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A review of biomaterial as an adsorbent: From the bibliometric literature review, the definition of dyes and adsorbent, the adsorption phenomena and isotherm models, factors affecting the adsorption process, to the use of typha species waste as a low-cost adsorbent

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Abstract

The aim of this paper is to describe an analysis of adsorption isotherms of some dyes taken from aqueous solutions by biomaterial. Here, Typha waste as a biomaterial model categorized as a low-cost adsorbent was reported. In addition, this paper presents a brief discussion of the literature information in view of the definition of dyes and adsorbents, bibliometric analysis, adsorption phenomena, adsorption isotherm models, and factors determining the adsorption, to the use of Typha species waste as an affordable adsorbent. The operational condition parameters are explained regarding pH, adsorbent amount, contact time, and initial dye amount determining the textile dye removal process. In the adsorption process, the pH solution becomes the most important aspect (e.g. the use of anionic dye requiring a low pH condition, and the cationic dye requiring higher pH). The adsorption capacity in terms of the adsorbent dosage is positively correlated to the use of high amount of adsorbent dosage, which is in relation to availability of the adsorption site. The dye removal efficiency is highly determined by the contact time between the adsorbent and dye in which a strong attraction force shortens the time. Increasing the initial concentration of dye will determine the the number of adsorbent surface active area required. A number of isotherm models are then described; a frequently used model for the evaluation of the adsorption capacity of the Typha species waste as adsorbents is Langmuir model. What is suggested from this review paper is that the accuracy level obtained from adsorption processes highly relies upon the successful modeling of adsorption isotherms. Typha biomaterial wastes can be seen as the new beneficial low-cost natural adsorbents for dye clean-up operations in aquatic systems.

Keywords: Typha; biomaterials; adsorption; toxics removal

1. Introduction

Water pollution today has been seen as a great defiance and a critical issue. Here, this paper attempts to present an analysis of adsorption isotherms of some dyes from aqueous solutions by biomaterial by presenting Typha waste as a biomaterial model as an affordable adsorbent. It also provides a step-by-step explanation started from the definition of dyes and adsorbents, bibliometric analysis, adsorption phenomena, adsorption isotherm models, and factors determining the adsorption to the use of Typha species waste as an affordable adsorbent.

2. Definition, Classification, and Strategies for Removing Dyes

Dyes refer to natural, synthetic, and organic compounds used in order to create bright and permanent color to other materials (Figure 1). Mostly, they are in the form of anionic dyes, cationic dyes, and non-ionic dyes (Figure 2) [1]. Here, cationic dyes are those of distinct type of chemical structures based upon substituted aromatic groups [2], which are classified as a toxic colorant potential to brings both the detrimental effects, e.g. skin irritation, allergic dermatitis, and carcinogenic effects and mutations [2]. This type is known as basic dyes that are dependent upon a positive ion and highly visible with high brilliance and intensity of colors [3]. Cationic functionality can be found in diverse types of dyes, primarily in cationic azo and methane dyes, di- and tri-arylcarbenium, anthraquinone, phthalocyanine, as well as polycarboxylic and solvent dyes.

Methylene blue and Malachite green are those mostly used in the cationic dyes. Methylene blue is a substance mostly employed dyes for dyeing cotton, silk and wood, but it can severely cause eye burnt leading to permanent injury to the eyes

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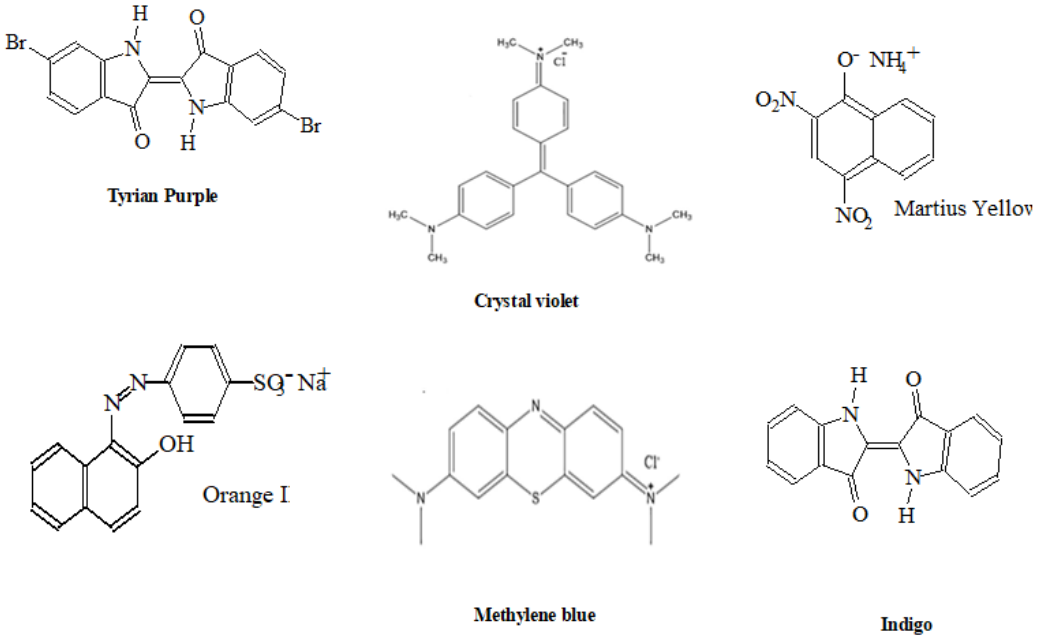

Fig.1. Chemical structures of some dyes

of humans and animals [4-6]. Meanwhile, Malachite Green is widely employed in dyeing paper, wool, cotton, leather, silk, as well as a biocide and disinfectant [7-9]; similar with Methylene blue, this dye is also responsible for some problems. Hence, in consideration to the toxicity and a serious hazardous condition to the aquatic system and human/animal health caused by these dyes [10], it is deemed important to formulate the way how to treat this dye.

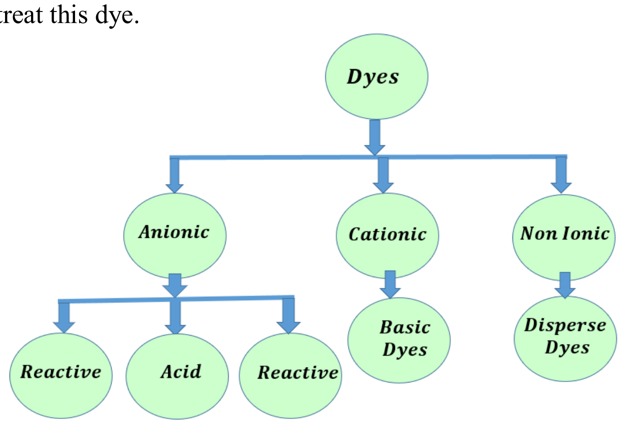

Fig. 2. Classification of dyes

Anionic dyes consist of many components in relation to their carrier as a negatively charged ion. From the most varied classes of dyes for anionic dyes, depending on its structure they show a number of characteristics. They include direct dyes and have a large proportion of the reactive dyes in which their releasement to the environment can create issue for having a low degree of fixation as well as hydrolysis of reactive groups in the aqueous phase [10]. Acid dyes are water soluble but hazardous for human and animal due to their ability to create organic sulphonic acids [11]. Congo red with its complex aromatic structure and high chemistry and thermal stability is harmful [12,13] and difficult to degrade [14-16].

In any kinds of industry such as textile, leather, paper, or plastics, dyes are functioned in product coloring. During the dyeing process, industries use the considerable amounts of water and simultaneously the unused water containing dyes as well as wastewater must be treated considering that the direct removal of these wastes can lead to environmental issues [17]. In brief, the higher the amount of water used, the more the wastewater produced [18] and it certainly becomes a major concern in both toxicological and esthetical aspects [19,20].

Dyes also contribute to a severe impairment of human organs such as liver brain, reproductive system, kidney dysfunction, as well as central nervous system in view of their carcinogenic, mutagenic, or teratogenic impacts [21]. For this reason, for many researchers, research in dyes becomes something interesting [22-27].

Table 1 depitcs the toxic dosages of some dyes with a number of references added to support the explanations [14,28-31]. The dyes removal is crucial but wastewater treatment might be challenging in consideration to that it is not simple to make dyes degradable. Thus, the dye treatment, for some cases, cannot be removed from wastewater by conventional wastewater treatment systems [28].

Some techniques such as photocatalytic degradation [32-34], sonochemical degradation [35-37], cation exchange membranes [38-40], electrochemical degradation [41-43], solar

Table 1. Toxicity of some dyes

Name	LD50 (mg/Kg rat)	Source
Malachite green	275	[28]
Acid orange 165	60	[29]
Basic blue 7	100	[29]
Basic blue 81	205	[29]
Basic violet 16	90	[29]
Basic yellow 21	171	[29]
Direct orange 62	150	[29]
Congo red	96	[30]
Crystal violet	10	[14]
Methylene blue	50	[31]

photo-Fenton [44-46], biological process [28,47,48], adsorption [49-66], solar photo-Fenton and biological processes[67], and Fenton-biological treatment [68] have been used for the wastewater treatment to remove the dyes from wastewater. Table 2 lists the advantages and disadvantages of the dye removal process technologies along with a number of references to support the explanation [28,69-81].

3. Adsorption Process

Adsorption is the very common way in pollutant removal [65] as it has a important role in controlling the environmental pollution [82-89]. The adsorbent-grade activated carbon is one of the issues due to its cost-prohibitive [90]. Many researchers, in response, have been attempting to find out some affordable and locally available chemical substitutes from natural sources as the alternative to the traditional carbon adsorbent [49-53,58,59,61]. The employmet of biomasses and plant-derived biomaterials has been one of the great interests, including several materials:

(i) Banana peel [91],
(ii) Orange peel [12],
(iii) Tree fern [92],
(iv) Pineapple [53],
(v) Wheat bran [93]
(vi) Rice straw and rice husk [49,61,66,94,95]
(vii) Castor tree leaves [96],
(viii) Grapefruit peel [97],
(ix) Date palm trees [98],
(x) Peanut shell [99],
(xi) Lotus leaf [100],
(xii) Coffee residues [101],
(xiii) Poplar leaf [102],
(xiv) *Citrus aurantium* [103],
(xv) Cypress products [104],
(xvi) Hyacinth leaves [105].

To support the adsorption process, the adsorption isotherm has been considerably used. It has been exploited to explain how the adsorbent contact and interact with the adsorbate. In addition, it arises an idea to obtain adsorption capacity during the process [65]. Figure 3 and Figure 4 respectively present the concept of adsorption and an example of the adsorption occurrences

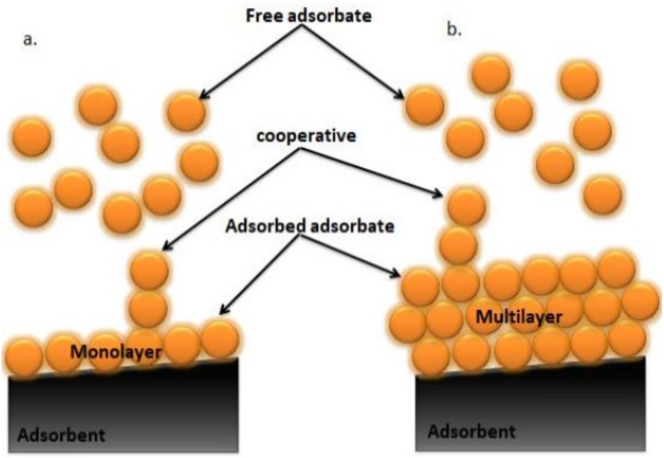

Fig. 3. Mechanism illustration of the interaction of adsorbate and adsorbent during the adsorption process. The interaction can be formed as a monolayer (a) and multilayer (b). The figure has been adopted from the literature[65]

4. Bibliometric analysis for Biomaterial Adsorption

Bibliometric analysis research involves 4 stages: data search with the use of Publish or Perish (PoP) 7 application, data processing with the use of Ms. Excel, data mapping with the use of the VOSviewer application, and data analysis from

Table 2. Advantages and disadvantages of the dye removal process technologies

Treatment technology	Materials used	Advantages	Disadvantages	Ref.
Chemical precipitation	Lime, surfactants, etc. (e.g. sulfides, hydroxides, and carbonates	Low capital cost, process simplicity	Sludge generation, the extra operational cost for sludge disposal, high-maintenance cost	[69,70]
Ion exchange	Ion-exchange resin, anion, and cation	No loss of sorbents during regeneration	Not effective for dispersing dyes	[71-73]
Membrane technologies	Membranes	Removal of all dye types, appreciable resistance to temperature, and chemical environment	A limited lifetime before membrane fouling occurs, concentrated sludge production, costlier, suitable for low volume of treatment	[28,74-76]
Flotation techniques	Surfactants or collectors (e.g. Polyvinyl Alcohol, Chitosan), gas bubbles	Low cost, shorter hydraulic retention time	Subsequent treatments are required to improve the removal efficiency	[77,78]
Electrochemical techniques	Electrode material (iron plates or aluminum), pH controller	The system is very robust, efficient, and easily controllable	The sacrificial anode requires to be replaced periodically, needs continuous monitoring and maintenance, cost of electricity	[76,79]
Coagulation and flocculation	Coagulants (ferrous sulfate, ferric chloride, alum, etc.)	Complete removal of dye, simplicity, and low capital cost	Produce highly toxic sludge, handling and disposal problem	[74]
Adsorption by commercial activated carbon	Commercial activated carbon	The high adsorption capacity for all dyes	Cost of regeneration, high cost of adsorbents, generation of sludge	[28,80,81]

VOSviewer mapping. In this study, the search for publication data used the PoP application in December 5, 2022 and on published data for the last 5 years in the period of 2018 - 2022. "Biomaterial Adsorption" became the keyword used in the data search. 997 articles were obtained from the search results published or perish and the data were in two file formats: *.ris and csv formats. The *.ris format was used to map data using VOSviewer and csv format was for data processing using Microsoft Excel. Then, data from the search results for publish or perish 7 in the csv format were processed with a help of Ms. Excel and the data processing using Ms. Excel was done to get data on the annual number of articles and to see the research done by researchers regarding the keywords used. Data stored in *.ris format were used in data mapping using VOSviewer. The mapped data were then analyzed to see the development of research on "Biomaterial Adsorption". The data from this mapping were analyzed to obtain any existing research trends and the results of terms often used as study material to find the for further research. Detailed information for the step-by-step procedure for the use of bibliometric analysis is shown elsewhere [106]. Bibliometric analysis has been used in many areas and utilized as a frontier to understand the research trend [107-116].

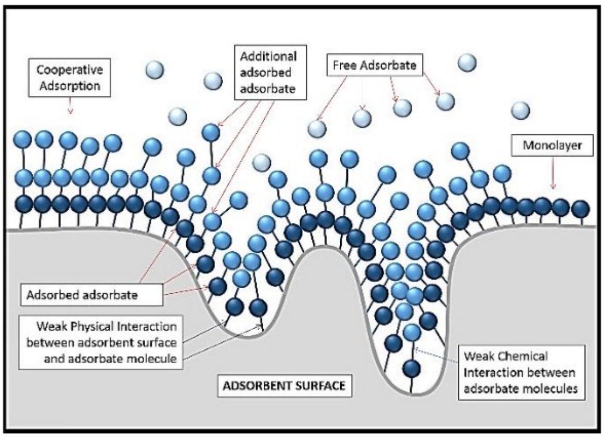

Fig. 4. Prediction model for adsorption process in silica from rice husk, adopted from the literature [65]

4.1 *Article search matrix on biomaterial adsorption*

A search for publications regarding Biomaterial Adsorption found 997 articles. Also, as shown in Table 3 from all these data, a research matrix was found in which the total number of citations of all articles regarding Biomaterial Adsorption was 37,939. Table 3 shows the number of citations in 3 types: annual citations with a total of 9,484, citations per article with a total of 37.98, and citations per author with a total of 10,784. Articles on biomaterial adoption showed an h-index of 90 and H-Index itself showed the author-level metrics in measuring productivity and the impact of citations from publications. The higher H index value can make the research better in that field. Publication on Biomaterial Adsorption has a g-index value of 4.25. Table 4 shows the 10 articles with the highest number of citations in which the article entitled "Chitosan as Biomaterial in drug delivery and Tissue Engineering", published in 2018 had the most citations with a total of 502 citations.

Table 3. Publication Metrix.

Type	Number
Paper	997
Citations	37939
year_first	2018
year_last	2022
Cites/Year	9484.75
Cites/Paper	37.98
Cites/Author	10784.16
Authors/Paper	4.25
h-index	90
g-index	131

4.2 *Progress of publication of biomaterial adsorption 2018 to 2022*

Figure 5 presents the progress of publication on "Biomaterial Adsorption" between 2018 and 2022 revealing a decrease of number of research on Biomaterial Adsorption in every year. The highest number of research was found in 2018 with 263 publications; however, from 2018 to 2022 it continued

Table 4. Publications on Bimaterioal Adsorption with the highest number of citations.

Authors	Title	Year	Citation
Ahsan et al.	Chitosan as biomaterial in drug delivery and tissue engineering	2018	502
Bakshi et al.	Chitosan as an environment friendly biomaterial–a review on recent modifications and applications	2020	419
Sezer et al.	Review of magnesium-based biomaterials and their applications	2018	418
Mariani et al.	Biomaterials: foreign bodies or tuners for the immune response?	2019	365
Bodratti et al.	Formulation of poloxamers for drug delivery	2018	352
Chai et al.	A review on conventional and novel materials towards heavy metal adsorption in wastewater treatment application	2021	315
Baino et al.	Bioactive glasses: where are we and where are we going?	2018	301
Dwivedi et al.	Polycaprolactone as biomaterial for bone scaffolds: Review of literature	2020	265
Fiyadh et al.	Review on heavy metal adsorption processes by carbon nanotubes	2019	251
Calzoni et al.	Biocompatible polymer nanoparticles for drug delivery applications in cancer and neurodegenerative disorder therapies	2019	229

to decline into 262 publications in 2019; 246 publications in 2020; 148 publications in 2021, and 78 publications as the lowest number of publications in 2022.

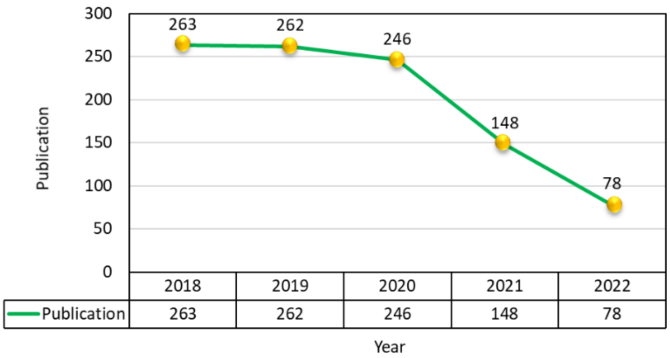

Fig. 5. Progress of Publication of Biomaterial Adsorption 2018 to 2022

4.3 Mapping visualization publication on biomaterial adsorption

The nodes in the network map visualization demonstrate an entity, including articles, authors, countries, institutions, keywords, and journals. Figure 6 illustrates a network visualization of publications on Biomaterial Adsorption in which several points can be concluded:

(i) The cover color size shows the keyword occurrence (i.e. how many times the keywords appear),
(ii) Relationships between nodes represent co-occurrence between keywords (i.e. keywords that occur together),
(iii) The thickness of the link shows the co-occurrence between keywords (i.e. how many times the keywords appear or occur together),
(iv) The bigger node correlates to the bigger keywords that appear, and
(v) The thicker links between nodes correlate to the greater co-occurrence between keywords.

As shown in Figure 6, protein adsorption is the most extensively researched type of adsorption and is related to the research theme of biomaterial adsorption. Term Protein Adsorption has a total link strength of 330 with a total of 203 occurrences and a total linkage with other terms of 60. Figure 7 shows the linkage of the term protein adsorption with other terms, which consist of Biofouling, incorporation, lactic acid, biomedical application, nano, polydopamine, adsorption process, natural biomaterial, kinetic, thermodynamic, mechanical property, blood compatibility, peg, adhesion, silicon, nonspecific protein adsorption, hydrophilic surface, bone tissue regeneration, bone tissue engineering, coating, and fibrinogen.

Table 5 depicts 6 clusters found in the network visualization. Several other terms are commonly related to research on Biomaterial Adsorption. This table can assist further researchers in determining the research focus to be carried out.

Table 5 shows the number of clusters found in the network visualization, namely 6 clusters. Several other terms are usually associated with research on Biomaterial Adsorption. This table can assist further researchers in determining the focus of the research to be carried out.

5. Applicability of Various Adsorption Isotherm Models on Dye Adsorption

Of many isotherm models provided in literature, such as Langmuir, Brunauer–Emmett–Teller, Freundlich, Temkin, Redlich– Peterson, Flory–Huggins, Dubinin–Radushkevich, Koble–Corrigan, Sips, Khan, Toth, Hill, and Radke–Prausnitz isotherms, [117], it has been found that, among researchers, Freundlich, Langmuir, and Redlich–Peterson isotherms are the most commonly used ones for both different adsorption

Table 5. VOSviewer Distribution of term mapping cluster

Cluster	Total items	Terms	Color code
1	36	Activated carbon. Adsorbate, adsorbent, adsorption isotherm, adsorption, kinetic, adsorption performance, adsorption process, adsorption removal, aqueous medium, aqueous solution, biochar, biomass, cadmium, carbon nanotube, copper, dye adsorption, dye removal, efficient adsorption, functional group, graphene oxide, heavy metal, heavy metal ion, high adsorption, high adsorption capacity, ion, isotherm, Langmuir, lignin, maximum adsorption, maximum adsorption capacity, metal ion, metal organic framework, methylene blue, polydopamine, predication, and silver nanoparticle.	Red
2	32	Adhesion, adsorbed protein, biomaterial surface, biomedical application, blood, blood combability, cell adhesion, coating, collagen, fibrinogen, hemocompatibility, hydrophobic surface, immune response, important role, inflammation, lactic acid, material surface, metallic biomaterial, nonspecific protein adsorption, peg, plasma protein, platelet, protein adsorption, roughness, silicon, surface chemistry, surface property, surface wettability, titanium implant, and wettability.	Green
3	27	Bioactive glass, biomaterial scaffold, biomaterials surface, bone regeneration, bone tissue engineering, bone tissue regeneration, cellular response, composition, differentiation, drug delivery system, enzyme, growth factor, implant, implantation, incorporation, nano, osteointegration, osteogenesis, peptide, potential application, proliferation, silk fibroin, smart biomaterial, tissue, tissue regeneration, titanium, and vitro.	Blue
4	15	Adsorption temperature, adsorption time, anionic dye, bio material, biosorption, chromium, equilibrium, kinetic, low cost, pectic, plant, thermodynamic, uranium, wastewater, and waste treatment.	Yellow
5	10	Adsorption mechanism, biomolecule, carbon, double hydroxide, enhanced adsorption, hexavalent chromium, mechanical property, methylene, natural biomaterial, and pollutant.	Violet
6	6	Bacterial adhesion, biofouling, dental implant, infection, prevention, and surface modification.	Blue Light

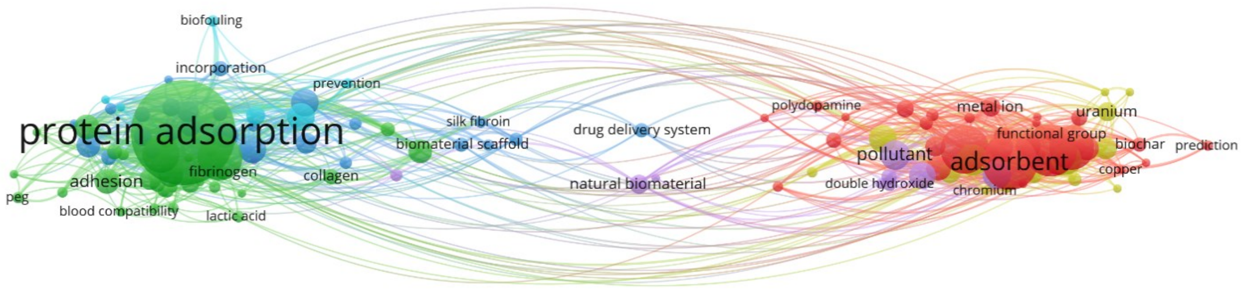

Fig. 6. Network Visualization of Biomaterial Adsorption Publication

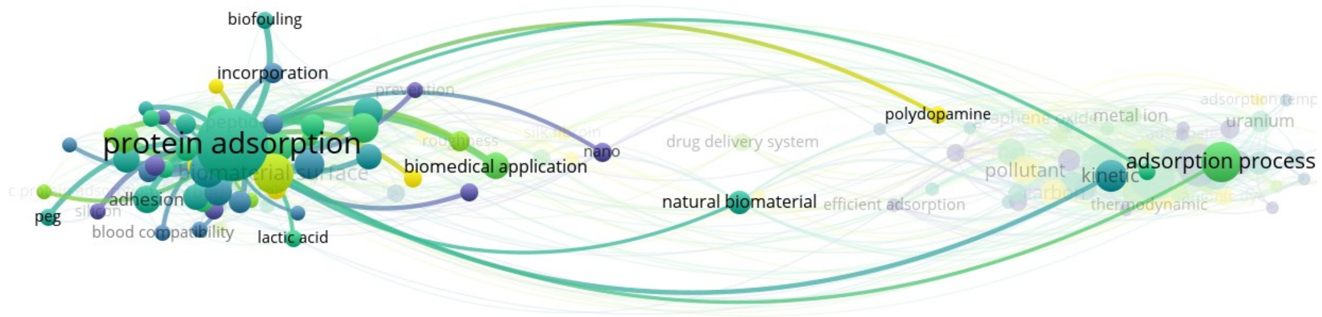

Fig. 7. Network Visualization of Protein Adsorption Term

processes and different adsorbent/ adsorbate systems [118]. Detailed information on how to calculate isotherm models is shown in the literature [65].

The Langmuir model focuses on adsorption occurred at specific homogeneous sites within the adsorbent. It has been successfully employed for taking care many adsorption processes of monolayer adsorption. The Langmuir equation is expressed in equation (1):

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \tag{1}$$

where q_e refers to the amount of dye adsorbed per unit mass of adsorbent (mg/g), C_e is the concentration of dye in the solution at equilibrium (mg/L), k_L is the Langmuir constant related to the adsorption capacity (L/g), q_m is the maximum uptake per unit mass of adsorbent (mg/g).

The focus of the Freundlich model is on a heterogeneous adsorption surface, which has unequal available sites with the different energies of adsorption. This model is shown in equation (2):

$$q_e = K_F C_e^{1/n} \tag{2}$$

where K_F (mg/g) (L/mg)^n and $1/n$ are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively.

The focus of the Temkin model is on the decrease in the heat of adsorption that is linear rather than logarithmic. The heat of adsorption of all the molecules in the layer, in view of adsorbate/adsorbent interactions, would linearly decrease with coverage. This model has largely been applied in the following non-linear form in equation (3):

$$q_e = B_1 Ln K_T C_e \tag{3}$$

where $B_1 = RT/b$ is a constant related to the heat of adsorption, b shows the variation of adsorption energy (J/mol) and K_T is a Temkin isotherm constant considering the interactions between adsorbate and adsorbent (dm^3/mg).

Jovanovic model and Langmuir isotherm model are alike with the approximation of monolayer that is localized adsorption without lateral interactions. The assumptions in this isotherm model resemble the Langmuir isotherm model besides the possibility of some mechanical contacts between the adsorption and desorbing model. The nonlinear Jovanovic isotherm model can be expressed by equation (4):

$$q_e = q_m(1 - e^{-K_J C_e}) \tag{4}$$

where q_m (mg/g) and K_J (L/mg) denote Jovanovic constants regarding the adsorption capacity and the rate of adsorption, respectively.

Sips model refers to a combination of the Langmuir and Freundlich isotherm models, showing systems for which one adsorbed molecule occupy more than one adsorption sites. The nonlinear representation of the Sips isotherm model is presented as in equation (5):

$$q_e = q_m \frac{K_S C_e^{n_S}}{(1+K_S C_e^{n_S})} \tag{5}$$

where q_m is the Sips isotherm maximum adsorption capacity (mg/g), K_S is the Sips isotherm equilibrium constant (L/mg), and n_S is the Sips model exponent describing heterogeneity.

The development of Toth model is intended to describe the heterogeneous adsorption systems, satisfying both low and high-end boundaries of adsorbate concentration, which is the modified form of the Langmuir model to correct any errors between the experimental and predicted data. The nonlinear representation of the Toth isotherm model is presented as in equation (6):

$$q_e = q_m \frac{C_e}{\left(1+\alpha_T C_e\right)^{1/n}} \quad (6)$$

where q_m is the Toth isotherm maximum adsorption capacity (mg/g), α_T is the adsorptive potential constant (mg/L), and n is the heterogeneity factor in the Toth isotherm.

The Redlich–Peterson model combines elements from both the Langmuir and Freundlich isotherm equations and the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption. It is used as a compromise to improve the fit by Langmuir or Freundlich isotherm. The nonlinear representation of the Redlich–Peterson isotherm model is presented as in equation (7):

$$q_e = \frac{K_{RP} C_e}{1+\alpha_{RP} C_e^n} \quad (7)$$

where K_{RP} (L/g) and α_{RP} (L/mol) are the Redlich-Peterson isotherm model constants, while n is the exponent, which lies between 0 and 1.

6. The use of Typha Waste as a Model of Biomaterial Adsorbent

As illustrated in Figure 8, Typha, also known as cattailis the only genus in *Typhaceae* family. This iconic genus comprises almost 40 species and hybrids and it is abundant across wetland ecosystems throughout the world. The highly increasing number of Thypa in comparison to aquatic weeds might lead to several problems such as mono-dominance, regime shifts, litter production, and flow disturbance condition in water flow, river, and water channels [119,120].

Fig. 8. *Typha australis* along the Senegal River

Typha, in spite of its harmful effects on natural systems, in fact can offer valuable ecosystem services. Under certain conditions, it gives bioremediation in constructed wetlands to reduce nutrient loads and pollution and provides biofuel feedstocks required to balance the global carbon dioxide emissions. Typha biomaterial wastes for being locally available and its chemical structure containing numerous types of functional groups, such as hydroxyl, carboxyl, and amino groups are employed as biosorbents [121].

Some researchers through a variety of batch experiments attempted to use Typha biomaterial wastes without chemical and/or physical treatment as adsorbents purposely to remove any cationic and anionic dyes. The effects of some variables (pH, contact time, adsorbent mass added, and initial dye concentrationon) on the efficiency of the adsorption process have been briefly discussed . It also included the description of the model of adsorption isotherms of dyes from aqueous solutions by Typha biomaterial wastes as the affordable adsorbents.

7. Removal of Dyes Using Typha as Biomaterial Adsorbent

Figure 9 presents the summary for the dyes removal by means of Typha as the biomaterial adsorbent. In short, this paper deals with advantages, process, modelling, important factors, and future perspectives of Typha.

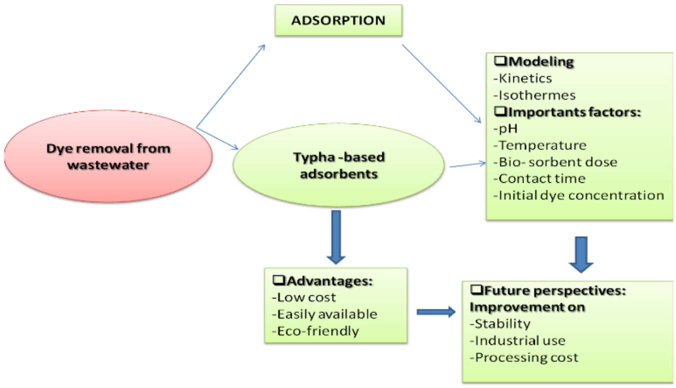

Fig. 9. Summary of the removal of dye using Typha as biomaterial adsorbent

7.1. *Factors affecting adsorption*

During the adsorption process, pH condition plays a crucial role . The pH condition of a medium controls the magnitude of electrostatic charges, as given by the ionized dye molecules. The adsorption rate, as a consequence, varies with the pH condition in the aqueous medium [122]. In the solution with a high pH condition, the positive charge at the solution interface decreases, and the adsorbent surface shows negatively charged [123]. For this reason, the cationic dye adsorption increases and anionic dye adsorption shows a decreasing value [124]. N'diaye et al. showed that the highest removal efficiency of methylene blue adsorption was obtained at pH 11.5 and evaluated at 92% [125]. The pHPZC condition for the Typha australis adsorbent was obtained at 6.36. For the values less than pHPZC condition, the Typha australis surface was positively charged, resulting in an electrostatic repulsion, thus leading to a decrease in methylene blue adsorption process (42.55% at pH 4). At pH > pHPZC the Typha australis surface was negatively charged, which then cause an electrostatic attraction, thus leading to an increase in methylene blue adsorption.

To obtain the optimal adsorption efficiencymis highly determined by the total amount of biomass. The impacts of amount of adsorbent on the adsorption can be conducted through the preparation of the adsorbent–adsorbate solution with various amounts of adsorbents added to a fixed initial dye concentration and mixed together until reaching the equilibrium time [124]. The experiment of Bouazza et al. was conducted using the different adsorbent doses (0.75–2.5 g/L) to observe the effects of different Typha angustifolia adsorbent dosages on methylene blue removal [126]. They showed that increasing the adsorbent dose from 0.75 to 2.5 g/L had made the removal percentage increased from 89.84 to 96.85%. Another researcher analyzed the effects of an adsorbent dose on the removal of Crystal Violet and Orange G by Typha angustata [127] with the results showing an increase of the adsorption percentage along with an increase in adsorbent dosage. In Typha angustata, the adsorbent surface carries basic sites, due to the presence of basic sites, the anionic dye adsorption decreases with the increasing dosage [124]. Subsequently, the impact of contact time on the dye adsorption was conducted by preparing adsorbent–adsorbate solution with a fixed adsorbent amount and initial dye concentration for various time intervals prior to mix it until obtaining equilibrium. To a certain extent, there was an increase of the dye removal rate with an increase in the contact time. Further increases in terms of the contact time brought no impact on the increase in the uptake in view of the dyes deposition process on the available adsorption site on adsorbent material [128]. Contact time between adsorbent and adsorbate significantly determined the performance of methylene blue dye removal [126]. The results showed that the biosorption capacity of methylene blue increased with an increase in the contact time - reaching a peak at 60 minutes. Also, methylene blue biosorption ran fast during the first 10 minutes, followed by a longer duration with a tendency to saturation until 60 minutes.

The relation between the dye concentration and the available binding sites on an adsorbent surface determined the effects of the initial dye concentration factor [124]. Such effect was done by shaking the adsorbent-adsorbate solution using a fixed adsorbent dosage with different initial dye concentrations for different processing time intervals until reaching equilibrium [124]. The biosorption equilibrium increased from 32.054 to 119.08 mg/g with an increase in initial concentration [126]. In contrast, the percentage of methylene blue absorbed decreased from 96.2 to 89.30% with an assumption that the low percentage in the methylene blue removal at high concentrations was from saturated adsorption sites that required a longer time to reach equilibrium.

7.2. Modeling of adsorption isotherms

Among the researchers, regarding the adsorption modeling, Freundlich, Langmuir, and Redlich–Peterson isotherm models are the most commonly employed isotherms for different Typha biomaterial wastes adsorbents/dye systems. [125,126,129-135]. The following results are briefly presented by researchers:

(i) Ashraf *et al.* examined the biosorption of acid yellow dye using a *Typha angustata* as a biosorbent in a batch experiment [136]. Langmuir model and Freundlich model here were used to describe the biosorption equilibrium at various temperatures. Here, equilibrium data were found fitted very well with the Freundlich model.

(ii) *Typha angustata* by Rehman and Han was used in the biosorption of methylene blue [137]. The monolayer adsorption of methylene blue was described using Langmuir model.

(iii) Employing *Typha angustifolia* leave as adsorbents, Guechi and Oualid Hamdaoui examined the biosorption of Malachite Green dye from aqueous solutions [129]. Equilibrium data were found to fit to the Langmuir, Freundlich, Redlich– Peterson, and Sips model and the results showed that the experimental equilibrium data were best represented by the Redlich–Peterson isotherm model.

(iv) Boumaza *et al.* researched the biosorption potential of *Typha angustifolia* in removing methylene blue dye [126]. Here, the Freundlich, Langmuir, and Temkin models were used. At this point, the Langmuir model adequately presented the experimental equilibrium data with the maximal monolayer biosorption capacity of *Typha angustifolia* to be 106.757 mg/g at 25°C.

(v) The observation of Sánchez Orozco *et al.* towards the potential of *Typha latifolia* stem and leaf powder as biosorbent was to remove methylene blue dye from aqueous solutions [130]. In the observation, equilibrium models were used for data analysis. Here, the experimental data fitted well to the Langmuir isotherm with a maximum adsorption capacity of 126.6 mg/g.

(vi) N'diaye *et al.* studied *Typha australis* leaf as a low-cost adsorbent with an aim to remove methylene blue dye from aqueous solutions [125]. Langmuir model and Freundlich model here were used to employ the equilibrium data. The results showed that Langmuir adsorption model fitted the data better than Freundlich model with the monolayer adsorption capacity for the Methylene blue -*Typha australis* leaf system of 103.12 mg/g. N'diaye *et al.* also studied and modeled the adsorption equilibrium isotherms of Malachite Green dye onto *Typha australis* leave as a affordable adsorbent [131]. The experimental equilibrium data were fitted to the two-parameter isotherms (i.e. Langmuir, Freundlich, and Jovanovic) and three-parameter isotherms (i.e. Sips, Redlich–Peterson, and Toth). The best-fitting isotherm was found to be the Langmuir model. The monolayer adsorption capacities of *Typha australis* were found to be 85.21 and 56.88 mg/g at 21.4 and 31.4°C, respectively. This homogeneity was confirmed by the constants of Sips and Redlich–Peterson models.

(vii) Ali *et al.* studied and modelled the adsorption equilibrium isotherms of Congo red dye onto *Typha australis* leaves as low-cost adsorbents [132]. The results showed that the Langmuir isotherm was a better model to explain the adsorption process. The monolayer adsorption capacities of *Typha australis* for Congo red at 20, 30 and 40°C was 17.40, 21.85, and 24.23 mg/g , respectively.

Table 6 depicts the adsorption capacity and other parameters for the dye removal by the different Typha biomaterials and other agricultural wastes as the affordable adsorbents. The studies of dyes adsorption by Typha species wastes as adsorbents presented a higher adsorption capacity for cationic dyes than an adsorption capacity for anionic dyes proving the viability of Typha biomaterial wastes as one of the most effective adsorbents for the dyes removal from aqueous solutions in comparison to other agricultural waste adsorbents as studied in the literature [91,125,126,129-135,138-145]. Therefore, the removal of cationic and anionic dye contaminants from wastewaters using Typha biomaterial

Table 6. Reported adsorption capacities q_m (mg/g) for the removal of dyes by different Typha biomaterials and other agricultural wastes as low-cost adsorbents

Adsorbent	Dyes	Q_m (mg/g)	References
Typha australis	Methylene blue	103.12	[125]
Typha angustoflia	Methylene blue	106.373	[126]
Typha angustoflia	Malachite green	72.25	[129]
Typha latifolia	Methylene blue	126.6	[130]
Typha australis	Malachite green	85.21	[131]
Typha australis	Congo red	17.40	[132]
Typha latifolia	Methylene blue	21.07	[133]
Typha latifolia	Methylene blue	54.73	[133]
Typha latifolia	Methyl orange	36	[134]
Typha angustota	Reactive red 4	100	[135]
Sugarcane dust	Malachite green	3.999	[138]
Sugarcane dust	Basic violet 10	3.240	[138]
Banana pith	Acid brilliant blue	4.42	[139]
Neem sawdust	Methylene blue	3.42	[140]
Coit pith	Acid violet	1.65	[141]
Orange peel	Basic violet 10	14.3	[91]
Beach sawdust	Basic blue 9	9.78	[142]
Water hyacinth root powder	Methylene blue	8.04	[143]
cashew nut shell	Congo red	5.184	[144]
de-oiled biomass	Acid fuchsin	9.9	[145]

wastes, in a natural form, offers the prospective outcomes with maximum adsorption efficiency in the field of adsorption technology for showing the outstanding removal capabilities for various classes of dyes and could be exploited as an alternative to the use of commercial activated carbon. Additionally, Typha biomaterial wastes adsorbent in a natural form have an advantage for requiring no overpriced pretreatment.

7.3. *Mechanism of adsorption occurring in the Typha biomaterial adsorbent*

An mathematical analysis done by Reichenberg [146] and Boyd *et al.* [147] was to differentiate particle, film diffusion, and mass-action-controlled mechanisms of exchange that have laid the obtainments of sorption/ ion-exchange kinetics. Typically, external transport is the rate-limiting step in systems, which have several essential aspects:

(i) poor mixing,
(ii) diluting the concentration of adsorbate,
(iii) small particle size,
(iv) the high affinity of the adsorbate for the adsorbent.

On the contrary, the intraparticle step limits the overall transfer for those systems with a consideration to several aspects:

(i) high concentration of adsorbate;
(ii) good mixing;
(iii) large particle size of the adsorbent;
(iv) low affinity of the adsorbate for the adsorbent.

During the adsorption of a solid chemical substance over a porous adsorbent, three consecutive steps occurred [7]:

(i) Transport of the adsorbate ions to the external surface of the adsorbent (film diffusion).
(ii) Transport of the adsorbate particles within the adsorbent pores, excluding the small amount of adsorption occurring at the external surface of the adsorbent (particle diffusion).
(iii) Adsorption of the adsorbate ions on the interior surface of the adsorbent.

The adsorption of Malachite green, a cationic dye, existing in an aqueous solution in the form of positively charged ions, was strongly pH-dependent [129]. As a charged species, the degree of its sorption by the biosorbent is mostly determined by the surface charge on the sorbent, which in turn is influenced by the solution pH. The lower absorption of Malachite Green at acidic pH condition is due to the presence of excess H^+ ions competing with the dye cation for sorption sites. As the pH condition in the adsorption system increases, the number of available positively charged sites decreases, while the number of negatively charged sites increases. The negatively charged sites favor the sorption of dye cation due to electrostatic attraction. A mechanism has been proposed for the biosorption of the methylene blue onto *Typha australis*. With the values of less than pH_{PZC} condition, the *Typha australis* surface was positively charged, which would result in an electrostatic repulsion; Thus, it led to a decrease in adsorbing methylene blue (42.55 % at pH = 4) [125]. At the condition of $pH > pH_{PZC}$, the *Typha australis* surface was negatively charged, causing an electrostatic attraction; therefore leading to an increase in adsorbing methylene blue.

8. Conclusion

This paper briefly presents the review of different sorts of Typha species as adsorbents. It also presents the potential of the adsorption process by means of Typha biomaterial wastes for the removal of dyes from textile wastewater. Furthermore, this paper provides a brief discussion about a number of determining factors (i.e. contact time, pH condition, adsorbent amount, and initial dye concentration) towards dye adsorption. In this case, in the adsorption process pH solution was found as the most critical point. Overall, it has been identified that, for anionic dyes, a low value of pH was preferable, in contrast to the one in cationic dyes more requiring a high pH value. In regard to the adsorbent amount, the adsorption capacity in view of the increase of the available number of sorption site increased along with the increment of adsorbent dosage. Meanwhile, it has been found that there was a determination of contact time between the adsorbent and dye to the efficiency of dye removal in which a strong attraction force would make adsorption time shorter. The increasing initial concentration of dyes would increase the increment of adsorbent surface area in dye adsorption. Here, Langmuir isotherm model became the one mostly followed in any dyes removal process. Typha species waste as affordable adsorbents have given better results for adsorbing the cationic dyes rather than the anionic dyes. Typha species wastes, which are an abundant, renewable, and free-cost adsorbent, could be successfully employed for the dye removal from aqueous solutions and can potentially substitute the high-cost adsorbents in the today market. Furthermore, it is suggested that the researchers should concentrate to predict the performance of the adsorption process for dye removal in the realistic industrial effluents.

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