



Research Article

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Agriculture waste biomass valorisation for cationic dyes sequestration: A concise review

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ABSTRACT

Wastes and by-products of agricultural industry are huge in amount and difficult to handle. These predominant waste materials could be utilised by converting them into a useful products such as biosorbents. The effluent holding the toxic cationic dyes from textile industry is a threatening factor now days due to environmental legalizations and their adverse effect on human biota. Under this circumstance the cheap form of the effective adsorbents from the agricultural waste for the removal of such kind of dyes can be considered. This paper reviews on the agricultural waste products for the removal of cationic dyes from the textile industry effluent and also briefly discusses about the model equations used for adsorption isotherms and kinetics.

Keywords: Cationic dye; biosorption; biomass; isotherms; kinetics

INTRODUCTION

1.1 Dye bearing effluents

The environment and everything connected with the environment are important for the public because most of our ecological systems such as air, water and soil are continuously contaminated by domestic and industrial pollutants. Dyes are the major pollutants present in the textile, tannery, paper and pulp, distillery, oil mill, and metal industries. It is estimated that 2% from over 7×10^5 tons of dyes annually are discharged in effluent from manufacturing operations whilst 10 % was discharged from textile and associated industries [1]. Today, there are more than 100,000 commercially available dyes, namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic, and sulphur dyes [2]. Moreover, even minor release of dye effluents into the environment may cause the appearance of color, for example in open waters, which attracts the critical attention of public and local authorities. There is, thus the requirement on industry to minimize environmental release of color, even in cases where a small but visible release might be considered as toxicologically rather innocuous. A major source of release of color into the environment is associated with the incomplete exhaustion of dyes onto textile fibre from an aqueous dyeing process and the need to reduce the amount of residual dye in textile effluent has thus become a major concern in recent years.

The colored effluents released from textile industries worsen the aesthetic value of the water bodies and adversely affects the photosynthesis of aquatic plants by hindering the penetration of light. Additionally, complete biodegradation of these dyes are very difficult due to their complex chemical structure having substituted chromophoric groups such as azo, anthraquinone, triarylmethane, etc. These dyes decompose into carcinogenic aromatic amines under anaerobic conditions, and therefore discharge of these dye bearing effluents into water bodies can cause harmful effects such as allergic dermatitis, skin irritation, mutations, and cancer [3, 4, 5].

1.2 CLASSIFICATION SYSTEMS FOR DYES

Dyes are classified usefully in two separate ways, either accordance to their chemical structure or according to the method of application [dyeing method]. In term of chemical structure, dyes may either be inorganic or organic compounds. Both groups can be further subdivided into natural and synthetic representatives. When classified according to dyeing method, one can be distinguish between anionic, direct, or disperse dyes, depending on whether these substances are used for dyeing protein, cellulose, or polyamide fibres.

For the two classifications based on chemical structure and on method of application overlap, there is hardly a chemical class of dye which occurs solely in one coloristic group, and vice versa. Furthermore, some coloristic groups can be applied to two or more substrates, whilst others are specified to a single substrate. Both classifications are used by the Color Index [C.I], which lists all dyes and pigments used commercially for large-scale coloration purpose, such as dyeing of textile fibres, for pigment coloration of plastics, paints, printing inks and for the coloration of liquids [solvents].

Table 1 summarizes the application classes of dyes and their chemical types. According to Griffiths [7], colorants can also be classified to the type of electronic excitation occurring on light absorption. However, Zollinger [8] classified colorants as absorption colorants, fluorescent colorants and energy transfer colorants, depending on whether the light energy absorbed is dissipated predominantly (i.e. high quantum yields) by internal conversion, by fluorescence or by intersystem crossing.

Table 1 Classification of dyes [9]

Dye Class	Description
Acid	Water-soluble anionic compounds
Basic	Water-soluble, cationic compounds, applied in weakly acidic dye baths; very bright dyes
Direct	Water-soluble, anionic compounds; applied directly to cellulose without moderants [or metals like chromium and copper]
Disperse	Not water-soluble
Reactive	Water-soluble, anionic compounds; largest dye class
Sulphur	Organic compounds containing sulphur or sodium sulphide
Vat	Water-soluble; oldest dyes; more chemically complex

1.3 CATIONIC DYES

These dyes are also called basic dyes and depend on a positive ion, which are generally hydrochloride or zinc chloride complexes [10]. Cationic dyes carry a positive charge in their molecule, furthermore it is water soluble and yield colored cations in solution. Cationic functionality is found in various types of dyes, mainly in cationic azo dyes and methane dyes, also in anthraquinone, di- and tri-arylcarbenium, phthalocyanine dyes, various poly carbocyclic and solvent dyes. The anthraquinone dyes are expensive and weak while the azo dyes have good properties, strong thus reducing cost [6]. Basic dyes are highly visible and have high brilliance and intensity of colors [11]. Cationic dyes are widely used in acrylic, wool, nylon, and silk dyeing. These dyes include different chemical structures based on substituted aromatic groups [12]. This group of dyes is considered as toxic colorants and can cause harmful effects such as allergic dermatitis, skin irritation, mutations, and cancer [13].

2 TECHNOLOGIES FOR CATIONIC DYES REMOVAL

Wastewater containing cationic dyes is very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion and are stable to light. Synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods. This is because of the high cost and disposal problems for treating dye wastewater at large scale in the textile and paper industries [14]. Table 2.2 shows a several reported methods for the removal of pollutants from effluents. The technologies for color removal can be divided into three categories: biological, chemical, and physical [1]. All of them have advantages and drawbacks (Table 2).

2.1 Biological Method

Biodegradation methods such as fungal decolorization, microbial degradation, adsorption by [living or dead] microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents because many microorganisms such as bacteria, yeasts, algae and fungi are able to accumulate and degrade different pollutants [15,16]. However, their application is often restricted because of technical constraint. Many organic molecules are degraded; many others are recalcitrant due to their complex chemical structure and synthetic organic origin [3-5]. According to Bhattacharyya & Sharma [17], biological treatment requires a large land area and is constrained by sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation. Further, biological treatment is incapable of obtaining satisfactory color elimination with current conventional biodegradation processes [1].

Table 2 Advantages and disadvantages of dye removal methods [1]

Methods	Advantages	Disadvantages
Chemical Methods		
Oxidative process	Simplicity of application	[H ₂ O ₂] agent needs to activate by some means
Fenton's reagent	Fenton's reagent is a suitable chemical means	Sludge generation
Ozonation	Ozone can be applied in its gaseous state and does not increase the volume of wastewater and sludge	Short half-life [20 min]
Photochemical	No sludge is produced and foul odours are greatly reduced	Formation of by-products
Sodium hypochloride [NaOCl]	Initiates and accelerates azo-bond cleavage	Release of aromatic amines
Electrochemical destruction	No consumption of chemicals and no sludge build up	Relatively high flow rates cause a direct decrease in dye removal
Biological Methods		
Decolorization by white-rot fungi	White-rot fungi are able to degrade dyes using enzymes	Enzyme production has also been shown to be unreliable
Other microbial cultures [Mixed bacterial]	Decolorized in 24–30 h	Under aerobic conditions cationic dyes are not readily metabolized
Adsorption by living/dead microbial biomass	Certain dyes have a particular affinity for binding with microbial species	Not effective for all dyes
Anaerobic textile dye bioremediation systems	Allows azo and other water-soluble dyes to be decolorized	Anaerobic breakdown yields methane and hydrogen sulphide
Physical Methods		
Adsorption by activated carbon	Good removal of wide variety of dyes	Cost of activated carbon
Membrane filtration	Removes all dye types	Concentrated sludge production
Ion exchange	Regeneration: no adsorbent loss	Not effective for all dyes
Irradiation	Adsorbent loss, effective oxidation at lab scale	Requires a lot of dissolved O ₂
Electro-kinetic coagulation	Economically feasible	High sludge production

2.2 Chemical Methods

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation-flocculation with Fe[II] / Ca[OH]₂, electro flotation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents [ozone], irradiation or electrochemical processes [18]. These chemical techniques are often expensive, and although the dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use. Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for the pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems.

2.3 Physical Methods

Different physical methods are also widely used, such as membrane – filtration processes [nanofiltration, reverse osmosis, electro dialysis] and adsorption techniques. The major disadvantages of the membrane processes are: (1) a limited lifetime before membrane fouling occurs and (2) cost of periodic replacement which needs to be included in any analysis of their economic viability. In accordance with the very abundant literature data, liquid-phase adsorption is one of the most popular methods for the removal of pollutants from wastewater, since proper design of the adsorption process will produce a high-quality treated effluent [19,20]. This process provides an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step before its application.

3 Adsorption Technology using activated biomass

Adsorption is a well-known equilibrium separation process and an effective method for water decontamination applications [21]. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Decolorization is a result of two mechanisms: adsorption and ion exchange [22], and is influenced by many physio-chemical factors such as dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time [23]. Adsorption also does not result in the formation of harmful substance.

Most of the solid adsorbents of great industrial applications possess a complex porous structure that consists of pores of different sizes and shapes. In terms of the adsorption science, total porosity is usually classified into three groups. According to International Union of Pure and Applied Chemistry [IUPAC] recommendation, the micropores are defined as pores of a width [< 2 nm], mesopores are pores of a width [2 - 50 nm], but macropores represent pores of a width [> 50 nm]. However, the importance of porous structure on adsorption of many contaminants in

aqueous solution is not well understood. As to physisorption on porous materials, it's generally accepted that adsorption mechanism and process may be significantly different as a consequence of porous structure. In the IUPAC classification of pore size, the definitions of 'macropores', 'mesopores' and 'micropores' depend on the different adsorption mechanism at pores with specified range of width: in micropores the whole accessible volume is regarded as adsorption space and the process occurs due to micropore filling [24], as distinct from surface coverage, which takes place on the walls of macropores. On the other hand, physisorption in mesopores takes place in two more or less stages (monolayer – multilayer adsorption and capillary condensation). For instance, Singh & Pant [25] concluded that mesopores are thought to be important in air/soil adsorption system for the diffusion of air and the transport and distribution of water, while the wider macropores provide channels for easy removal of surplus water and allow air to penetrate rapidly to the required depth. Further, a powder is easily recognized as a mass of small dry particles, but the precise definition is inevitably somewhat arbitrary.

The term fine powder is also used in an imprecise manner, but it seems reasonable to apply it to a material consisting of particles less than about 1 μ m. The unit mass of a fine powder contains a large number of small particles and exhibits an appreciable surface area. In addition to the performance, a number of other factors greatly influence the choice and viability of waste materials as adsorbents, for example the cost of processing materials, wastewater selectivity, and regeneration of materials. Cost is a very important factor when considering materials for use as adsorbents. It is generally recognized that a material can be deemed 'low-cost' if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry [26].

3.1 Indigenous adsorbents for dyes removal

The by-products from the agriculture and industry could be assumed to be low-cost adsorbents, since they are abundant in nature, inexpensive, and require little processing.

Commercially available Activated Carbons (AC) are usually derived from natural materials such as wood, coconut shell, lignite or coal, but almost any carbonaceous material may be used as precursor for the preparation of carbon adsorbents [27]. Because of its availability and cheapness, coal is the most commonly used precursor for AC production [28]. Coal is a mixture of carbonaceous materials and mineral matter, resulting from the degradation of plants. The sorption properties of each individual coal are determined by the nature of the origin vegetation and the extent of the physical-chemical changes occurring after deposition [29]. Plentiful agricultural and wood by-products may also offer an inexpensive and renewable additional source of AC. These materials have little or no economic value and often present a disposal problem. Therefore, there is a need to valorize these low cost by-products. So, their conversion into AC would add economic value, help reduce the cost of waste disposal, and most importantly provide a potentially inexpensive alternative to the existing commercial activated carbons.

Agricultural materials, particularly those containing cellulose show potential sorption capacity for various pollutants. The basic components of the agricultural waste materials include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch containing variety of functional groups. Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable nature and low cost are viable option for water and wastewater remediation. Agricultural waste is a rich source for activated carbon production due to its low ash content and reasonable hardness [30], therefore, conversion of agricultural wastes into low-cost adsorbents is a promising alternative to solve environmental problems and also to reduce the preparation costs. In the last several decades, various agricultural wastes have been explored as low-cost adsorbent. These agricultural waste materials have been used in their natural form or after some physical or chemical modification. Table 3 presents the various biomass related adsorbents, model dyes selected and their adsorption capacities values.

4 Effect of process factors on dye adsorption

The adsorption capacity of an adsorbent depends on the source of raw material, preparation, and treatment conditions. The process factors including solution pH, temperature, initial dye concentration, adsorbent dosage and others, can affect the dye removal efficiency [3-5].

The pH is a measure of acidity ($\text{pH} < 7$) or basicity ($\text{pH} > 7$) of an aqueous solution. The pH factor is very important in the adsorption process especially for dye adsorption. The pH of a medium will control the magnitude of electrostatic charges, which are imparted by the ionized dye molecules. As a result, the rate of adsorption will vary with the pH of an aqueous medium [71]. The isoelectric point or point of zero charge (pH_{pzc}) is an important factor that determines the linear range of pH sensitivity, the type of surface active centres and the adsorption ability of the surface [73]. Many researchers studied the isoelectric point [pH] of adsorbents that prepared from agricultural solid wastes to better understand the adsorption mechanism. Cationic dye adsorption is favored at $\text{pH} < \text{pH}_{\text{pzc}}$, due to presence of functional groups such as OH – and COO – groups [74,75].

Table 3 Various biomasses and model dyes taken for adsorption studies

S.No.	Adsorbent	Dye	Adsorption Capacity [mg g ⁻¹]	References
1	Bagasse pith	Basic blue 69 basic red 22	158 177	31
2	Bagasse pith	Acid red 114 acid blue 25	23 22	31
3	Maize cob	Telon blue and Erinoyl red	47.7 41.4	32
4	Maize cob	Astrazone blue, Maxilon red	160 94.5	32
5	Sunflower stalks	Methylene blue basic red 9	205 317	33
6	Rice husk	Methylene blue Safranin	312 838	34
7	Rice husk	Basic blue 9	19.83	35
8	Rice husk ash	Acid violet 54 acid red 119	99.4 155	36
9	Coir pith waste	Rhodamine B Acid violet	2.56 8.06	37
10	Coir pith	Congo red	6.72	38
11	Orange peel	Acid violet 17	19.88	39
12	Banana peel	Methyl orange Methylene blue Rhodamine B Congo red Methyl violet Amidoblack 10B	17.2 15.9 13.2 11.2 7.9 7.9	40
13	Orange peel	Methyl orange Methylene blue Rhodamine B Congo red Methyl violet Amido black 10B	15.8 13.9 9.1 7.9 6.1 3.8	40
14	Jack fruit peel carbon	Malachite green	166.37	41
15	Pearl millet husk	Methylene blue	82.37	42
16	Hazelnut shell	Basic blue 9	8.82	43
17	Rice husk	Acid yellow 36	86.9	44
18	Date pits	Basic blue 9	17.3	45
19	Pinewood	Acid blue 264 Basic blue 69 Basic blue 9	1176 1119 556	46
20	Orange peel	Direct Red 23 Direct Red 80	10.72 21.05	47
21	Rice husk ash	Methylene blue	690	48
22	Rice husk H ₂ SO ₄ activated ZnCl ₂ activated	Crystal violet	64.87 61.57	49
23	Coconut male flower H ₂ SO ₄ treated H ₃ PO ₄ treated	Crystal violet	60.42 85.84	50
24	Wheat bran	Reactive blue 19 Reactive yellow 145	117.6 196.1	51
25	Silk cotton hull	Reactive blue MR	12.9	52
26	Coconut bunch waste	Methylene blue	70.92	53
27	Rubber seed coat	Basic blue 3	227.27	54
28	Peanut husk	Neutral Red	37.5	55
29	Brazil nut shell	Methylene blue, Indigo carmine	7.81 1.09	56
30	Wood apple shell	Methylene blue, Crystal violet	95.2 130	57
31	Spent tea leaves	Methylene blue	300.05	58
32	Papaya seed	Methylene blue	555.55	59
33	Garlic peel	Methylene blue	82.64	60
34	Pineapple stem waste	Methylene blue	119.05	61
35	Cotton hull	Remazol Black B	50.9	62
36	Cotton stalk, Cotton hull	Remazol Black B	35.7 50.9	63
37	Tea waste	Methylene blue	86.16	64
38	Palm kernel fibre	Basic violet 3	40.12	65
39	Sugar beet pulp	Basic red 2	20.17	66

40	Zizania latifolia	Basic red 9	150.7	67
41	Spirogyra	Direct Brown	5.46	68
42	Acacia arabica	Metylene blue	78.2	69
41	Activated Cotton seed	Basic red 9	86.24	23
		Basic violet 10	113.11	70

Temperature is an indicator for the adsorption nature, whether it is an exothermic or endothermic process. If the adsorption capacity increases with increasing temperature, then the adsorption is an endothermic process and it is vice versa for the exothermic process. This may be due to increasing the mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature [50]. This effect depends mainly on the movement of dye molecules of each dye class. The decrease of adsorption capacity with increasing temperature indicates that the adsorption is an exothermic process [76]. Increasing temperature may decrease the adsorptive forces between the dye species and the active sites on the adsorbent surface as a result of decreasing adsorption capacity [66].

The percentage removal of dye is highly dependent on the initial amount of dye concentration. The effect of the initial dye concentration depends on the immediate relation between the concentration of the dye and the available binding sites on an adsorbent surface. Generally, the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface [66]. At a low concentration, there will be unoccupied active sites on the adsorbent surface, and when the initial dye concentration increases, the active sites required for adsorption of the dye molecules will lack [77]. On the other hand, the increase in initial dye concentration will cause an increase in the loading capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration [78].

Table 4 Effect of process parameters and their range for batch adsorption

S. No	Adsorbent	Dye	Dosage [g l ⁻¹]	Concentration	Contact time	pH	Temperature [°C]	Particle size	Agitation Speed [rpm]	Reference
1	Olive stone	BR2	0.5–1	25–150 mg l ⁻¹	0–1 h	4–10	25–45	-	-	72
2	Sugar beet pulp	BR2	0.05–0.5	100–800 mg l ⁻¹	1110 min	2–10	-	-	150	66
3	Sun flower stalks	BR9	1	50–1000 mg l ⁻¹	0–180 min	-	25–50	-	-	79
4	Powdered carbon	BR9	0.01	0–250 mg l ⁻¹	0–48 h	8	32–40	-	95	80
5	Bottom ash and de-oiled soya	BR9	0.05–0.15	1×10 ⁻⁵ – 8×10 ⁻⁵ M	0–24 h	3–10	30–50	0.08–0.15 mm	-	81
6	Magnetic nanoparticles	BR9	0.2–0.5	20–60 mg l ⁻¹	-	3–10	25	-	-	82
7	Zizania latifolia carbon	BR9	0.5–1	200 mg l ⁻¹	0–12 h	3–12	20–40	-	125	67
8	Cellulose	BR9	-	10–80 mg l ⁻¹	5–600 min	3–8	10–50	-	180	83
9	Banana pith	BV10	0.25–3	20–100 mg l ⁻¹	0–240 min	2–10	30	53 µm–1 mm	140	84
10	Neem sawdust	BV10	0.5	6–12 mg l ⁻¹	0–30 min	2–10	25–45	50–100 mesh	-	85
11	Coir pith carbon	BV10	0.5–8	10–40 mg l ⁻¹	0–80 min	2–10	30	3 mm	160	86
12	Carbon slurry waste	BV10	0.01	10 ⁻⁵ –10 ⁻⁴ M	1–30 min	5–6	25–45	100–250 mesh	-	87
13	Orange peel	BV10	0.01–0.04	10–50 mg l ⁻¹	0–60 min	4–10	30	-	140	88
14	Sago waste	BV10	1	10–40 mg l ⁻¹	0–180 min	2–10	30	125–750 µm	-	89
15	Activated sludge	BV10	-	100 µm l ⁻¹	1–5 h	5–9	5–45	-	-	90
16	Powdered carbon	BV10	0.01	0–250 mg l ⁻¹	0–48 h	8	32–40	-	95	82
17	Anaerobic sludge	BV10	1–15	10–200 µm l ⁻¹	0–150 min	7	20–60	-	150	91
18	Coir pith	BV10	0.2–0.3	20–100	0–90 min	-	32–50	-	160	92
19	Cellulose	BV3	-	10–80	5–600 min	3–8	10–50	-	180	83
20	Palm kernel fibre	BV3	0.01–0.25	20–160	0–120 min	2–11	25–55	-	50–350	93
21	Ginger waste	BV3	0.05	5–20	0–180 min	2–9	30–50	-	80	94
22	Bottom ash and De-oiled soya	BV3	0.01–0.05	5×10 ⁻⁶ – 8×10 ⁻⁵ M	0–24 h	2–8	30–50	36–170 mesh	-	95
23	Grapefruit peel	BV3	0.1–3.0	5–600	0–240 min	2–10	20–45	-	100	96
24	Wood apple shell	BV3	0.1	0–200	0–6 h	2–10	32	-	200	97
25	Coniferous pinus bark	BV3	0.2–1.0	10–50	0–120 min	2–8	30–50	-	-	98
26	Coconutmale flower	BV3	0.01–0.2	5–40	0–3 h	2–9	28–48	0.15–0.25 mm	120	50
27	Powdered carbon	BV3	0.01	0–250	0–48 h	8	32–40	-	95	82

Usually, the percentage of dye removal increases with increasing adsorbent dosage, where the number of sorption sites at the surface will increase by increasing the dose of the adsorbent. As a result it increases the percentage of dye removal from the solution. Study of the effect of adsorbent dosage gives an idea of the effectiveness of an adsorbent and the ability of a dye to be adsorbed with a minimum dosage, so as to identify the ability of a dye from an economical point of view [23].

Table 5 Isotherm equations

S.No	Isotherm	Significance	Equation	Remarks
1	Henry's law[109]	Describes the adsorption of solutes on a uniform surface of adsorbent at sufficiently low concentrations such that all solute molecules are isolated from their nearest neighbors	$q_e = HC_e$	The higher value of H indicates a stronger interaction between the adsorbent and the solute molecules.
2	Langmuir[103]	Accounts the monolayer adsorption taking place on a structurally homogeneous adsorbent where all the adsorption sites are identical and energetically equivalent [i.e., constant heat of adsorption for all sites]	$q_e = \frac{q_{mL}b_L C_e}{1 + b_L C_e}$ $R_L = \frac{1}{1 + C_0 b_L}$	It predicts a constant monolayer adsorption capacity at high solute concentrations. If $R_L > 0$ unfavourable adsorption, $R_L < 0$ favourable adsorption, and $R_L = 0$ no adsorption.
3	Freundlich[109]	Accounts the non-ideal and reversible nature of multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface.	$q_e = K_F C_e^{1/n_F}$	The magnitude of $1/n_F$ ranges between 0 and 1 is a degree of surface heterogeneity. Additionally n_F value < 1 indicates chemisorption where > 1 implies cooperative adsorption.
4	Temkin[110]	Relates the effects of heat of adsorption that decreases linearly with the coverage of the solute and the adsorbent interactions on the surface at moderate values of solute concentrations. It assumes that the adsorption is characterized by a uniform distribution of binding energies up to some maximum energy.	$q_e = \frac{RT}{b_T} \{ \ln[a_T C_e] \}$	b_T value relates to heat of sorption and helps to understand the nature of adsorption.
5	Dubinin-Radushkevich[111,112]	States that the characteristic sorption curve is associated to the porous structure of the adsorbent. It facilitates to find the value of mean free energy of adsorption per mole of solute as it is transferred from the solution to the solid surface.	$q_e = q_{mDR} \exp(-K_{DR} \epsilon^2)$ $\epsilon = \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2$ $E = \frac{1}{\sqrt{2K_{DR}}}$	If the values of E is around 8–16 kJ/mol, the adsorption is ion-exchange reaction.
6	Smith[113]	Takes into account the progressive enlargement of the adsorptive surface which must inevitably result in an increase in the number of adsorptive sites. It also assumes that in the desorption process, the solute molecules bound to rigid structural elements of appreciably superior dimensions get involved to block the collapse of the structure.	$q_e = W_{s1} - W_{s2} \ln(1 - C_e)$	Obedience to this equation indicates progressive enlargement of the adsorptive surface and swelling of adsorbent molecule.
7	Redlich-Peterson[114]	Comprises the characteristics of both Langmuir and Freundlich isotherms into a single equation which represents the adsorption equilibrium over a wide range of concentrations.	$q_e = \frac{K_{RP1} C_e}{1 + K_{RP2} C_e^{\beta_{RP}}}$	If β_{RP} value tends to zero it approaches Freundlich isotherm and β_{RP} value tends to unity it approaches Langmuir isotherm.
8	Sips[115]	A combined form of Langmuir and Freundlich isotherms deduced for predicting the heterogeneous adsorption systems.	$q_e = \frac{K_s q_{mS} C_e^{\frac{1}{n_S}}}{1 + K_s C_e^{\frac{1}{n_S}}}$	This model overcomes the disadvantage of the increasing solute concentration linked with Freundlich isotherm.
9	Toth[116]	An improved form of Langmuir isotherm proposed for describing heterogeneous adsorption systems which assumes the majority of the active sites have adsorption energy lower than the maximum or mean value.	$q_e = \frac{q_{mT} C_e}{(K_T + C_e^{n_T})^{n_T}}$	n_T is a scale of surface heterogeneity. If n_T approaches unity, the process occurs on a homogenous surface.
10	Hill[117]	Describes the binding of different solutes onto a homogeneous adsorbent on the assumption that adsorption is a cooperative occurrence, owing to the ligand binding ability at one site on the macromolecule which tends to influence different binding sites on the same macromolecule.	$q_e = \frac{q_{mH} C_e^{n_H}}{K_H + C_e^{n_H}}$	If $n_H > 1$, positive cooperativity in binding, $n_H = 1$, non-cooperative or hyperbolic binding, and $n_H < 1$, negative cooperativity in binding.
11	Khan[118]	A combined form of Langmuir and Freundlich isotherms for bi-solute adsorption from dilute aqueous solutions.	$q_e = \frac{q_{mK} b_K C_e}{(1 + b_K C_e)^{a_K}}$	If a_K is equal to unity it reduces to Langmuir isotherm and at large values

				of C_e reduces to Freundlich isotherm.
12	Brouers–Sotolongo[119]	A model in the form of deformed exponential [Weibull] function developed for heterogeneous adsorption systems	$q_e = q_{mBS}(-K_{BS}C_e^{n_{BS}})$	The sorption energy distribution and the energy heterogeneity of the adsorbent surface can be measured from model exponent n_{BS} at the given temperature.
13	Unilin[120]	An empirical correlation which helps to understand the heterogeneous adsorption systems	$q_e = \frac{q_{mU}}{2b_U} \ln \left(\frac{a_U + C_e e^{b_U}}{a_U + C_e e^{-b_U}} \right)$	Obedience to this equation indicates the adsorption system is heterogeneous.
14	Marczewski–Jaroniec[121]	Accounts the distribution of adsorption energies in the active sites and developed based on the assumptions of Langmuir isotherm	$q_e = q_{mMJ} \left(\frac{(K_{MJ}C_e)^{n_{MJ}}}{1 + (K_{MJ}C_e)^{n_{MJ}}} \right)^{\frac{m_{MJ}}{n_{MJ}}}$	Fit to this equation is an indication of heterogeneous adsorption system.
15	Weber–van Vliet[121]	An empirical relation with four parameters to illustrate the heterogeneous equilibrium adsorption data.	$C_e = P_1 q_e^{(P_2 q_e^{P_3 + P_4})}$	Fit to this equation explains it is a heterogeneous adsorption system.
16	Fritz–Schlunder–III[122]	Langmuir–Freundlich type of empirical equations which can fit a wide range of experimental data.	$q_e = \frac{q_{mFS} K_{FS} C_e}{1 + q_{mFS} C_e^{n_{FS}}}$	If n_{FS} value tends to zero it approaches Freundlich isotherm and n_{FS} value tends to unity it approaches Langmuir isotherm.
17	Fritz–Schlunder–IV[122]		$q_e = \frac{A_{FS} C_e^{a_{FS}}}{1 + B_{FS} C_e^{b_{FS}}}$	It is valid only at $a_{FS} \leq 1$ and $b_{FS} \leq 1$.
18	Fritz–Schlunder–V[122]		$q_e = \frac{q_{mFS5} K_1 C_e^{a_{FS}}}{1 + K_2 C_e^{b_{FS}}}$	It is valid only in the range of $a_{FS} \leq 1$ and $b_{FS} \leq 1$.

Therefore, such process factors are to be continuously monitored and maintained in order to obtain maximum dye removal by the prepared adsorbent. Some of the process factors selected for batch adsorption system to attain maximum dye removal are shown in Table 4.

4.1 Isotherms

In the endeavor to explore novel adsorbents in accessing an ideal adsorption system, it is essential to establish the most appropriate adsorption equilibrium correlation [23,99], which is indispensable for reliable prediction of adsorption parameters and quantitative comparison of adsorbent behavior for different adsorbent systems [or for varied experimental conditions] [19,100]. In the perspective, equilibrium relationships, generally known as adsorption isotherms, describe how pollutants interact with the adsorbent materials, and thus are critical for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and effective design of the adsorption systems [20,101,102].

Over the years, a wide variety of equilibrium isotherm models [Table 5], have been formulated in terms of three fundamental approaches [19,20,103]. Kinetic consideration is the first approach to be referred. Hereby, adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal [104]. Whereas, thermodynamics, being a base of the second approach, can provide a framework of deriving numerous forms of adsorption isotherm models [105,106], and potential theory, as the third approach, usually conveys the main idea in the generation of characteristic curve [23,107]. However, an interesting trend in the isotherm modeling is the derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters [23,108].

4.3 Kinetics

In the past decades, several mathematical models have been proposed to describe adsorption data, which can generally be classified as adsorption reaction models and adsorption diffusion models. Both models are applied to describe the kinetic process of adsorption; however, they are quite different in nature. Adsorption diffusion models are always constructed on the basis of three consecutive steps [19,20]:

- [1] diffusion across the liquid film surrounding the adsorbent particles, i.e., external diffusion or film diffusion;
- [2] diffusion in the liquid contained in the pores and/or along the pore walls, which is so-called internal diffusion or intra-particle diffusion; and
- [3] adsorption and desorption between the adsorbate and active sites, i.e., mass action.

However, adsorption reaction models originating from chemical reaction kinetics are based on the whole process of adsorption without considering these steps mentioned above. At present, adsorption reaction models have been widely developed or employed to describe the kinetic process of adsorption [19,20,23,123-129]

Table 6 Kinetic equations

S.No.	Kinetics	Description	Equation	Remarks
1	Ho–McKay[130]	Describes that adsorption process is controlled by chemisorption which involves valence forces through sharing or exchange of electron between the solute and the adsorbent.	$q_t = \frac{q_e^2 k_{Ho} t}{1 + k_{Ho} q_e t}$ $h = k_{Ho} q_e^2$	It helps to calculate the initial sorption rate h.
2	Blanchard[131]	A second order kinetic model which assumes that the solute adsorption on the adsorbent follows ion exchange mechanism.	$q_t = \frac{k_{Bla} q_e t + \alpha_{Bla} q_e - 1}{k_{Bla} t + \alpha_{Bla}}$	It reduces to Ho model when $\alpha_{Bla} = 1/q_e$.
3	Elovich[132]	States the second–order kinetic on the assumption that the actual solid surfaces are energetically heterogeneous.	$q_t = \beta_E \ln(r_E \beta_E) + \beta_E t$	β_E relates the extent of surface coverage and activation energy for chemisorption.
4	Avrami[133]	Developed based on thermal decomposition process and applied to adsorption. It determines the adsorption rates in terms of the initial concentration and the adsorption time in addition to the determination of fractional kinetic orders.	$q_t = q_e [1 - e^{(-k_{Av} t)^{n_{Av}}}]$	n_{Av} accounts to the adsorption mechanism changes.
5	Ritchie[134]	Accounts the second–order kinetic adsorption of gases on solids based on the assumption that the rate of adsorption of solute onto adsorbent depends solely on the fraction of surface sites $[\theta]$, which are occupied by adsorbed gas.	$\theta = \frac{q_t}{q_e}$ $= \left\{ 1 - \left[\frac{1}{\beta_R + k_R t} \right] \right\}$	β_R represents initial particle loading.
6	Sobkowski–Czerwi[133]	Similar to Ritchie model but proposed based on the maximum adsorption capacity of adsorbents.	$q_t = \frac{q_e k_{SC} t}{k_{SC} t + 1}$	Fit to this equation stands for second order kinetics.
7	Modified Freundlich [134]	An empirical kinetic equation to evaluate the effect of solute surface loading and ionic strength on the adsorption process.	$q_t = k_{mF} C_i t^{1/m_{mF}}$	The values of k_{mF} accounts for effect of solute surface loading and m_{mF} predicts the ionic strength.

CONCLUSION

The agricultural waste products are predominant in the agricultural practicing country like India. The effluent holding the toxic dye from textile industries in India requires an proper alternative for their treatment. Under this circumstance the cheap form of the effective adsorbents from the agricultural waste for the removal of dye can be considered. This paper reviewed the recent literatures of biosorbents for cationic dye removal.

Appendix A. List of Symbols

H – Henry constant (l/mg)

q_{mL} – Maximum monolayer adsorption capacity by Langmuir isotherm (mg/g)

b_L – Langmuir model constant (l/mg)

R_L – Separation factor

S_{sp} – Specific surface area ($m^2 g^{-1}$)

K_f – Freundlich isotherm constant (l/g)

n_f – Freundlich exponent

a_T – Temkin isotherm constant (l/g)

b_T – Temkin isotherm constant (J/mol)

q_{mDR} – Maximum monolayer adsorption capacity by Dubinin–Radushkevich isotherm (mg/g)

K_{DR} – Dubinin–Radushkevich constant

ϵ (mol^2/KJ^2) – Polanyi potential

E – Mean free energy (kJ/mol)

W_{s1} & W_{s2} – Smith isotherm constant

K_{RP1} – Redlich–Peterson isotherm constant (l/g)

K_{RP2} – Redlich–Peterson isotherm constant (l/mg)

β_{RP} – Redlich–Peterson model exponent

q_{mS} – Maximum monolayer adsorption capacity Sips isotherm (mg/g)

K_S – Sips model isotherm constant (l/g)

n_S – Sips model exponent

q_{mT} – Maximum monolayer adsorption capacity by Toth isotherm (mg/g)

K_T – Toth isotherm constant

n_T – Toth isotherm exponent

q_{mH} – Maximum monolayer adsorption capacity by Hill isotherm (mg/g)

K_H – Hill isotherm Constant

n_H – Hill cooperativity coefficient

q_{mK} – Maximum monolayer adsorption capacity by Khan isotherm (mg/g)

α_K – Khan isotherm exponent

b_K – Khan isotherm constant
 q_{mRP} – Maximum monolayer adsorption capacity by Radke–Prausnitz–III isotherm (mg/g)
 K_{RP} – Radke–Prausnitz–III equilibrium constant
 n_{RP} – Radke–Prausnitz–III model exponent
 q_{mBS} – Maximum monolayer adsorption capacity predicted by Brouers–Sotolongo isotherm (mg/g)
 K_{BS} – Brouers–Sotolongo equilibrium constant
 n_{BS} – Brouers–Sotolongo model exponent
 q_{mFS} – Maximum monolayer adsorption capacity predicted by Fritz–Schlunder–III isotherm (mg/g)
 K_{FS} – Fritz–Schlunder–III equilibrium constant
 n_{FS} – Fritz–Schlunder–III model exponent
 q_{mMJ} – Maximum monolayer adsorption capacity by Marczewski–Jaroniec isotherm (mg/g)
 K_{MJ} – Marczewski–Jaroniec equilibrium constant
 n_{MJ} & m_{MJ} – Marczewski–Jaroniec model exponent
 A_{FS} & B_{FS} – Fritz–Schlunder–IV equilibrium constant
 a_{FS} & b_{FS} – Fritz–Schlunder–IV model exponent
 q_{mFSS} – Maximum monolayer adsorption capacity by Fritz–Schlunder–V isotherm (mg/g)
 K_1 & K_2 – Fritz–Schlunder–V equilibrium constant
 α_{FS} & β_{FS} – Fritz–Schlunder–V model exponent
 k_{Ho} – Ho constant ($\text{g mol}^{-1} \text{min}^{-1}$)
 h – initial sorption rate ($\text{mg g}^{-1} \text{min}^{-1}$)
 k_{Blc} – (min^{-1}) Blanchard kinetic rate constant
 a_{Blc} – is Blanchard model constant
 r_E – initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$)
 β_E – extent of surface coverage (g mg^{-1})
 k_{Av} – Avrami rate constant (min^{-1})
 n_{Av} – Avrami model exponent
 k_R – Ritchie rate constant (min^{-1})
 β_R – Ritchie model constant
 k_{SC} – Sobkowsk–Czerwi second order kinetic rate constant (min^{-1}).

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