

Application of Agricultural Waste for the Adsorption of Textile Colorant: A Review

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Abstract - Adsorption treatments are simple with no side product as the pollutants are adsorbed on the surface of the adsorbent and in many cases, can be regenerated and reused. Activated carbon is widely used for this purpose as it has excellent adsorption properties due to its high surface area and porous structure. However, its application is limited due to its expensive cost [1]. Recent development in adsorption treatment as in use of different adsorbents for wastewater treatment has developed many researches on materials that have low or no values such as agro waste, clay, mud, yeast and fungi. In addition to good removal of pollutants from aqueous solution, these materials are abundant, environmental friendly and low cost, making adsorption treatments to be more attractive than the conventional treatments. The use of adsorption technique offer much potential and reliable in the treatment of dye containing wastewater.

Key Words: Adsorption, aqueous solution, low cost adsorbent, agro waste

1. INTRODUCTION

Over the years, the quality of water is deteriorating mainly due to the anthropogenic activities, population growth, unplanned urbanization, rapid industrialization and unskilled utilization of natural water resources. Furthermore, the increased awareness of the importance of providing impacts due to the current environmental strategies has pushed the research community towards the development of robust, economically feasible and environmentally friendly processes capable of removing pollutants from water and at same time to safeguard the health of affected populations [2].

A variety of treatment technologies are available with different degree of success to control and minimize water pollution [3]. However, the shortcomings of most of these methods are high operational and maintenance costs, generation of toxic sludge and complicated procedure involved in the treatment [4]. Comparatively, adsorption process is considered a better alternative in water and wastewater treatment because of convenience, ease of operation and simplicity of design [5,6,7]. In wastewater treatment plants (WWTPs), adsorption processes are

applied for the removal of dissolved pollutants that remain from the subsequent biological phases or after chemical oxidation treatments. Today, the most commonly adopted adsorbent is the activated carbon. It is commonly used for the removal of various pollutants from water such a dyes and heavy metals [2,3]. However, its widespread use in wastewater treatment is sometimes restricted due to its higher cost [5] besides other issues such as the adsorbent regeneration capacity or the disposal of the end-of-life sorbent following different strategies than disposal [7].

2. WASTEWATER GENERATION IN TEXTILE INDUSTRIES

The wastewater from textile ventures is very factor, contingent upon the kind of color, sort of texture and the grouping of the additional operators. These effluents are edifices of numerous constituents, including a general classification of colors, normal dirtying impacts removed from the filaments and diverse items, for instance, acids, soluble bases, and metals [1]. The wastewater released from textile industry is tremendously shaded having high organic oxygen request (BOD), concoction oxygen request (COD), high conductivity and antacid nature. The textile shading industry uses huge volume of water and creates gigantic amounts of wastewater from different strides in the coloring and completing procedures. An expansive segment of wastewater delivered by material enterprises is amid the wet handling stages which incorporate estimating, desizing, scouring, blanching, mercerization, coloring, printing, completing and at last washing (EPA 1997). Table 1 below explicit contaminations from each procedure of textile. Furthermore, the centralization of some significant toxins is built up in Table 2 [8].

Table -1: Process involved in textile industries and pollutants released at every stage

Textile process	Main pollutants	Textile effluent characteristics
Desizing	Sizing agents, enzymes, starch, waxes, ammonia	High BOD, high TS, neutral pH

Scouring	Residues of disinfectants and insecticides; sodium hydroxide, surfactants, detergents, fats, waxes, pectin, oils, sizes, spent solvents, enzymes	High BOD, high TS, high alkalinity, high temperature
Bleaching	H ₂ O ₂ , adsorbable organic halogens, sodium silicate or organic stabilizer, high pH	High BOD, high TS, alkaline wastewater
Mercerizing	High pH, NaOH and other salts	Wasted dyes, high BOD, COD, solids, neutral to alkaline wastewater
Dyeing	Dyes, metals, salts, surfactants, organic processing assistants, sulfide, acidity/alkalinity, formaldehyde	
Printing	Urea, solvents, color, metals	
Finishing	Resins, waxes, chlorinated compounds, acetate, stearate, spent solvents, softeners	

Table 2: Main pollutants and concentration from textile industry

Parameters	Value
pH	7.0-9.0
Biochemical Oxygen Demand (mg/L)	80-6,000
Chemical Oxygen Demand (mg/L)	150-12,000
Total Suspended Solid (mg/L)	15-8,000
Total Dissolved Solid (mg/L)	2,900-3,100
Chloride (mg/L)	1000-1600
Colour (Pt-Co)	50-2500
Total Kjeldahl Nitrogen (mg/L)	70-80

These dyes are imperative wellsprings of natural contamination present dangerous impact on amphibian life on account of its harmful effect, high COD, BOD and low biodegradability. Notwithstanding the colors, textile emanating also contains variable pH and ionic quality, and high salts fixation as well. Notwithstanding water use, the effect of textile wastewater on water quality must be considered. After every single textile process water for the most part came back to our biological system without treatment - implying that the wastewater contains synthetic concoctions, for example, formaldehyde (HCHO), chlorine and substantial metals, for example, lead and mercury. These synthetic substances cause both ecological harm and human sickness. The World Bank evaluates that 17-20 percent of modern water contamination originates from textile coloring and treatment. They've additionally recognized 72 dangerous synthetics in our water exclusively from textile coloring, 30 of which are can't be evacuated. This speaks to an unpleasant natural issue for the attire originators and other material makers. In spite, numerous endeavors have been made to decrease or reuse water use through zero release frameworks. Be that as it may, selection has been ease back because of the failure to reliably repeat exact shading, and the mind-boggling expense of treatment to meet water quality gauges for the coloring forms.

2.1 TOXICITY OF DYES

An incredible assortment of substances got from dyes has been tried, in laboratorial creatures, to decide the genuine dangerous impacts of these mixes on living life forms. The assessment of the danger of textile dye is critical, mostly because of the distinctive impacts that they cause in nature and the life forms presented to them. The organic exercises additionally vary incredibly between the dyes and, in spite of the similitudes of the structures; the toxicological properties can't be summed up as per the reference of just a single substance gathering. The danger isn't caused just by textile dye yet by an extensive number of various material synthetic concoctions.

The synthetic compounds used to create dyes today are frequently exceedingly dangerous, cancer-causing, or even hazardous. Single or different exposures in brief timeframe causes intense poisonous quality, for example, skin disturbance, spewing, runs into human body.

Dye HSA (Human Serum Albumin), goes about as an antigen in human body delivering immunoglobulin and through the arrival of synthetic concoctions, for example, histamine, causes unfavourably susceptible responses.

The intense harmfulness of azo dyes, as characterized by the EU criteria for grouping of perilous substances, is somewhat low. Direct lethal dimensions of azo dyes will never be come to by expending azo dyes shaded nourishment.

Sulphonation of azo dyes seems to diminish poisonous quality by improving urinary discharge of the dyes and its metabolites. Sulphonated dyes, basically mono-, di- and trisulphonated mixes are world-wide allowed for use in nourishments, beautifying agents and as medications for oral application. As a few of the debasement results of the dyes have been observed to be mutagenic or cancer-causing and thus, a few dyes were never again allowed as nourishment dyes.

The compound aniline, the reason for a prominent group of dyes known as Azo dyes (explicitly assemble III A1 and A2) which are viewed as lethal toxic substances (emitting cancer-causing amines) and unsafe to work with, likewise being very combustible has its destructive impacts.

2.2 WASTEWATER TREATMENT METHODS

Different kinds of pollutants come from different textile processes, the treatment of different pollutants should be considered separately. For instance, the highly polluting effluent should be segregated and treated separately. The other low polluting wastewater should be treated by primary, secondary and tertiary treatment processes in order to reach the standards before disposal.

The treatments of wastewater from textile industry processes are complicated because of the complex components of organic matters and high colour. As one of the oldest industries, the treatment processes of textile effluent have been developed in order to find an economic and efficient method to treat wastewater in the past decades. These technologies consist of physicochemical, biochemical, combined treatment processes and other technologies. A whole treatment procedure of wastewater is normally a mixture of different units which contain some physical, chemical and biological steps.

2.3 CONVENTIONAL TREATMENT METHODS

Some conventional methods of textile wastewater treatments are listed below: coagulation and flocculation, oxidation, and biological methods. Coagulation and flocculation is a conventional method which mainly used to remove organic matters, such as dyeing substance. Some electrolytic products like aluminum sulphate ferric chloride are added into wastewater to eliminate the surface electrical charges of the colloids. This process is called coagulation. The coagulants are normally inorganic or organic cationic coagulants with positive charge in water. Moreover, it can help to increase the sedimentation. Biological process can remove dissolved substances like a self-depuration process. The efficiency of biological process depends on the ratio between biomass quantity and organic load in the tank, the oxygen concentration and the temperature. The biological treatment can be divided into aerobic and anaerobic treatment according to the different oxygen demand by different kinds of biomass. Oxidation is another widely used

method in textile wastewater treatment. It relies on variety of chemical reactions between chemical matters with contaminants to remove pollutants from wastewater. Oxidation process is a very important part of the whole wastewater treatment processes. It can oxidize the pigment in dyeing water and remove the colour of effluent. Nowadays, Fenton and ozone oxidation are mainly used in the wastewater treatment.

2.3.1 DRAWBACKS OF CONVENTIONAL TREATMENT

Physical and chemical strategies for dye removal are successful just if the wastewater volume is little. This restricts the utilization of physico-chemical strategies, for example, film filtration and cucurbituril, to small scale in situ expulsion. A restricting component of these techniques is cost. This is genuine even in lab-scale studies, and strategies, in this manner, can't be utilized by expansive scale industry. Biological activity, in fluid state maturations, is unequipped for expelling colors from emanating on a persistent premise. This is because of the time period of a few days required for decolorization-maturation forms. With the goal for this to be a practical choice for industry, the dye containing gushing must be held in huge tanks; this presents issues because of the sheer site estimate required.

Adsorption has been observed to be better than different procedures for water re-use regarding beginning cost, adaptability and straight forwardness of configuration, simplicity of activity and obtuseness to lethal contaminations. Adsorption likewise does not result in the arrangement of harmful substances.

3. ADSORPTION MECHANISM

Adsorption is a mass transfer process which involves the accumulation of substances at the interface of two phases, such as, liquid-liquid, gas-liquid, gas-solid or liquid-solid interface. The substance being adsorbed is the adsorbate and the adsorbing material is termed the adsorbent. The properties of adsorbates and adsorbents are quite specific and depend upon their constituents. If the interaction between the solid surface and the adsorbed molecules has a physical nature, the process is called physisorption. In this case, the attraction interactions are van der Waals forces and, as they are weak the process results are reversible. Furthermore, it occurs lower or close to the critical temperature of the adsorbed substance. On the other hand, if the attraction forces between adsorbed molecules and the solid surface are due to chemical bonding, the adsorption process is called chemisorption. Contrary to physisorption, chemisorption occurs only as a monolayer and, furthermore, substances chemisorbed on solid surface are hardly removed because of stronger forces at stake. Under favourable conditions, both processes can occur simultaneously or alternatively. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic [9].

In a solid-liquid system adsorption results in the removal of solutes from solution and their accumulation at solid surface. The solute remaining in the solution reaches a dynamic equilibrium with that adsorbed on the solid phase. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm according to the general Eq. (1):

$$q_t = \frac{(C_0 - C_t) \cdot V}{m}$$

where q_t (mg/g) is the amount of adsorbate per mass unit of adsorbent at time t , C_0 and C_t (mg/l) is the initial and at time t concentration of adsorbate, respectively, V is the volume of the solution (l), and m is the mass of adsorbent (g) [14].

4. LOW COST NOVEL ADSORBENTS

The agricultural solid wastes from cheap and readily available resources such as agave bagasse [10,11,12], almond shell[13], apricot shell[13], barley straw[14], cashew nut shell[15], citric acid[16],corncob [17], cotton and gingelly seed shell[18], depectinated pomelo peel [19], Egyptian mandarin peel [20], fruit juice residue [21], garden grass [22], garlic peel [23], grapefruit peel[24],hazelnut shell[25], lentil shell[26], mango peel waste[27], Mosambi (Citrus limetta) peel[28],muskmelon peel[29], pine sawdust[30], pongam seed shell[35],groundnut shell[31], olive stone[32], pomegranate peel[33], , potato peel[34],rice shell[35], rice straw[36], sugarcane bagasse [37,38],walnut shell[39], banana peel[40] cane pith[41],coirpith[42], yellow passion fruit [43], orange peel[44,45-47], rice husk[48-53],soy meal hull[54],sunflower stalk[55], white ash[56], white rice husk ash , wood derived biochar[57], pinewood[58], mixture almond shells[59], cassava peels[60],ash gourd peel[61], Cucumis sativa peel[62], lentil husk[63], neem bark[64], pomegranate peel[65],sunflower hull[66], wheat stem[67],carbon cloth[68], sky fruit husk[69]and coconut shells[70] have been investigated for the removal of numerous dyes from aqueous solutions. The basic components of the agricultural waste materials include hemicelluloses, lignin, lipids, proteins, simple sugars, water, hydrocarbons and starch, containing a variety of functional groups with a potential sorption capacity for various pollutants. Agricultural waste products are used in the natural and modified form. In the natural form, the product is washed, ground and sieved until reaches the desired particle size and subsequently used in adsorption tests. While, in the modified form, the product is pre-treated by-means of well known modification techniques [4]. The goal of these pre-treatments is to enhance and reinforce the functional group potential and, consequently, increase the number of active sites. Agricultural waste products have been extensively studied in relation to the adsorption process.

Below, the most significant experiences are described, starting from agriculture and household waste sorbents for the removal of dyes from single compound aqueous solution.

[10] Low cost by products from horticultural, household and industrial divisions have been perceived as a reasonable answer for wastewater treatment. They permit accomplishing the expulsion of toxins from wastewater and at same time to add to the waste minimization, recuperation and reuse. In spite of various surveys have been distributed over the most recent couple of years, an immediate correlation of information acquired utilizing distinctive sorbents is troublesome these days due to irregularities in the information introduction. In this circumstance, the aim was to change the study of the use of minimal effort adsorbents for wastewater treatment featuring, deliberately, both adsorbents characteristics and adsorption capacities. For this extension, low cost sorbents have been isolated into the accompanying five gatherings: (I) Agricultural and household wastes, (ii) industrial by-products, (iii) sludge, (iv) sea materials, (v) soil and ore materials and (vi) novel low-cost adsorbents. The affinity of sorbents in expelling different contaminations, their applications on wastewater, expenses and contemplations on their reuse after adsorption forms, has been talked about. At last, so as to better features the partiality of sorbents for more pollutants (colors, substantial metals biorecalcitrant mixes, nitrogen and phosphate mixes), simple methodological apparatuses, for example, "adsorbents-contaminations" grids have been proposed and applied. As such, the adsorbent contender for supplanting business activated carbons has been distinguished.

Kamraj et al. [71] depicts about the planning of ease and eco-accommodating groundnut shell activated carbon (GSAC) by joined physical-and chemical activity in a research centre scale office. The primary goals in this examination are: (1) to deliver groundnut shell activated carbon (GSAC); and (2) to assess their methylene blue color evacuation effectiveness through segment strategy alongside examination of their microbiostatic movement. As indicated by strategy gave in research paper, the ground nutshells were surface activated and a section adsorption process was embraced.

Dahri et al. [72] shows the utilization of Casuarina equisetifolia needle as minimal effort adsorbent for the expulsion of colors from fluid arrangement by clump mode tests. Distinctive parameters, for example, impact of adsorbent dose, pH, contact time and temperature were assessed. Lagergren-first-order and pseudo-second-order Models, Weber- Morris intraparticle dissemination and Boyd energy models were applied. Langmuir, Freundlich and Dubinin-Radushkevich isotherms were applied. The investigations were led at 180 min contact time with no modification of pH. Expanding temperature builds the adsorption of the both dyes onto CEN. The adsorption procedure was not seriously influenced by high ionic quality. The pseudo-second-order best spoke to the energy trial

information. The Weber– Morris intra-particle dissemination display demonstrated that intra-particle dispersion isn't the rate-restricted advance for the both adsorbents while the Boyd show recommended the two frameworks could be constrained by the film dissemination. The Langmuir isotherm display best spoke to the adsorption procedure for the both frameworks (CEN-MB and CEN-MG) which anticipated q_m at 110.8 and 77.6 mg g⁻¹, individually, at 25°C. Thermodynamic investigations demonstrated that both adsorption frameworks are unconstrained and endothermic in nature.

Malik et al. [73] examined groundnut shell, an agricultural waste, was utilized for the readiness of an adsorbent by compound activated utilizing ZnCl₂ under enhanced conditions and its relative characterization was directed with cost accessible powdered activated carbon (CPAC) for its physical, chemical and adsorption properties. The groundnut shell based powdered activated carbon (GSPAC) has a higher surface area, iodine and methylene blue number contrasted with CPAC. Both of the carbons were utilized for the expulsion of malachite green color from aqueous solution and the impact of different working factors, viz. adsorbent portion (0.1– 1 g⁻¹), contact time (5– 120 min) and adsorbate fixations (100– 200 mg/l) on the expulsion of color, has been considered. The test results demonstrate that at a portion of 0.5 g/l and introductory convergence of 100 mg/l, GSPAC indicated 94.5% expulsion of the color in 30 min balance time, while CPAC evacuated 96% of the color in 15 min. The exploratory isotherm information was analyzed utilizing the linearized types of Freundlich, Langmuir and BET conditions to decide greatest adsorptive limits. The balance information fit well to the Freundlich isotherm, despite the fact that the BET isotherm likewise indicated higher co-relation for both of the carbons. The consequences of similar adsorption limit of the two carbons show that groundnut shell can be utilized as an ease option in contrast to business powdered actuated carbon in watery answer for color evacuation.

Abigail et al. [74] investigated; Microbes play a vital role in the expulsion of Hexavalent chromium from defiled wastewater and soil. They build up an opposition towards chromium by an assortment of instruments, for example, adsorption to cell surfaces, complexation by exopolysaccharides, intracellular aggregation or precipitation. This made ready for secluding organisms from contaminated locales which could be abused for bioremediation purposes. In the present examination, as comparative marvel was utilized to confine parasites from tannery dumpage site which contains elevated amounts of chromium. Among the microbial adsorbents tried, contagious adsorbents appear to be all the more encouraging because of its astounding metal take-up limit on account of the nearness of numerous utilitarian gatherings on their phone divider, which pulls in and sequesters the metal on the biomass. Distinctive parameters i.e. impact of time,

temperature, pH, starting colour focus, adsorbent measurement was considered. Active models like zero, partial, first request, second request, pseudo first request, pseudo second request and so forth were examined. Isotherms like Langmuir, Freundlich, Hasley, Harkins, Temley, D-R were examined and thermodynamic conduct was additionally surveyed.

Senthil et al. [75] studied removal of cadmium ion by adsorption process using surface-modified *Strychnos potatorum* seeds and raw *Strychnos potatorum* seeds. Various effects of pH, adsorbent dose, initial dye concentration, contact time and temperature were studied. SMSF showed higher adsorption capacity than RSP. The adsorption data found to be following pseudo second order kinetic model. Boyd kinetic model and shrinking core model were also taken into consideration along with Langmuir and Freundlich. Langmuir adsorption isotherm model described equilibrium data well.

Ponnusami, et al [76] Removal of methylene blue utilizing novel minimal effort adsorbent Guava (*Psidium guajava*) leaf powder is considered. Batch adsorption was conducted to examine adsorbent dosage, initial dye concentration, pH, and temperature on percentage dye removal by varying these conditions one at a time. The percentage dye removal was found to increment with increment in contact time, pH, and adsorbent dose. With increasing initial dye concentration and temperature dye uptake increased initially and then decreased. Kinetic models and isotherms, thermodynamic nature was assessed. Kinetic model like first order, second order and intra particle diffusion were studied. Thomas model and Langmuir isotherm showed equilibrium data.

Abdelmajid et al [77] Adsorption investigation of Basic Blue 41 color onto activated carbon from *Persea americana* nuts with phosphoric acid activation was accomplished. The impact of working parameters, the impact of pH (2– 12), adsorbent sum (5– 30 mg/50 mL), color focus (25– 125 mg/L), contact time (0– 200 min) and temperature (298– 323 K), on the adsorption limit was analyzed. The experimental isotherm information were investigated utilizing Langmuir and Freundlich models, which demonstrated that the best fit was accomplished by the Langmuir show with the most extreme monolayer adsorption limit at 625 mg/g. The adsorption dynamic process pursued pseudo-second-order kinetics. Thermodynamic assessment demonstrated that the procedure was endothermic (DH0 = 144.60 kJ/mol) and unconstrained (DG0 shifted from to - 11.64 to - 19.50 kJ/mol), while the positive estimation of entropy (DS0 = 524.3 J/mol K) revealed increased randomness at the adsorbent–adsorbate interface. It was observed to be an extremely proficient adsorbent and a promising option for color expulsion from fluid arrangements.

Mallampati, et al [78] investigated three materials, avocado, hamimelon and dragon fruit peels, were chosen and utilized

as simple and sustainable adsorbents for water purification. The nearness of surface functional groups, for example, $-CO_2H$, $-OH$ and morphologies of the peels were described utilizing spectroscopic and electron microscope techniques, separately. The Langmuir isotherm display was helpful to clarify the adsorption procedure, commanded by electrostatic interaction between adsorbent and adsorbates, demonstrating a monolayer adsorption at the binding sites on the surface of the peels. In any case, the adsorption demonstrates for methylene blue and neutral red is as yet a matter of guess. The adsorbents can be recovered at acidic pH and could reuse for a couple of cycles.

Kiruba, et al [79] studied Adsorption of Cu (II) particles by on sulfuric acid-modified Eucalyptus seeds was considered. Sulphuric corrosive wash for 24 hr was given to grinded seeds for adsorption. Adsorption kinetics, mechanism, isotherms, and thermodynamic parameters were estimated. It was found that the adsorption of Cu(II) particles onto SMES pursues pseudo-second-order kinetic. Freundlich adsorption isotherm display concurred with the test information to a more prominent degree, demonstrating the multilayer adsorption of Cu(II) particles onto SMES. The conclusions from the thermodynamic examination demonstrate that the procedure was feasible, spontaneous, and exothermic in nature

Kanjilal, Babu et al, [80] Paper outlines the removal of heavy metal lead (Pb) (II) from paint industry effluent utilizing the mango seed integuments. The model fit rundown demonstrate the hugeness of the model and proposes the intensity of utilizing mango seed integument as the bio-adsorbent of lead particles from aqueous solution. From the outcomes, it tends to be reasoned that inexhaustibly. Under the ideal mix of the factors, most extreme evacuation accomplished was 75.23% with initial metal particle concentration of 49.79 g/L, adsorbent loading weight of 1.62 g/L, and contact time of 118.7 min. Langmuir, Freundlich, DKR Isotherm models were examined.

Senthil Kumar et al., [81] this study shows removal of Congo Red (CR) dye from aqueous solution by cashew nut shell. Various effects of pH, adsorbent dose, initial dye concentration, contact time and temperature were studied. CNS is locally viable adsorbent. Pseudo second order kinetic model agreed well with behaviour for adsorption of CR onto CS at different concentration. Langmuir, Freundlich, Redlich-Peterson, Koble-Corrigan, Toth, Temkin, Dubinin-Redushkevich isotherm models were studied. The experimental data showed astounding fits within the following isotherms order for: Redlich- Peterson >Toth >Koble-Corrigan >Sips >Freundlich >Langmuir >Temkin >Dubinin-Radushkevich, based on its correlation coefficient values. The thermodynamic study showed that the adsorption process is spontaneous and exothermic. The pseudo-first and pseudo-second-order kinetic model concurs very well with the adsorption process study on for the sorption of CR onto CNS is also discussed.

T. Calvete et al., 2010[82] shows Activated (AC-PW) and non-activated (C-PW) carbonaceous materials were prepared from the Brazilian- pine fruit shell (*Araucaria angustifolia*) and tested as adsorbents for the removal of reactive orange 16 dye (RO-16) from aqueous effluents. Adsorption studies for the evaluation of the C-PW and AC- PW adsorbents for the removal of RO-16 dye from aqueous solutions by kinetic models such as Avrami, Pseudo first order, Pseudo second order, Elovich, Intra particle diffusion were studied. The effects of shaking time, adsorbent dosage and pH on the adsorption capacity were studied. RO-16 up take was favourable at pH values ranging from 2.0 to 3.0 and from 2.0 to 7.0 for C-PW and AC-PW, respectively. The contact time required to obtain the equilibrium using C-PW and AC-PW as adsorbents was 5 and 4 hat 298K, respectively. The fractionary-order kinetic model provided the best fit to experimental data compared with other models. Equilibrium data were better fit to the Sips isotherm model using C-PW and AC-PW as adsorbents. The enthalpy and entropy of adsorption of RO-16 were obtained from adsorption experiments ranging from 298 to 323K.

5. GIST OF LITERATURE REVIEW

Activated carbons are the most popular and widely used adsorbents in wastewater treatment throughout the world [83]. It has several properties that make it particularly suitable for the purpose such as the high specific surface, the affinity with many compounds as well as its easy of regeneration. In spite of large use, the overall idea is to reduce the use of activated carbon because of high costs. Therefore, scientific world is looking at low-cost adsorbents as sustainable alternatives for wastewater treatment. Although numerous articles have been published in recent years, to the best of our knowledge, there are no studies which aimed to highlight the affinity of low-cost adsorbents in respect more pollutant classes. In our opinion, this is an important aspect. In fact, in order to replace the commercial activated carbon(CASs), a suitable non-conventional low-cost adsorbent should (i) be efficient to remove many and different contaminants, (ii) have high ad-sorption capacity and rate of adsorption and (iii) have high selectivity for different concentrations[83].

6. STUDY OF ADSORPTION ISOTHERM

Adsorption isotherm is a significant curve, which depicts the marvel administering the versatility of a substance from aqueous phase to a solid phase at a steady temperature and pH. The relationship between adsorbed particle and remaining particle in the solution is characterized when adsorbate is in contact to adsorbent for defined contact time which are communicated with mathematical calculation by means of adsorption isotherms Foo et al., [84]. A wide assortment of equilibrium isotherm models has been detailed over the years. In our experimental investigation, we have used the two dimensional isotherm models

(Langmuir, Freundlich, Dubinin– Radushkevich (D– R), Temkin, Harkins– Jura and Hasley isotherm) for fitting the got biosorption information of CEP and SCEP biosorbent.

6.1 THE LANGMUIR ISOTHERM

The theoretical Langmuir sorption isotherm Langmuir et al., [85] is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The non-linear equation of Langmuir isotherm model is expressed as follow:

$$q_e = \frac{q_{\max} k_L C_{eq}}{1 + k_L C_{eq}}$$

where C_{eq} is the equilibrium dye concentration (mg/L), q_m and K_L are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption respectively.

6.2 THE FREUNDLICH ISOTHERM

The Freundlich isotherm show Freundlich et al., [86] is the most well known relationship describing the sorption procedure. The model applies to adsorption on heterogeneous surfaces with interaction between adsorbed atoms and the use of the Freundlich condition likewise recommends that sorption vitality exponentially decreases on completion of the sorptional centers of an adsorbent. This isotherm is an experimental equation which can be utilized to depict heterogeneous conditioned solution and is evaluated from below equation:

$$q_e = K_f C_{eq}^{\frac{1}{n}}$$

where K_f is the Freundlich constant (L/g) indicating adsorption capacity. $1/n$ is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n is equal to unity, the adsorption is linear; if the value is below to unity, this implies that adsorption process is chemical; if the value is above unity adsorption is a favorable physical process.

6.3 DUBININ-RADUSHKEVICH (D-R) ISOTHERM

The Dubinin–Radushkevich Dubinin et al., [87] has the following form

$$q_e = q_{\max} e^{-\beta \epsilon^2}$$

where q_m is the Dubinin–Radushkevich monolayer capacity (mg/g), β constant related to sorption energy, and ϵ is the Polanyi potential which is related to the equilibrium concentration as follows

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$$

where R is the gas constant (8.314 J/mol K) and T is the absolute temperature. The constant β gives the mean free energy, E , of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship:

$$E = \frac{1}{\sqrt{2\beta}}$$

6.4 TEMKIN ISOTHERM MODEL

The Temkin isotherm model Temkin et al.,[88] contains a factor that explicitly takes into account -adsorbate interactions. This model assumes the following: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has commonly been applied in the following form:

$$q_e = \frac{RT}{B_T} (\ln A_T C_{eq})$$

where A and B are Temkin isotherm constants.

6.5 HARKINS-JURA ISOTHERM MODEL

Harkin-Jura isotherm model assumes the possibility of multilayer adsorption on the surface of absorbents having heterogeneous pore distribution Y Foo et al., 2010[84]. This model is expressed as follows:

$$\frac{1}{q_e^2} = \left(\frac{B}{A} \right) - \left(\frac{1}{A} \right) \log C_e$$

where B and A are Harkin-Jura constants that can be obtained from plotting $1/q_e^2$ versus $\log C_e$.

6.6 HASLEY ISOTHERM MODEL

The Halsey isotherm is used to evaluate multilayer adsorption at a relatively large distance from the surface Halsey G et al., & Ayawei et al [89,90]. The adsorption isotherm can be given as follows:

$$q_e = \left(\frac{K_H}{C_e}\right)^{\frac{1}{nH}}$$

where K_H and n are Halsey isotherm constant and they can be obtained from the slope and intercept of the plot of $\ln q_e$ versus $\ln C_e$.

6.7 SCATCHARD ISOTHERM MODEL

As Langmuir model is formulated for homogeneous adsorption, the negative-slope linearity shown on the Scatchard plot can be considered as an index for adsorption homogeneity. In other words, a nonlinear or positive-slope linear Scatchard plot indicates the adsorption heterogeneity. The negative-slope linear relation between q_e/C_e and q_e is called the Scatchard analysis Shing Yi-shen., [91]. The equations used for analyzing the data are shown in Table 3.

Table 3 Summarized isotherm model used in adsorption study

Isotherms	Non-linearized form	Linearized form
Langmuir	$q_e = \frac{q_{max} k_L C_{eq}}{1 + k_L C_{eq}}$	$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{k_L q_{max}} + \frac{1}{C_{eq}}$
Freundlich	$q_e = K_f C_{eq}^{\frac{1}{n}}$	$\log q_e = \log K_f + \frac{1}{n} \log C_{eq}$
Dubinin-Radushkevich	$q_e = q_{max} e^{-\beta \epsilon^2}$	$\ln q_e = \ln q_{max} - \beta \epsilon^2$
Temkin	$q_e = \frac{RT}{B_T} (\ln A_T C_{eq})$	$q_e = B_T \ln A_T + B_T \ln C_{eq}$
Harkins	-	$\frac{1}{q_e^2} = \left(\frac{B}{A}\right) - \left(\frac{1}{A}\right) \log C_e$
Hasley	$q_e = \left(\frac{K_H}{C_e}\right)^{\frac{1}{nH}}$	$\ln q_e = \left(\frac{1}{n}\right) \ln k - \left(\frac{1}{n}\right) \ln C_e$
Scatchard	-	$\frac{q_e}{C_e} = q_m K_L - q_e K_L$

7. ADSORPTION KINETICS

Till date, various kinetic models have been utilized to the reaction order and mechanism of adsorption systems. In this, the biosorption of MB dye by CEP and SCEP biosorbent was tried with the equation of kinetic models, such as fractional power, zero-order, pseudo-first order, Elovich, second order, pseudo second order, Weber Morris model and External diffusion model kinetics (Table 4) for investigating the rate controlling step and biosorption mechanism.

7.1 FRACTIONAL POWER

The fractional-power or modified Freundlich equation, which can be expressed as Aharoni et al., [92]

$$\ln q_t = \ln K + v \ln t$$

where q is the amount sorbed, k and v are constants and v is positive and smaller than one, and t is time. This expression is generally considered empirical, except for the case in which $v = 0.5$, where it becomes indistinguishable from the parabolic-diffusion equation.

7.2 PSEUDO FIRST ORDER

The pseudo first order kinetic model has been widely used to predict dye adsorption kinetics. The pseudo-first-order rate expression suggested originally by Lagergren based on solid capacity is expressed as follows.

$$\log(q_e - q_t) = \log q_{eq} - \frac{k_1 t}{2.303}$$

Values of q_e and K_1 can be obtained from the slope and intercept of the plot $\log (q_e - q_t)$ versus $t/2.303$.

7.3 SECOND ORDER

A linear form of the typical second-order rate equation is

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t$$

Where q_e is equilibrium dye concentration in solid phase (mg/g), q_t is amount of dye adsorbed per unit mass of adsorbent at time t (mg/g), K_2 is pseudo second order rate constant ($g\ mg^{-1}\ min^{-1}$).

7.4 PSEUDO SECOND ORDER

Pseudo-second order model is expressed by the equation Ponnusami et al., [76]

$$\frac{dq_t}{dt} = K_2 (q_e - q_t)^2$$

Integrating and applying boundary conditions $q_t|_{t=0} = 0$ and $q_t|_{t=t} = q_t$ we get,

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t$$

Rearranging the above equation we get,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

Values of q_e and K_2 can be obtained from the slope and intercept of the plot t/q_t versus t .

7.5 ELOVICH MODEL

The Elovich equation is generally expressed as follows YS Ho et al., [93]

$$\frac{dq_t}{dt} = a \exp(-bq_t)$$

where q_t is the sorption capacity at time t (mg/g), a is the initial sorption rate (mg g⁻¹ min⁻¹) and b is the desorption constant (g/mg) during any one experiment.

To simplify the Elovich equation, Chien and Clayton assumed $abt \gg 1$ and by applying the boundary conditions $q_t=0$ at $t=0$ and $q_t=q_t$ at $t=t$ equation becomes:

$$q_t = \frac{1}{b_e} (\ln a_e b_e) + \frac{1}{b_e} \ln t$$

7.6 WEBER MORRIS MODEL

It is important to recognize the steps involved during adsorption so as to interpret the mechanism of adsorption. It is expected that the adsorption procedure comprises of a few stages. Relocation of the dye from the bulk of the solution to the sorbent surface, diffusion of the dye through the boundary layer, intraparticle diffusion, and adsorption of the dye on the internal sorbent surface. The intraparticle dispersion rate can be communicated as far as the square root time. The equation of q_t versus $t^{0.5}$ is obtained if the sorption process is considered to be influenced by diffusion in the spherical particles and convective diffusion in the solution Bulut et al., [94]. The equation is as below:

$$q_t = K_p t^{\frac{1}{2}} + c$$

The plot q versus $t^{0.5}$ is given by multiple linear regions representing the external mass transfer followed by intra particle pore diffusion [95].

Table 4 List of Linearized form of kinetic models

Kinetic model	Linearized form
Fractional power	$\ln q_t = \ln K + v \ln t$
Zero order	$(q_t - q_e) = q_e - k_o t$
Pseudo-first order	$\log(q_e - q_t) = \log q_{e0} - \frac{k_1 t}{2.303}$

Second order	$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + K_2 t$
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$
Elovich	$q_t = \frac{1}{b_e} (\ln a_e b_e) + \frac{1}{b_e} \ln t$
Weber Morris Model	$q_t = K_p t^{\frac{1}{2}} + c$
External diffusion model	$\ln C_t = \ln C_o - K_{ext} t$

8. THERMODYNAMIC STUDY

Various parameters such as energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) change of adsorption can be evaluated from the following equations for studying thermodynamic behavior of adsorbent onto adsorbate at different temperature range Foo et al., [84].

$$\Delta G^\circ = -RT \ln K_c$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$\ln K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT}$$

where K_c is the equilibrium constant, ΔG° , ΔH° and ΔS° are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol) and entropy (J/mol/K), R is the gas constant (8.314 J/mol/K), T is the temperature (K) Ayawei et al., [90].

7. CONCLUSION

Based on the extensive literature reviewed, the following outcomes can be drawn: There is a lack of data concerning the characteristics of the investigated novel by-products. In many cases, adsorption tests were conducted without highlighting the characteristics of the adsorbents such as their average particle size or specific surface area. Furthermore, with reference to adsorption tests in batch mode, it was not always possible to acquire information on important parameters such as adsorption dose, contact time and initial pollutant concentration. Consequently, there is still much study to be done in order to standardize the outputs. According to the literature reviewed, novel low-costs adsorbents represent a promising green technology. Potentially, they can be applied at full-scale wastewater treatment. However, most of studies published in literature were referred to experimentations at lab-scale. Furthermore, the majority of the studies focused on synthetic solutions with only few studies using real wastewater. Ultimately, in order to take into account the new frontiers of

research, the regeneration of the novel adsorbents as well as the study of their end of life should be carefully evaluated.

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