant dyes and vat dyes.

- Mordant dyes are water-insoluble compounds formed by the reaction of metal salts (which have been fixed after a preliminary treatment on the fiber) with the functional groups present in the dye molecule (İşmal and Yıldırım, 2019). Kermes (natural red 3) and carmine (natural red 4) are included in this category and originate from insects of the genus Coccus (Dastgerdi et al., 2019; Serrano et al., 2015).
- Vat dyes: These dyes are initially insoluble in water and contain at least two ketone functions. However, an alkaline reduction process makes it possible to dissolve them via an alkaline enolic form, called leuco-soluble. Substituted with enolate groups, the solubilized dye shows an affinity for cellulosic fibers (Berradi et al., 2019; John et al., 2020). Tyrian purple, indigo, and pastel are vat dyes (Gürses, 2019).

2.1.2. Synthetic dyes

Synthetic dyes are dyes derived from organic or inorganic molecules. These textile dyes are classified into several groups using the general chemistry of the dyes as the basis for their classification:

- Organic pigments are colored organic compounds with pigmentary properties, they have no affinity with the colored substance but are rather fixed to its surface by an adhesive or a film-forming material. They are characterized by resistance to solar radiation (Órdenes-Aenishanslins et al., 2016), resistance to acids (Wu et al., 2017), resistance to organic solvents and water (Marzec et al., 2019), thermo resistance (Kanbur et al., 2019), and excellent dispersion in the application medium (Ali et al., 2019; Nagose et al., 2019).
- Direct dyes are anionic dyes with an affinity for cellulosic fibers, applied in an aqueous bath containing an electrolyte (Gurr, 1971).
- Reactive dyes are dyes with one or more reactive groups capable of forming a covalent bond between the dye and the fiber (Shang, 2013). The most important reactive systems are sulfone vinyls, halotriazines, and halopyrimidines (Asgher, 2012; Irfan et al., 2020). Unsaturated groups, sulfonated vinyls, for example, react with cellulose by the addition to the double bond, while dyes with an activated halogenated substituent involve a nucleophilic substitution (Shore, 2002).
- Disperse dyes are dyes without solubilization groups and with a low molecular weight. The dye-fiber affinity is the result of three types of interactions: hydrogen bonds with oxygen and nitrogen atoms on the fiber, dipole-dipole interactions (between the dye molecules and the fiber) which result from l dye asymmetry, and the Van der Waals forces that come into play when the molecules of the fiber and the dye are aligned and close to each other (Lacasse and Baumann, 2004).

2.2. Chemical classification of dyes

The classification according to the chemical structure of the dyes is mainly based on their nature: chromophore or auxochrome.

- According to the nature of the chromophore: This classification is based on the chemical structure of the dyes. The main types of dyes in this class are azo, anthraquinone, indigo, xanthenes, phthalocyanine, nitrated, and nitrosated and triphenylmethane dyes (Berradi et al., 2019; Yagub et al., 2014).
- According to the nature of the auxochrome: This category of dyes is based on the mode of use and application of the dye. It contains acid or anionic dyes, basic or cationic dyes, vat dyes, direct dyes, mordant dyes, reactive dyes, azo dyes, and dispersed dyes (Pereira and Alves, 2012; Yagub et al., 2014).

2.3. Classification according to nuclear structure

Although this classification is not very popular, dyes can be classified into two categories using this method:

- Cationic or basic dyes: This is a class of dyes that carry positive ions and known for their brilliant nuances. Basic dyes are made up of large molecules and are water-soluble salts. They are often dedicated to dyeing acrylic fiber, and printing polyester, and nylon (Mansour et al., 2011).
- Anionic or acid dyes: They are water-soluble and dedicated to dyeing animal fibers (wool and silk) and some modified acrylic fibers (nylon, polyamide) in a slightly acid bath by their carboxylate groups. The dye-fiber affinity is the result of ionic bonds between the sulfonic acid part of the dye and the amino groups of the textile fibers (Salleh et al., 2011).

3. Environmental impact of textile pollutants

3.1. On the worldwide level

The whole world faces a dangerous threat linked to an imminent water crisis and its natural reserves. Indeed, wastewater management is one of the most serious dilemmas of modern times especially since it is discharged into the environment without any treatment: the *United Nations* has alerted that more than 80% of the world's wastewater and more than 95% in some least developed countries are released into the environment without having been first treated (UNESCO, 2017). This wastewater contains coloring molecules which are stable and persistent organic pollutants in the environment (Hussain et al., 2019). Regardless of the intrinsic characteristics of the dyes, it should be noted that 10 to 50% of the dyes used for dyeing are not fixed on the fibers and are found in industrial effluents (Drumond Chequer et al., 2013; Woolley et al., 2002). These colored effluents have an impact on the aesthetics of the environment and contribute to the eutrophication of watercourses, increasing turbidity, generating odors, and reducing the rate of oxygen available to the aquatic ecosystem (Kanu and Achi, 2011). It is important to emphasize that the textile industry is one of the most polluting industries in the world, given the annual consumption of water and toxic chemicals added during the coloring process (Núñez et al., 2019). Many regions of the world already suffer from a medium-to-high level of water stress, and the situation is more critical if we consider the anticipation of a 50% increase in water consumption by industries related to dyeing by 2030 (Dimitrijević et al., 2019).

3.2. At the national level (Morocco)

With the increased industrial activity, the aquatic environment remains the most affected by collectors who discharge industrial wastewater containing dyes, grease, flammable hydrocarbons, and acidic substances which seriously pollute the waters. The 3rd report of the *"Ministry delegated to the Minister of Energy, Mines, Water and the Environment, in charge of the environment"* entitled *"The state of the environment of Morocco, 2015"* provides information on the main activities source of pollution of aquatic environments: 964 million m^3 is annually produced from industrial wastewater in Morocco, i.e. 92% of the water initially withdrawn from the sea and water resources soft. The main responsibility for the discharge of wastewater with a volume of 931 million m^3 belongs to the chemical and parachemical industry. The agro-industry, textile, and leather sectors are the other sources impacting the volume of wastewater, to a lesser extent followed by the mechanical and metallurgical industries. The total volume for the latter reaches an average of 32 million m^3 annually (Department of Water, 2009). The numerous pollutant released come from hydrocarbons (petroleum refining and storage industries), phosphorus (phosphate industry at Safi and Jorf Lasfar), and other solid, liquid, or gaseous pollutants. The tanneries, given their great need for water, are often installed near watercourses (example: Sebou and Tensift) or are discharged with liquid waste; 500 L of chrome waste or vegetable tannins per ton of skin treated, are the waste production volume by the tanneries. The clothing and carpet manufacturing industries also generate polluting liquid discharges. The artisanal rejects from the copperware are considered the most harmful because of their richness in heavy metals and very toxic salts (Ministry of the Environment, the summary note of the document of preparation of the "National program for the prevention of Industrial pollution"). The leather and textile industries represent 31% of all industries, play a strategic role in the Moroccan economy (Gebrati et al., 2019; Talouizte et al., 2020), and consume large amounts of water and produce liquid discharges, estimated at 10 million m^3 per year for Morocco and 400 m^3 per day for the city of Fez, Morocco, having a high load not only of dyes but also in other toxic substances

Table 2 Comparison between physical and chemical adsorptions.

Properties	Chemisorption	Physisorption
Kinetic	Very slow	Fast and temperature independent
Desorption	Difficult	Easy
Binding energy	100-1000 kJ/mol	10-100 kJ/mol
Molecules individuality	Destroyed	Preserved
Process temperature	Higher than the boiling temperature of the adsorbate	Relatively low compared to the boiling temperature of the adsorbate
Formation Type	Monolayer formation	Multilayer and monolayer formation
Binding types	Chemical bond	Van der Waals
Mechanism	Shrinking core	Diffusion

Table 3 Equations of the linear forms of the Langmuir isotherm

Linear form	Equation
Lineweaver-Burk	$\frac{C_e}{Q_e} = \frac{1}{k_L Q_L} + \frac{C_e}{Q_L}$ (2)
Hanes-Woolf	$\frac{1}{Q_e} = \frac{1}{k_L Q_L C_e} + \frac{1}{Q_L}$ (3)
Eadie-Hofstee	$Q_e = Q_L - \frac{Q_e}{C_e k_L}$ (4)
Scatchard	$\frac{Q_e}{c_e} = k_L(Q_L - Q_e)$ (5)

and various types of pollutants(Fatta-Kassinos et al., 2016; Giorgetti et al., 2011; Talouizte et al., 2020).

4. Different parameters influencing the adsorption capacity

Adsorption is the phenomenon of attraction and retention of the molecules of a liquid "adsorbate" by a solid "adsorbent" on its surface, which leads to a higher concentration of molecules on the surface. The classic adsorption mechanism takes place in three stages: The diffusion of the adsorbate on the surface of the adsorbent: By the intermolecular forces between the adsorbent and the adsorbate, the migration of the adsorbate in the pores of the adsorbent, and monolayer formation of the adsorbate on the adsorbent: When the particles of the adsorbate are distributed on the surface and fill the pore volume, particles of adsorbate from the monolayer of molecules, ions and atoms which reacted to the active sites of the absorbent (Kammerer et al., 2019). The latter is one of the most used methods to treat this water before being discharged into the environment. The transfer of pollutants in aqueous media is governed by three physicochemical phenomena: the thermodynamic equilibrium between the two phases which expresses the limit of the process, the kinetics of adsorption, and the competition between the different dyes. Several factors will therefore influence these phenomena: particle size, adsorbent mass, initial concentration of the dye, pH, and temperature of the solution.

- Initial dye concentration: Both for cationic and anionic dyes, the higher the dye concentration in the solution, the greater the adsorption capacity (amount of compound adsorbed per unit mass of adsorbent) (Ji et al., 2021; Liu et al., 2020; Sukla Baidya and Kumar, 2021).
- Adsorbent mass: For cationic dyes, the increased adsorbent mass implies a decrease in adsorbent capacity. This behavior may be associated with the fact that as long as the amount of adsorbent added to the dye solution is small, the cations of the dye can easily access the adsorption sites; as it could be attributed to the fact that a large amount of adsorbent can create agglomerations of particles, resulting in a reduction in the total adsorption area and, therefore, a decrease in the amount of adsorbate per unit of adsorbent mass (Alene et al., 2020; Boukhemkhem and Rida, 2017). In the case of anionic dyes, the rise in the adsorbent mass leads to a reduction in the potential of adsorption. Owing to the increased amount of empty active sites on the adsorbent surface at a higher adsorbent dose, such a pattern could be predictable by the adsorbate molecules' number constancy (Wong et al., 2020).

- Granulometry (the adsorbent particle size): this is a parameter closely linked to the specific adsorption surface area: Small particles have a large specific adsorption surface area and therefore perform much better than large particles (Wekoye et al., 2020).
- the pH of the solution: Anionic dyes are better adsorbed in acidic solutions while adsorption of cationic dyes is more effective in alkaline solutions (Zhao et al., 2021).
- The temperature of the solution: If the adsorption is favored by low temperatures, it is exothermic, otherwise it is endothermic (Wang et al., 2020).

5. Descriptive approach on the adsorption method

Although several approaches have been suggested for removing dyes, the adsorption processes remain the most attractive techniques, due to their simplicity and cost-effectiveness (Li et al., 2019).

5.1. Different types of adsorption

Two types of adsorption are defined according to the nature of the forces responsible for the formation of the interfacial layer: Physical adsorption or chemical adsorption, each has its properties as shown in Table 2 (Brandani, 2020; Cheng et al., 2019; Gupta and Suhas, 2009; Yagub et al., 2014).

5.2. Adsorption Isotherms

5.2.1. Langmuir's Isotherm
The solid adsorbent has a limited adsorption capacity. All active sites are identical and can only complex a single molecule of solute (monolayer adsorption). No interactions exist between the adsorbed molecules (Langmuir, 1918).

The mathematical equation of the Langmuir isotherm can be written in a non-linear form Eq.(1) (Chawla et al., 2017; Foo and Hameed, 2010; Hu et al., 2018; Sahin and Tapadia, 2015):

$$Q_e = \frac{K_L Q_L C_e}{1 + K_L C_e} \tag{1}$$

This isotherm also takes four linear forms gathered in Table 3 (Eq.(2-5)) (Chu et al., 2011; Foo and Hameed, 2010; Sahin and Tapadia, 2015).

where Q_L is Maximum monolayer coverage capacities (mg g^{-1}); K_L: Langmuir isotherm constant (L mg^{-1}); C_e: Equilibrium concentration (mg L^{-1}); and Q_e: Amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}).

This isotherm is the most used by scientific researchers in the fields of environmental adsorption because it is applicable at low concentrations, easy to use, and flexible with computer simulations especially when coupled with equations of transport phenomena (Laskar and Hashisho, 2020).

According to Al-Ghouti and Da'ana (2020), Langmuir relied on the structure and surface of solid materials and therefore classified adsorption into six mechanisms (Al-Ghouti and Da'ana, 2020) :

- First mechanism: Single-site adsorption in a surface of identical elementary adsorption sites capable of uptaking a single adsorbed molecule.
- Second mechanism: Multi-site adsorption in a surface containing more than one type of elemental adsorption sites and each site adsorbing a single molecule, is characterized by the independence of the binding sites and the neglect of the adsorbent-adsorbate interactions.
- Third mechanism: Generalized adsorption (case of continuum amorphous materials): several adsorption sites and several adsorbent affinities. The adsorption isotherm is dependent on the binding energy since adsorbent-adsorbate interactions are negligible.
- Fourth mechanism: Cooperative adsorption in a surface of identical elementary adsorption sites capable of uptaking several adsorbed molecules.
- Fifth mechanism: Dissociative adsorption by chemical bonding, molecular dissociation, and desorption
- Sixth mechanism: Multilayer adsorption where each adsorption site is independent and identical, and an unlimited number of molecules could be adsorbed.

5.2.2. Freundlich Isotherm

There are different types of different energy adsorption sites, but with the same entropy, distributed according to an exponential law as a function of the heat of adsorption. The density of sites decreases exponentially (Freundlich, 1907).

This isotherm can be represented using the nonlinear Eq.(6) or linear Eq.(7) models below (Foo and Hameed, 2010; Freundlich, 1907; Qian et al., 2018; Sahin and Tapadia, 2015):

$$Q_e = k_F(C_e)^{\frac{1}{n}} \tag{6}$$

$$Ln(Q_e) = Ln(K_F) + \frac{1}{n} Ln(C_e) \tag{7}$$

where C_e: equilibrium concentration (mg/L); K_F: Freundlich isotherm constant (mg/g) (L g^{-1})^n related to adsorption capacity; n: adsorption intensity; and Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}).

5.2.3. Bohart Adams Isotherm

It is an isotherm applied during adsorption by column and fixed bed (continuous adsorption). The assumptions taken by Bohart and Adams (1920) to implement their model are as follows (Bohart and Adams, 1920):

- The transfer area is symmetrical (negligible axial dispersion)
- The temperature, the inlet concentration of the adsorbate solution, the speed of passage, and the flow are constant,
- The column is at adsorption equilibrium (equilibrium between the adsorbent and the adsorbate).

The Bohart-Adams equation can be expressed using nonlinear Eq. (8) or linear Eq. (9) models represented below (Chu et al., 2011; El Hamidi et al., 2012; Yu et al., 2017):

$$\frac{C_t}{C_i} = \frac{e^{K_{BA}C_it}}{e^{K_{BA}N_0Z/U} - 1 + e^{K_{BA}C_it}}$$
$$= \frac{1}{1 + (e^{K_{BA}N_0Z/U} - 1)e^{-K_{BA}C_it}} \tag{8}$$

$$Ln\left(\frac{C_i}{C_t} - 1\right) = \frac{K_{BA}NZ}{U} - K_{BA}C_it \tag{9}$$

where C_i: Feed solution concentration; C_t: Solution concentration at fixed bed outlet at time t;

K_{BA}: Bohart-Adams rate constant; N_0: sorption capacity of sorbent per unit volume of fixed bed; t: time (minute); U: Superficial velocity; and Z: Total bed depth.

There exists in the literature of environmental adsorption, an isotherm called the "Thomas model" which resembles the model of Bohart Adams (the two isotherms ignore the dispersive effects) except that the model of Thomas is based on the isotherm of Langmuir with a pseudo-second-order velocity expression while the Bohart Adams model is a rectangular isotherm with a quasichemical velocity expression. Bohart Adams isotherm is applied to model the initial part of a breakthrough curve (Ratio of the adsorbate concentration at time t over its initial concentration is less than 0.5) and therefore it could be a limiting form of the isotherm of Thomas (Baghdadi et al., 2017; Chu, 2010).

5.2.4. Brunauer Emmett Teller (BET) Isotherm

This model admits the formation of adsorbent multilayers, a homogeneous distribution of the sites on the surface of the adsorbent, and the existence of adsorption energy which retains the first layer of adsorbed molecules, and second energy which retains the layers following. The model also accounts for the saturation phenomenon and involves the solubility of the solids in the solvent, in the form of saturation concentration. The relationship between adsorption capacity and concentration at equilibrium can be described using this isotherm in its non-linear Eq. (10) or linear Eq. (11) form (Brunauer et al., 1938; Foo and Hameed, 2010):

$$Q_e = \frac{Q_sC_{BET}C_e}{(C_s - C_e)\left(1 + (C_{BET} - 1)\left(\frac{C_e}{C_s}\right)\right)} \tag{10}$$

$$\frac{C_e}{Q_e(C_s - C_e)} = \frac{1}{Q_sC_{BET}} + \frac{(C_{BET} - 1)\left(\frac{C_e}{C_s}\right)}{Q_sC_{BET}} \tag{11}$$

where C_{BET} is BET adsorption isotherm relating to the energy of surface interaction (L/mg); C_e: equilibrium concentration (mg L^{-1}); C_s: adsorbate monolayer saturation concentration (mg L^{-1}); Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); and Q_s: theoretical isotherm saturation capacity (mg g^{-1}).

5.2.5. Dubinin Radushkevich Isotherm

The Dubinin-Radushkevich model is more general than the Langmuir model since it is not based on the assumption of a homogeneous surface and a constant adsorption potential (Dubinin, 1947a). Dubinin Radushkevich assumes that micropore volume filling is based on the fact that the adsorption's capacity is variable and that the adsorption's free enthalpy depends on the pores' filling degree (Thiam et al., 2020). This isotherm has a non-linear and linear form represented respectively by Eq. (12) and Eq. (13) (Dubinin, 1947b; Foo and Hameed, 2010; Ghaffari et al., 2017):

$$Q_e = Q_{DR}e^{-\beta\varepsilon^2} \tag{12}$$

$$Ln(Q_e) = Ln(Q_{DR}) - K_{DR}\varepsilon^2 \qquad (13)$$

where K_{DR}: Dubinin–Radushkevich isotherm constant (mol^2 kJ^{-2}); Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); and Q_{DR}: theoretical isotherm saturation capacity (mg g^{-1}).

ε: Potential of Polanyi (J/mol);

$$\varepsilon = RTLn\left(1 + \frac{1}{C_e}\right) \qquad (14)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and $T(K)$ is the absolute temperature.

5.2.6. Flory Huggins Isotherm

The theory of Flory–Huggins solutions is a mathematical model of the thermodynamics of polymer solutions that take into account the large dissimilarity of molecular sizes to adapt the usual expression of the entropy of the mixture (Flory, 1942). This isotherm can be presented using a nonlinear Eq. (15) or linear Eq.(16) model (Foo and Hameed, 2010; Hossain et al., 2016; Nechifor et al., 2015):

$$\frac{\theta}{C_i} = K_{FH}(1 - \theta)^{n_{FH}} \qquad (15)$$

$$log\left(\frac{\theta}{C_i}\right) = log(K_{FH}) + n_{FH}log(1 - \theta) \qquad (16)$$

where C_i: adsorbate initial concentration (mg L^{-1}); K_{FH}: Flory–Huggins isotherm equilibrium constant (Lg^{-1}); n_{FH}: Flory–Huggins isotherm model exponent; and θ: the degree of surface coverage.

5.2.7. Frenkel-Halsey-Hill Isotherm

It is assumed that an adsorbate atom interacts with the other species (adsorbate and substrate) only through pair potentials. Thus, the total interaction can be broken down into a sum of the different adsorbate/substrate and adsorbate/adsorbate contributions. In other words, this approximation assumes that the adsorbate/substrate interaction does not introduce a coupling between adsorbate atoms via interaction terms with three bodies (Coasne, 2003). The isotherm can be expressed using a non-linear model Eq. (17) (Foo and Hameed, 2010; Hill, 1952):

$$\ln\left(\frac{C_e}{C_s}\right) = \frac{-\alpha}{RT}\left(\frac{Q_s}{Q_e d}\right)^r \qquad (17)$$

where C_e: equilibrium concentration (mg L^{-1}); C_s: adsorbate monolayer saturation concentration (mg L^{-1}); d: Interlayer spacing (m); Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); Q_s: theoretical isotherm saturation capacity (mg g^{-1}); R: universal gas constant (8.314 J mol^{-1} K^{-1}); r: inverse power of distance from the surface; T: temperature (K); and α: Frenkel–Halsey–Hill isotherm constant (J m^r mole^{-1}).

5.2.8. Khan Isotherm

The important variables in evaluating the adsorption properties of an adsorbent for a given adsorbent-adsorbate device are surface heterogeneity, pore surface. The hydrophilic and hydrophobic nature of chemical molecules (adsorbate) is also important when aqueous solutions are used for adsorption.

Adsorption on activated carbon decreases in high pH values, but the addition of neutral salts accelerates adsorption. The effect of pH is due to the electrostatic relationship between the adsorbent surface and the adsorbate or ion-molecule (Khan et al., 1997). This isotherm can be expressed using the linear model Eq. (18) (Foo and Hameed, 2010):

$$Q_e = \frac{Q_S b_k C_e}{(1 + b_k C_e)a_k} \qquad (18)$$

where a_k: Khan isotherm model exponent; b_k: Khan isotherm model constant; C_e: equilibrium concentration (mg L^{-1}); Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); and Q_s: theoretical isotherm saturation capacity (mg g^{-1}).

5.2.9. Koble Corrigan Isotherm

The Koble-Corrigan isotherm is a three-parameter equation that integrates the Langmuir and Freundlich isotherms to represent the adsorption data at equilibrium. The model is generally applied to the heterogeneous adsorption surface (Saadi et al., 2015). The mathematical expressions of this isotherm in its non-linear and linear forms are represented by Eq. (19) and Eq. (20) respectively (Foo and Hameed, 2010; Koble and Corrigan, 1952):

$$Q_e = \frac{A(C_e)^n}{1 + B(C_e)^n} \qquad (19)$$

$$\frac{1}{Q_e} = \frac{1}{A(C_e)^n} + \frac{B}{A} \qquad (20)$$

where A: Koble–Corrigan isotherm constant (L^{n}mg^{1-n} g^{-1}); B: Koble–Corrigan isotherm constant (L mg^{-1})^n; C_e: equilibrium concentration (mg L^{-1}); n: adsorption intensity; and Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}).

According to Shahbeig et al. (2013), the Koble-Corrigan model's mean relative percent error is the same as the Hill model, and therefore the two models are similar and have the same structure (Shahbeig et al., 2013).

5.2.10. MacMillan-Teller Isotherm

The MacMillan-Teller isothermal model has been extended taking into account the surface tension effects in the Brunauer Emmett-Teller isotherm (Saadi et al., 2015). This isotherm can be presented using a non-linear model Eq. (21) (Foo and Hameed, 2010):

$$Q_e = Q_S\left(\frac{k}{ln\left(\frac{C_S}{C_e}\right)}\right)^{\frac{1}{3}} \qquad (21)$$

where C_e- equilibrium concentration (mg L^{-1}); C_s - adsorbate monolayer saturation concentration (mg L^{-1}); K - MacMillan–Teller isotherm constant; Q_e - the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); and Q_s - theoretical isotherm saturation capacity (mg g^{-1}).

5.2.11. Radke Prausnitz Isotherm

The thermodynamic foundations used by Myers and Prausnitz (1965) to develop the Theory of the Ideal Adsorbed Solution are taken from the ideal behavior of gases and the classical

Gibbs equation (Myers and Prausnitz, 1965). This theory was then modified to be able to apply it to the case of the solutions of Radke and Prausnitz (1972). The advantage of this model is that it is not based on a particular pure body isothermal model, but thermodynamic foundations. Consequently, all pure body isotherm models (e.g., Freundlich, and Langmuir) can be integrated into it. This approach is based on the following thermodynamic assumptions:

- The adsorbent is assumed to be thermodynamically inert, that is to say, that the variation in its thermodynamic properties (internal energy for example) is negligible throughout the adsorption, carried out at constant temperature. The available surface is invariant and equivalent for all the compounds.
- The thermodynamic definition of adsorption, presented by Gibbs, is applicable (Ruthven, 1984; Tien, 1995).
- The adsorbed phase consisting of n compounds behaves like an ideal solution.

The isotherm can be modeled under this non-linear formula (Eq. (22)) (Foo and Hameed, 2010; Vijayaraghavan et al., 2006):

$$Q_e = \frac{a_{RP} r_R (C_e)^{\beta_R}}{a_{RP} + r_R (C_e)^{\beta_R - 1}} \tag{22}$$

where a_{RP}: Radke–Prausnitz isotherm model constant; C_e: equilibrium concentration (mg L^{-1}); Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); r_R: Radke–Prausnitz isotherm model constant; and β_R: Radke–Prausnitz isotherm model exponent.

5.2.12. Redlich Peterson isotherm

The Redlich-Peterson isotherm model can be used over a wide range of concentrations to describe the adsorption equilibrium and can be implemented due to its flexibility in homogeneous or heterogeneous systems (Ayawei et al., 2017). This isotherm can be modeled by a nonlinear equation Eq. (23) and a linear equation Eq. (24) (Foo and Hameed, 2010; Redlich and Peterson, 1959):

$$Q_e = \frac{K_R C_e}{1 + a_R (C_e)^g} \tag{23}$$

$$\ln \left(K_R \frac{C_e}{C_s} - 1 \right) = g \ln (C_e) - \ln (a_R) \tag{24}$$

where a_R: Redlich–Peterson isotherm constant (L mg^{-1}); C_e: equilibrium concentration (mg L^{-1}); g: Redlich–Peterson isotherm exponent; K_R: Redlich–Peterson isotherm constant (L g^{-1}); and Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}).

5.2.13. Sips isotherm

This mathematical model is valid if the adsorption is localized and there are no interactions between the adsorbates (Sips, 1948). This isotherm can be modeled using a nonlinear Eq. (25) and linear Eq. (26) equation (Foo and Hameed, 2010; Sips, 1948):

$$Q_e = \frac{K_S (C_e)^{\beta_S}}{1 + a_S (C_e)^{\beta_S}} \tag{25}$$

$$\beta_s \ln (C_e) = -\ln \left(\frac{K_S}{Q_e} \right) + \ln (a_S) \tag{26}$$

where a_s: Sips isotherm model constant (L mg^{-1}); C_e: equilibrium concentration (mg L^{-1}); K_S: Sips isotherm model constant (L g^{-1}); Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); and β_s: Sips isotherm model exponent.

5.2.14. Temkin isotherm

The isothermal model of Temkin suggests that with the increased coverage of the adsorbent surface where adsorption is defined by a uniform distribution of binding energies, the heat of adsorption of all molecules decreases linearly to maximum bond energy (Temkin, 1940). This isotherm can be modeled using Eq. (27) (Foo and Hameed, 2010; Ghaffari et al., 2017):

$$Q_e = \frac{RT}{b_T} \ln (A_T C_e) = \frac{RT}{b_T} ln(A_T) + \frac{RT}{b_T} ln(C_e) \tag{27}$$

where A_T: Temkin isotherm equilibrium binding constant (L g^{-1}); b_T: Temkin isotherm constant; C_e: equilibrium concentration (mg L^{-1}); Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); R: universal gas constant (8.314 J mol^{-1} K^{-1}); and T: temperature (K).

The main advantage of Temkin isotherm is that it allows the evaluation of the heat of the adsorption: if the constant b$_T$ is positive, the adsorption process would be exothermic (Rossetto et al., 2020).

5.2.15. Toth Isotherm

Toth's model is based on Langmuir's model with a reduced experimental error. Toth's model takes into account lateral interactions, surface heterogeneity within the system, and other deviations from ideality. This isotherm can be modeled using a nonlinear equation Eq.(28) and a linear equation Eq. (29) (Foo and Hameed, 2010; Toth, 1971):

$$Q_e = \frac{K_T C_e}{(a_T + C_e)^{\frac{1}{t}}} \tag{28}$$

$$\ln \left(\frac{Q_e}{K_T} \right) = \ln (C_e) - \frac{1}{t} ln(a_T + C_e) \tag{29}$$

where a_T: Toth isotherm constant (L mg^{-1}); C_e: equilibrium concentration (mg L^{-1}); K_T: Toth isotherm constant (mg g^{-1}); Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); and t: Toth isotherm constant.

5.2.16. Wolborska Isotherm

The Wolborska model describes the adsorption dynamics using the mass transfer equations associated with the diffusion mechanisms at low concentrations of the rupture curve ($C_t/C_i < 0.05$) (Quintelas et al., 2008). The isotherm can be modeled using this nonlinear formula Eq. (30) (Yu et al., 2017):

$$\frac{C_t}{C_i} = e^{\left(\frac{\beta C_i}{N_0} t - \frac{\beta Z}{U} \right)} \tag{30}$$

where C_i: adsorbate initial concentration (mg L^{-1}); C_t: solution concentration at fixed bed outlet at time t; N_0: the maximum volumetric sorption capacity; U: the linear flow rate; Z: total bed depth; and β: kinetic coefficient of the external mass transfer.

5.2.17. Yoon Nelson Isotherm

The Yoon-Nelson adsorption model assumes that the rate of decrease in the rate of adsorption probability on the adsorbate molecule is proportional to the breakthrough on the adsorbent (Ahmad and Hameed, 2010). The isotherm can be modeled under the following nonlinear formula Eq.(31) (Yu et al., 2017):

$$\frac{C_t}{C_i} = \frac{1}{1 + e^{-K_{YN}(t-\tau)}} \tag{31}$$

where C_i: adsorbate initial concentration (mg L^{-1}); C_t: Solution concentration at fixed bed outlet at time t; K_{YN}: Yoon–Nelson rate constant; and τ: the time required for reaching 50 % adsorbate breakthrough (min).

5.2.18. Harkin Jura Isotherm

With the inclusion of heterogeneous pore distribution on the surface of the adsorbent, the Harkin Jura isotherm determines the multilayer adsorption system (Imran and Latif, 2018). The isotherm can be modeled under the following linear formula Eq.(32) (Hossain et al., 2016):

$$\frac{1}{Q_e^2} = \frac{B_{HJ}}{A_{HJ}} - \frac{1}{A_{HJ}} log(C_e) \tag{32}$$

where Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); A_{HJ}: Harkin-Jura isotherm constants (slope); B_{HJ}: Harkin-Jura isotherm constants (intercept); and C_e: equilibrium concentration (mg L^{-1}).

5.2.19. Halsey Isotherm

The isothermal model of Halsey primarily specifies the multilayer adsorption mechanism for adsorbate at a relatively wide distance from the surface of the adsorbent with a heterogeneous porous design (Al-Ghouti and Da'ana, 2020). The isotherm can be modeled under this linear formula Eq. (33) (Hossain et al., 2016):

$$Ln(Q_e) = \frac{1}{n_H} Ln(K_H) - \frac{1}{n_H} Ln(C_e) \tag{33}$$

where Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); C_e: equilibrium concentration (mg L^{-1}); K_H: Halsey Constant (slope); and n_H: Halsey Constant (intercept).

5.2.20. Elovich-Larionov Isotherm

The Elovich-Larionov isotherm describes the adsorption of non-electrolytes from a solution on a solid surface (Elovich and Larionov, 1962). The isotherm can be modeled under this linear formula Eq. (34) (Hossain et al., 2016):

$$Ln\left(\frac{Q_e}{C_e}\right) = Ln(K_E Q_E) - \frac{1}{Q_E} Q_e \tag{34}$$

where Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); C_e: equilibrium concentration (mg L^{-1}); K_E: Elovich-Larionov isotherm constant; and Q_E: Elovich-Larionov maximum adsorption capacity (mg g^{-1}).

5.3. Kinetic Models

Adsorption is a complex phenomenon, which generally follows a path that includes a combination of surface adsorption and diffusion into the pores.

5.3.1. Kinetic model of Lagergren's pseudo-first-order

The Lagergren kinetic is the most commonly used for the liquid-solid adsorption system based on the pseudo-first-order equation (Lagergren, 1898). According to Rodrigues and Silva (2016), the pseudo-first-order model describes the adsorption kinetics of a species in an adsorbent particle by the following ordinary first-order differential equation Eq. (35) (Rodrigues and Silva, 2016):

$$\frac{dQ}{dt} = K_1(Q_e - Q_t) \tag{35}$$

The differential equation Eq. (35) shows that the adsorption capacity is proportional to the "distance to equilibrium" and which is expressed by the difference between the final concentration of the phase adsorbed in equilibrium with the fluid phase and the average concentration of the species in the adsorbed phase: At time $t = 0$, for a clean particle, the average concentration of species in the adsorbed phase is zero and the distance at equilibrium is equal to the final concentration of the adsorbed phase in equilibrium with the fluid phase; as time increases, the distance at equilibrium decreases and becomes nullified when equilibrium is reached: The difference between the concentration of the final adsorbed phase in equilibrium with the fluid phase and the average concentration of species in adsorbed phase is zero (Rodrigues and Silva, 2016).

By integration of this differential equation Eq. (35) for the boundary conditions: $qt = 0$ to $t = 0$ and $qt = qt$ to $t = t$, the following pseudo-first-order Lagergren equation was obtained Eq. (36) (Çiftçi and Henden, 2015; Moussout et al., 2018):

$$Ln(Q_e - Q_t) = Ln(Q_e) - K_1 t \tag{36}$$

where Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}); Q_t: the amount of adsorbate in the adsorbent at time t (mg g^{-1}); K_1: constant rate of Lagergren's first order; and t: time of contact (min).

To test this isotherm, it is convenient to represent $Ln\ (Qe-Qt)$ graphically as a function of the contact time t and to note the coefficient of determination R^2.

5.3.2. Kinetic model of Pseudo Second Order

Adsorption takes place on two surface sites in pseudo-second-order kinetics (some authors call it "*Blanchard's model*"), and therefore, can be expressed by the following second-order differential equation Eq. (37) (Naderi et al., 2018; Rout et al., 2015):

$$\frac{dQ}{dt} = K_2(Q_e - Q_t)^2 \tag{37}$$

by the integration of this differential equation Eq. (37) for the boundary conditions: $qt = 0$ to $t = 0$ and $q_t = qt$ to $t = t$, the mathematical equation of the following pseudo-second-order kinetic model Eq.(38) was obtained (Çiftçi and Henden, 2015; Moussout et al., 2018):

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{1}{Q_e} t \tag{38}$$

where Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg/g); Q_t: the amount of adsorbate in the adsorbent at time t (mg g^{-1}); K_2: constant rate of Pseudo second order; and t: time of contact (min).

To test this isotherm, it is convenient to represent graphically t/Qt according to the contact time t and to note the coefficient of determination R^2.

5.3.3. Kinetic model of Avrami

This model implies that the reaction is located on the active surface sites of the solid support and its equation takes the following two forms, exponential and double logarithmic, respectively represented by Eq. (39) and Eq. (40) (George and Sugunan, 2014; Georgin et al., 2018):

$$Q_t = Q_{av}\left(1 - e^{(k_{av}t)^{n_{av}}}\right) \tag{39}$$

$$\ln\left(-\ln\left(1 - Q_t\right)\right) = \ln(K_{av}) + n_{av}\ln\left(t\right) \tag{40}$$

where Q_{av}: Avrami theoretical value of the amount of the adsorption (mg g^{-1}); K_{av}: Avrami constant rate; t: time of contact (min); n_{av}: Avrami order model; and Q_t: the amount of adsorbate in the adsorbent at time t (mg g^{-1}).

To test this isotherm, it is convenient to graph Q_t as a function of the contact time t for the exponential model or Ln $(-Ln$ $(1-$ $Q_t))$ as a function of Ln (t) for the double logarithmic model and to note the coefficient of determination R^2.

According to equations Eq. (39) and Eq. (40), the Avrami model depends on two parameters derived from the Kolmogorov – Erofeev – Kazeeva – Avrami – Mampel equation:

- The overall speed of adsorption (k)
- The specific parameter linked to the adsorption mechanism (n), the values of which can be used to check for possible alterations in the adsorption mechanisms as a function of contact time and temperature. In general, n can be considered as the criterion determining the domain in which these heterogeneous reactions occur. The value determines whether the adsorption process can be limited by a surface reaction ($n > 1$) or not. If $n = 1$, the interaction is therefore instantaneous (George and Sugunan, 2014).

The main drawback of this model is that it sometimes shows the presence of two and/or three linearized regions, as a function of time and temperatures of adsorption (George and Sugunan, 2014). Therefore, it may be necessary to take into account 2 and/or 3 independent sets of values of n {n_1, n_2, n_3} and k {k_1, k_2, k_3}(George and Sugunan, 2014). George and Sugunan (2014) used this model in its double logarithmic form to describe the kinetics of adsorption of the lipase enzyme of *Candida rugosa* on pure and mesoporous silica materials synthesized hydrothermally and modified by glutaraldehyde. Their results showed that the enzyme-support interaction was well adjusted to the Avrami model (the coefficient of determination R^2 is between 0.90 and 0.98 for the different mesoporous materials), the adsorption is controlled by the surface kinetics (n greater than 1), and the enzyme had a relatively high affinity for the active sites of mesoporous silica according to the values obtained from the speed constant k and the activation energy, around 49 kJ/mol (George and Sugunan, 2014).

According to Ahmad et al. (2020), the Avrami kinetic model could be used in the case where adsorption is slow and/or when there is more than one mechanism of adsorption (Ahmad et al., 2020).

5.3.4. Bangham kinetic model

Bangham kinetic model explores the stage of slow diffusion in the pores of the adsorption process thus (Malana et al., 2011). The model can be represented by the empirical mathematical equation Eq. (41):

$$\log\left(\log\left(\frac{C_t}{C_i}\right) - Q_t m\right) = \log K_0 + Q_t \log(t) \tag{41}$$

where C_t: solution concentration at fixed bed outlet at time t; C_i: adsorbate initial concentration (mg L^{-1}); Q_t: the amount of adsorbate in the adsorbent at time t (mg g^{-1}); m: the mass of the adsorbent in 1 L of the adsorbate (g L^{-1}); K_0: constant rate of Bangham's model; and t: time of contact (min).

To test this isotherm, it is convenient to graph $\log\left(\log\left(\frac{C_t}{C_i}\right) - Q_t m\right)$ as a function of $\log(t)$ and to note the coefficient of determination R^2.

5.3.5. Boyd kinetic model

It is a model that makes it possible to distinguish between extraparticle and intraparticle diffusion: If the plot of B_t as a function of time is a straight line that passes through the origin, the sorption is controlled by intraparticle diffusion; otherwise, it is governed by the diffusion in the film (it is limited by extraparticular transport). This model corresponds to the following equation Eq. (42) (Okewale et al., 2013):

$$B_t = -0.4977 - \ln\left(1 - \frac{Q_t}{Q_e}\right) \tag{42}$$

where B_t: Boyd constant; Q_t: the amount of adsorbate in the adsorbent at time t (mg g^{-1}); and Q_e: the amount of adsorbate in the adsorbent at equilibrium (mg g^{-1}).

To test this isotherm, it is convenient to represent B_t graphically as a function of the contact time t and to note the coefficient of determination R^2.

5.3.6. Elovich kinetic model

The Elovich equation has been widely used to describe not only the kinetics of gas adsorption on solids but also the adsorption of pollutants from aqueous solutions in recent years (Ho, 2006). This model corresponds to the following equation Eq.(43) (Chien and Clayton, 1980):

$$Q_t = \beta \ln\left(\alpha\beta\right) - \ln\left(t\right) \tag{43}$$

where Q_t: the amount of adsorbate in the adsorbent at time t (mg g^{-1}); β: the number of sites available for adsorption; α: the initial adsorption rate (mg g^{-1} min); and t: time of contact (min). To test this isotherm, it is convenient to graph Q_t as a function of Ln (t) and to note the coefficient of determination R^2.

5.3.7. Kinetic model of intraparticle diffusion

Generally, there are four stages in the adsorption process by porous solids:

1) Transfer of the solute from the solution to the boundary layer surrounding the particle
2) Transfer of the solute from the boundary layer to the adsorbent surface
3) Transfer of the solute to the adsorbent sites: Diffusion in the micropores and macropores

Table 4 Main characteristics and adsorption capacities of various adsorbents for the treatment of dyes

Adsorbent	Adsorbate	Amount of adsorption (mg g⁻¹)	Kinetic Model	Adsorption isotherm	Specific Surface (m² g⁻¹)	Reference
Heulandite	Safranin T	41.6	Pseudo second order	-	-	(Abukhadra and Mohamed, 2019)
Clinoptilolite	Safranin T	42.9	Pseudo second order	-	-	(Abukhadra and Mohamed, 2019)
Phillipsite	Safranin T	65.35	Pseudo second order	-	-	(Abukhadra and Mohamed, 2019)
Almond shell activated carbon	Crystal Violet	625	Pseudo second order	Langmuir	2054	(Ait Ahsaine et al., 2018)
Nanoparticles of magnetites (Azolla)	Crystal Violet	30.21	Pseudo second order	Langmuir	-	(Alizadeh, 2017)
Nanoparticles of magnetites (Figleaves)	Crystal Violet	53.47	Pseudo second order	Langmuir	-	(Alizadeh, 2017)
Glyricidia sepium woodchip based activated carbon	Basic Green 4	230.47	Avrami	Fritz–Schlünder (for discontinuous adsorption), Thomas and Yoon-Nelson (for continuous adsorption)	633.30	(Ahmad et al., 2020)
Tunisian almond shell	Eriochrome Black T	123.92	Pseudo second order	Freundlich	-	(Arfi et al., 2018)
Tunisian almond shell	Malachite green	126.9	Pseudo second order	Freundlich	-	(Arfi et al., 2018)
Azola filiculoides aquatic fern	Reactive Black 5	41.73	Pseudo second order	Langmuir	-	(Balarak et al., 2020)
Tea waste	Astrazon Blue FGRL	263.16	-	Freundlich	0.871	(Balkaya, 2019)
Waste Mussel Shells	Orange G	1000	Pseudo second order	Langmuir	-	(Delali et al., 2019)
Biomass compound of pine, oak, hornbeam, and fir sawdust	Malachite green	48.261	Intraparticle diffusion	Freundlich	-	(Deniz, 2017)
Persea americana avocado shell (sulfuric acid)	Procion Red	167	-	Sips	5.32 ±0.20	(Georgin et al., 2018)
Persea americana avocado shell (nitric acid)	Procion Red	212.6	-	Sips	8.45 ±0.71	(Georgin et al., 2018)
Peanut shell (sulfuric acid reflux)	Tetracycline	303	Pseudo second order	Langmuir	3.7	(Islam et al., 2019)
Carbonized Watermelon (*Citrus lanatus*)	Methylene Blue	200	Pseudo second order	Langmuir	-	(Jawad et al., 2019)
Corn stalk-walnut shell mix-based activated carbon	iodine	720.5	Pseudo second order	Langmuir	1187	(Kang et al., 2018)
Pseudevernia furfuracea activated carbon	Methylene Blue	243.90	Pseudo Second Order, Elovich and Intraparticle Diffusion	Langmuir, Freundlich and Dubinin Radushkevich	851.24	(Koyuncu and Kul, 2020)
Water hyacinth	Crystal Violet	322.58	Pseudo second order	Langmuir	-	(Kulkarni et al., 2017)
Psyllium seed powder	Reactive Orange 16	206.6	-	Langmuir	-	(Malakootian and Heidari, 2018)
Calcite	Methylene Blue	18.776	Pseudo second order	Langmuir	-	(Miyah et al., 2015)
Pyrophyllite	Methylene Blue	19.608	Pseudo second order	Langmuir	-	(Miyah et al., 2015)
Pyrophyllite	Crystal Violet	9.58	Pseudo second order	Langmuir	-	(Miyah et al., 2017)
Walnut shells powder	Methylene Blue	178.9	Pseudo second order	Langmuir	-	(Miyah et al., 2018)
Banana Peel Powder	Congo Red	164.6	Pseudo second order	Langmuir	-	(Munagapati et al., 2018)
Chemical iron nanoparticles	Crystal Violet	454.5	Pseudo second order	Langmuir	34.38	(Nasiri et al., 2019)
Biological Iron	Crystal	454.5	Pseudo second	Langmuir	46.68	(Nasiri et al.,

Table 4 (*continued*)

Adsorbent	Adsorbate	Amount of adsorption (mg g^{-1})	Kinetic Model	Adsorption isotherm	Specific Surface (m^2 g^{-1})	Reference
nanoparticles	Violet		order			2019)
Organometallic nanomaterials of the Lavoisier Institute	Basic Blue 41	1257	-	Langmuir	1350	(Oveisi et al., 2018)
Organometallic nanomaterials of the Lavoisier Institute	Basic Red 46	1296	-	Langmuir	1350	(Oveisi et al., 2018)
Persea americana-activated carbon prepared by phosphoric acid action	Basic Blue 41	625	Pseudo second order	Langmuir	1593	(Regti et al., 2017)
Goat polishing dust	Brilliant Cresyl Blue	-	Pseudo second order	Langmuir -Brunauer Emmett Teller	-	(Roy et al., 2019)
Rhizopus arrhizus	Fast Red	108.8	Pseudo second order	Langmuir	-	(Salvi and Chattopadhyay, 2017)
Natural cocoa shell	Azur II	12.03	Pseudo second order	Langmuir-Freundlich	-	(Takam et al., 2017)
Plasma treated cocoa shell	Azur II	14.04	Pseudo second order	Langmuir-Freundlich	-	(Takam et al., 2017)
Natural cocoa shell	Reactive Red II	32.78	Pseudo second order	Langmuir-Freundlich	-	(Takam et al., 2017)
Plasma treated cocoa shell	Reactive Red II	40.32	Pseudo second order	Langmuir-Freundlich	-	(Takam et al., 2017)
Hydrochar of golden pods	Methylene Green 5	59.6	-	-	6.65-14.7	(Tran et al., 2017)
Basic sawdust acacia	Methylene Blue	267.04	-	Langmuir	-	(Tounsadi et al., 2020)
3.5-Diacrylamidobenzoic acid-based resin	Rhodamine B	23.28	-	Langmuir and Temkin	64.78	(Waheed et al., 2019)
bis-N,N,N-dodecyldimethyl-p-phenylenediammonium dibromide	Rhodamine B	234	Pseudo second order	Freundlich	-	(Wang et al., 2019)
1,3-bis (dodecyldimethylammonio)-2-hydroxypropane dichloride	Rhodamine B	267	Pseudo second order	Langmuir	-	(Wang et al., 2019)
1,9-bis(dodecyl)-1,1,9,9-tetramethyl-5-imino-1,9-nonanediammonium dibromide	Rhodamine B	528	Pseudo second order	Langmuir	-	(Wang et al., 2019)
Apricot shell activated carbon	Atrazine	57.18	Pseudo second order	Freundlich	276.15	(Wu et al., 2018)
Walnut shell activated carbon	Atrazine	156.25	Pseudo second order	Freundlich	553.33	(Wu et al., 2018)
Apricot shell activated carbon	Atrazine in co-solution with bisphenol a	45.05	Pseudo second order	Freundlich	614.21	(Wu et al., 2018)
Walnut shell activated carbon	Atrazine in co-solution with bisphenol a	105.26	Pseudo second order	Freundlich	553.33	(Wu et al., 2018)
Apricot shell activated carbon	Bisphenol a	52.91	Pseudo second order	Langmuir	276.15	(Wu et al., 2018)
Walnut shell activated carbon	Bisphenol a	136.98	Pseudo second order	Langmuir	614.21	(Wu et al., 2018)
Sugar cane bagasse (diethylenetriamine)	Congo red	780	Pseudo second order	Langmuir	-	(Yu et al., 2017)
Cedar cone forest waste	Crystal Violet	7.7	Pseudo second order	Freundlich	-	(Zamouche et al., 2020)

Table 4 (*continued*)

Adsorbent	Adsorbate	Amount of adsorption (mg g^{-1})	Kinetic Model	Adsorption isotherm	Specific Surface (m^2 g^{-1})	Reference
Walnut shell activated carbon	Phenanthrene	247.54	Pseudo second order	Langmuir	-	(Zheng et al., 2018)
Magnetic microparticles of chitosan	Tartrazin	666.67	Pseudo second order	Langmuir	1.50-2.94	(Zheng et al., 2019)
Magnetic microparticles of chitosan	Yellow food 3	833.33	Pseudo second order	Langmuir	1.50-2.94	(Zheng et al., 2019)

4) Interactions between the molecules of the solute and the active sites on the surface: Adsorption, complexation, and precipitation

Several studies referring to this kinetic approach to intra-particulate diffusion are generally based on work by Weber and Morris (1963) on the adsorption of simple aromatic compounds on activated carbon and show that the concentration of adsorbate (C_t) is a linear function of the square root of the contact time ($t^{1/2}$), whose slope is assimilated to the speed constant according to the following equation Eq.(44) (Weber and Morris, 1963):

$$Q_t = K_{ID}\sqrt{t} + I \qquad (44)$$

where Q_t: the amount of adsorbate in the adsorbent at time t (mg g^{-1}); K_{ID}: constant rate of intraparticle diffusion; t: time of contact (min); and I: intercept of intraparticle diffusion kinetic model. To test this isotherm, it is suitable to graph Q_t as a function of the square root of the contact time and to note the coefficient of determination R^2.

5.4. Results of the application of adsorption

One of the main contributors to environmental pollution is colored industrial waste present in wastewater. However, particular attention has been paid to these industries by developing research for the identification of economical methods of treating their colored waste and meeting the required standards. In this context, several studies relating to the elimination of dyes were undertaken by increasingly less developed physic-chemical or biological means. Adsorption has attracted considerable attention in dye wastewater treatment due to its technical feasibility, flexibility, and ease of operation. Consequently, it is the subject of several research works, the results of which are mentioned in Table 4.

6. Adsorption in the continuous system

The sizing of column adsorption units is based on hydrodynamic and physicochemical considerations:

- Fluid Flow Rate: *Owing to the increase of contact time between the adsorbent surface and the dye in solution, equilibrium adsorption capability increases as the flow rate is decreased* (Camara et al., 2020).
- pH: It could be inferred from the work of Vieira et al.(2019) that in the case of the adsorption of anionic dyes such as FD&C Red 40 is greater efficient in acidic conditions due to electrostatic interaction between the negative charge of the dye and the positive charge of the adsorbent (Vieira et al., 2019). However, cationic dyes are better adsorbed on alkaline pH due to their elimination by the hydroxide anions (Miyah et al., 2020).
- Filter Bed Height: The growth in bed height leads to an increase in breakthrough time and a longer bed height, the dye solution needs further to be in contact with the adsorbent and thus to increase the adsorption of the dye. This phenomenon could be explained by the assumption that, owing to a reduction in the axial dispersion of the mass transition, the rise in the adsorbent mass results in an increase in the dye molecules diffusion to the adsorbent (Akbar et al., 2020; Faraj et al., 2020).
- Particle size: The dye adsorption capacity is greater when the adsorbent particles are thin dye to the higher number of active sites in their larger surface area (El mouhri et al., 2021).

To describe the adsorption of the solute in the case of a liquid phase flowing through the adsorbent bed, transfer relationships between the mobile (liquid) and solid (fixed) phases are used. For this, the benefit of concentration in the two phases must be known as a function of time and space. A mathematical calculation makes it possible to write, in the form of equations, the different stages taking place during the process. Three approaches are possible: stochastic, mathematical, and experimental methods (Baharlouei et al., 2018; Gritti, 2018; Patel, 2019; Rahbaralam et al., 2020).

6.1. Stochastic Method

The phenomenon that takes place in the adsorption column is considered random. The evolution of the adsorbate concentration in the two phases does not follow any defined rule and the study must therefore be the subject of statistical analysis (Namane and Hellal, 2006).

6.2. Mathematic Method

This method takes into account all the parameters involved in the adsorption process. It consists of a mathematical spatial and temporal description of the distribution of the adsorbent between the two phases. It is advantageous for two reasons: First, it allows a complete description of the adsorption mechanism, second, once the mathematical relationships are established, the influence of the various parameters can be predicted (Fallah and Taghizadeh, 2020). But taking into account all the

factors involved in the continuous adsorption process is a difficult and tedious job, moreover, the resolution of the global equations always requires simplifying considerations, which means that the solutions found are limited cases (Xu et al., 2013).

6.3. Experimental Method (Mass Transfer Zone)

The concept of the mass transfer zone was developed by Michaels (1952) for ion exchange and later adapted by Lukchis (1973) for adsorption (Lukchis, 1973; Michaels, 1952). It is a simple, efficient, and very reliable method for practice and allows correlations to be established for adsorption systems (Naja and Volesky, 2006). However, the operating conditions must be set: A uniform bed, a volume flow rate, and a uniform concentration for the liquid phase, no phase change, negligible absorption energy, and no interaction between the adsorbed molecules. It has been noticed that during the adsorption process, it is not the whole filter that participates in the transfer phenomenon, but only a portion of the bed whose depth is variable, and where practically 95% of the exchange takes place of the solute between the two phases: mobile and fixed. This portion of the bed called the "mass transfer zone" moves through the bed at a constant speed until it is saturated (Khalfa et al., 2021; Namane and Hellal, 2006). The sizing of an adsorption column can be done by calculating the parameters characterizing the mass transfer zone: the fractional capacity, the height of the mass transfer zone, and the movement rate of the mass transfer zone.

6.3.1. Fractional Capacity

The Fractional Capacity determines the effectiveness of the adsorbent in removing adsorbate. It could be defined as the quantity which participates in the phenomenon of adsorption relative to the total quantity of adsorbent, or else as the quantity of adsorbate removed relative to the potential elimination capacity of the adsorbent inside the mass transfer zone (Namane and Hellal, 2006). It is calculated graphically according to the equation Eq. (45) :

$$F = \frac{A_Z}{A_{max}} = \frac{\int_{V_{Bp}}^{VE} (C_0 - C_i) dV}{C_0 (V_E - V_{Bp})} \tag{45}$$

Where F: Fractional Capacity; A_z: is the amount removed within the mass transfer zone (mg); A_{max}: represents the maximum amount of adsorbate that can be removed by the filter inside the mass transfer zone (mg); V_{Bp}: volume of treated effluent at the breakthrough point (where concentration is less than 5% of the initial concentration) (ml); V_E: Volume treated at the saturation point (ml); C_0: Initial concentration of adsorbate (mg/l); C_i: Concentration of the solute of species i at equilibrium (mg/l); and V: Volume of solute solution.

6.3.2. Height of the mass transfer zone

It is in this portion of the bed that practically takes place most of the phenomenon. It determines the rate of elimination of the adsorbate by the adsorbent (Namane and Hellal, 2006). It is an effective parameter for quantifying the global exchange rates, it is calculated as follows in Eq.(46) and Eq.(47):

$$t_z = t_E - t_{Bp} \tag{46}$$

$$H_z = U_z \times t_z \tag{47}$$

Where t_z: the time required for the mass transfer zone to settle at the top of the column (minutes); t_E: Saturation time (minutes); t_{Bp}: Time at breakthrough point (minutes); H_z: height of mass transfer zone (cm); and U_z: Movement rate of the mass transfer zone (cm minute^{-1})

Apart from its training period, the mass transfer zone moves along the column of the adsorbent bed and is calculated by Eq. (48):

$$t_E - t_F = \frac{H_b}{U} \tag{48}$$

Where t_E: Saturation time (minutes);t_F: Time required for the formation of the adsorption zone (minutes); and H_b: Adsorption bed height (cm).

Since the movement rate of the mass transfer zone is constant, we obtain Eq. (49) :

$$U_Z = \frac{H_z}{t_z} = U = \frac{H_b}{t_E - t_F} \tag{49}$$

Where t_z: the time required for the mass transfer zone to settle at the top of the column (minutes); H_z: height of mass transfer zone (cm); t_E: Saturation time (minutes);t_F: Time required for the formation of the adsorption zone (minutes); H_b: Adsorption bed height (cm); and U_z: Movement rate of the mass transfer zone (cm minute^{-1}).

Since the only unknown in Eq. (49) is t_F, it could be estimated, based on Eq. (50), by the fact that if the fractional capacity is zero, it means that the adsorbent is entirely saturated, $t_F = t_z$ and therefore the mass transfer zone travels a distance equal to its depth. On the other hand, if the fractional capacity is equal to 1, then the adsorbent is an example of adsorbate, t_F should be very short, at the limit equal to zero.

$$t_F = (1 - F)t_z = (1 - F)(t_E - t_{Bp}) \tag{50}$$

Where t_F: Time required for the formation of the adsorption zone (minutes); F: Fractional Capacity; t_z: the time required for the mass transfer zone to settle at the top of the column (minutes); t_E: Saturation time (minutes); and t_{Bp}: Time at breakthrough point (minutes).

From Eq. (49) and Eq. (50), we could deduce Eq. (51) by which we could determine the height of the filter bed H_z :

$$H_z = \frac{H_b . t_z}{t_E - t_F} = \frac{H_b(t_E - t_{Bp})}{t_{Bp} + F(t_E - t_{Bp})} \tag{51}$$

Where H_z: height of mass transfer zone (cm); H_b: Adsorption bed height (cm); t_z: the time required for the mass transfer zone to settle at the top of the column (minutes); t_E: Saturation time (minutes); t_F: Time required for the formation of the adsorption zone (minutes); t_{Bp}: Time at breakthrough point (minutes); and F: Fractional Capacity.

Finally, knowing that the operating time (in hours) is equal to the ratio of the volume (in liters) to the volumetric flow rate (in liters per hour), we obtain the equation Eq. (52):

$$H_z = \frac{H_b(V_E - V_{Bp})}{V_{Bp} + F(V_E - V_{Bp})} \tag{52}$$

Where H_z: height of mass transfer zone (cm); H_b: Adsorption bed height (cm); t_z: the time required for the mass transfer zone to settle at the top of the column (minutes); V_{Bp}: Volume of effluent treated at the breakthrough point (ml); V_E: Volume treated at the saturation point (ml); and F: Fractional Capacity.

6.3.3. Movement rate of the material transfer zone

It is a measure of the equilibrium nature of the adsorption process under continuous flow conditions. It measures the bed saturation rate and is directly linked to the height of the mass transfer zone by Eq. (53) (Namane and Hellal, 2006) :

$$U_z = \frac{H_z}{t_z} = \frac{H_b Q}{V_{Bp} + F(V_E - V_{Bp})} \qquad (53)$$

Where U_z: Movement rate of the mass transfer zone (cm minute^{-1}); H_z: height of mass transfer zone (cm); t_z: the time required for the mass transfer zone to settle at the top of the column (minutes); H_b: Adsorption bed height (cm); Q: Volumetric flow (l h^{-1}); V_E: Volume treated at the saturation point (ml); F: Fractional Capacity; and V_{Bp}: Volume of effluent treated at the breakthrough point (ml).

6.3.4. Removal capacity at the breakthrough time

This is the quantity of the product eliminated at the breakthrough point, which corresponds to the volume of purified water with an instantaneous concentration less than or equal to the concentration chosen as that of discharge. It is determined by Eq. (54) (Namane and Hellal, 2006) :

$$X_{Bp} = \int_0^{V_{Bp}} \frac{(C_0 - C_i)dV}{m} \qquad (54)$$

Where X_{Bp}: Removal capacity at breakthrough time (mg g^{-1}); C_0: Initial concentration of adsorbate (mg l^{-1}); C_i: Concentration of the solute of species i at equilibrium (mg l^{-1}); V_{Bp}: Volume of effluent treated at the breakthrough point (ml); V: Volume of solute solution (l); and m: adsorbent mass (g).

6.3.5. Removal capacity at saturation time

This is the amount removed by the bed until it is saturated. It is calculated according to Eq. (55) (Namane and Hellal, 2006) :

$$X_E = \int_0^{V_E} \frac{(C_0 - C_i)dV}{m} \qquad (55)$$

Where X_E: Removal capacity at saturation time (mg g^{-1}); C_0: Initial concentration of adsorbate (mg l^{-1}); C_i: Concentration of the solute of species i at equilibrium (mg/l); V_E: Volume of effluent treated at the saturation point (ml); V: Volume of solute solution (l); and m: adsorbent mass (g).

7. Conclusion

The purpose of this review was to respond to a major environmental issue, water pollution, and its repercussions on recipient environments by industrial effluents discharged in large quantities of wastewater loaded with toxic products such as dyes which the classification could be based on the source of materials (natural or synthetic dyes), on their chemical structure (chromophore or auxochrome) or their nuclear structure (cationic or anionic). For the protection of the environment,

it is essential or compulsory to treat the toxicity generated by the presence of these colored effluents in the waters of industrial discharges by adsorption that is one of the simplest environmental protection methods to design and use. The growing demand for adsorbents has made their price more and more expensive which prompted research complementary for the manufacture of new, less expensive adsorbent materials from available biomass in Morocco (food waste, medicinal aromatic plants, etc.) that may be used, instead of expensive commercial activated carbon, to remove dyes from an aqueous solution due to their very large porous structure, their large specific surface, and their great adsorption capacity. This manuscript also describes the empirical models of adsorption kinetics (pseudo-first-order, pseudo-second-order, Avrami, Bangham, Boyd, Elovich, and intraparticle diffusion) and its isotherms (Langmuir, Freundlich, Bohart-Adams, Brunauer-Emmett-Teller, Dubinin Radushkevich, Florry Huggins, Frenkel-Halsey-Hill, Khan, Koble Corrigan, MacMillan Teller, Radke Prausnitz, Sips, Temkin, Wolborska, Yoon Nelson, Harkin Jura, Halsey, and Elovich-Larionov) which represent the relationship between the concentration of a substance in solution and the quantity adsorbed at a constant temperature and which are often used to establish the maximum adsorption capacity of dyes on adsorbents. Indeed, for most studies, the adsorption capacities at equilibrium are better represented by the Langmuir isotherm (monolayer adsorption) and the pseudo-second-order kinetic model. Information regards adsorption in continuum systems was also provided. The development of natural biosorbents without generating pollutants is a great challenge and is recommended for sustainable industrial development to preserve the environment. This study opens up many perspectives such as the assessment of *the novel adsorbents regeneration as well as the study of their end of life in addition to their adsorbent potential at full-scale wastewater treatment*.

Conflict of Interest

The authors declare that there is no conflict of interest regarding the publication of this article. The authors confirmed that the paper is free of plagiarism.

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