REVIEW

Low Cost Adsorbents for Sustainable Dye Containing-Wastewater Treatment

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Dyes are coloured substances that can be applied to various substrates such as textile materials, leather, paper and hair. The usage of dyes has continuously increased in many industries but the removal of this pollutant remains as a problematic issue as they are generally stable to light and oxidizing agents and are resistant to aerobic digestion. This literature review paper provides and lists several low cost adsorbents to serve as an alternative method for dye removal. Adsorption using low cost materials can be viewed as a sustainable treatment process because most of these materials are of naturally occurring, locally available and inexpensive materials. This paper covers an overview of dyes waste treatments for 5 years period, from 2008-2012. Some of the noteworthy adsorbents include agricultural by-products, industrial waste and natural clay materials. Besides, the combination processes involving adsorption and other methods was also discussed.

Keywords: Adsorbent, Dyes, Colour, Low-cost process, Wastewater treatment.

INTRODUCTION

The application of adsorption techniques employing solid sorbents are widely used for the removal of dyes from aqueous environment. However, dyes removal in wastewater treatment through adsorption technique can only be applicable and sustainable, if the sorbent is of great abundance, readily available and relatively low cost. In this regard, agricultural by-products, industrial waste and natural clay materials can be viewed as attractive alternatives and yet economical sorbents with their own suitability in removing different types of dyes.

Agricultural waste/products/by-products: Agricultural-based activated carbon. Tandon and Nandini[1] studied the possibility of using activated carbon prepared from the sugarcane bagase and paddy straw to remove methylene blue. It was found that both H_3PO_4 and HNO_3 were good activating agents and more than 90 % of adsorption efficiency can be obtained from the solution containing 10 mg/L of dye with an adsorbent dosage of 0.1 g after 45 min of contact time at all the selected pH. Verma and Mishra[2] concluded that rice husk carbon has the ability to adsorb crystal violet (CV), direct orange and magenta

from aqueous solution. The adsorption of dyes have been best described by pseudo-first-order mechanism and Freundlich adsorption isotherms. Wheat straw carbon and saw dust carbon also demonstrated its potential to remove the same dyes[3]. Kulyakorn *et al.*[4] tested the applicability of burned rice husk to remove acid red dye under packed bed condition. Thomas model was used to predict the breakthrough time and the results indicated that the burned rice husk has a potential to be low-cost adsorbent for removal of acid red dye. Soy meal hull activated carbon was being investigated for its possibility in removing acid red 14 and acid red 18. The experimental data followed Langmuir isotherm and the tested adsorbent was concluded to be a suitable low-cost alternative for dye removal[5].

Senthilkumar *et al.*[6] evaluated the adsorption of direct blue 2B onto silver wood sawdust carbon. The kinetic study showed that the adsorption process is better explained by the pseudo-second-order rate equation whereas the equilibrium data fitted well with the Langmuir model. Analysis of adsorption data using a Boyd kinetic plot confirms that external mass transfer is the rate determining step in the sorption process. Neem sawdust carbon appeared to be an effective adsorbent for the

removal of Congo red (CR). Three simplified kinetic models based on pseudo-first-order, pseudo-second-order and intraparticle diffusion equations were used to describe the adsorption process and result shown that the adsorption of Congo red could be described by the pseudo-second-order equation, suggesting that the adsorption occurs as a chemisorption process[7]. Palanisamy and Sivakumar[8] used various kinetic models for the analysis of adsorption kinetics involving activated carbon prepared from *Euphorbia antiquorum* L wood and acid blue 92 as the model pollutant. Amongst all, pseudo-second-order model appeared to be providing a reasonably fitting for the selected study. The positive enthalpy of adsorption substantiates that the adsorption process is endothermic in nature. In the adsorption process of Congo red using Eucalyptus Globules Bark Carbon (EGBC) as the adsorbent, Kannan and Pagutharivalan[9] found that the percentage removal of Congo red was pH, initial dye concentration, particle size and adsorbent dosage dependent. Kinetics of adsorption is observed to be first order with intra-particle diffusion as one of the rate determining steps.

Cracked shea nut shell activated carbon was tested as an adsorbent for textile dyestuff wastewater[10]. The adsorbent shown a high adsorption capacity (4.169 mg/g) and ΔG was found to be more negative with sorbent-dye contact time, within the equilibration limit. In other study involving activated carbon from pomegranate and tamrind shell, Sundaram *et al.*[11] found that both adsorbents were efficient in removing Azure A dye from aqueous solution. The potential applicability of activated carbon prepared from *Myrtus communis* (AC-MC) and pomegranate (AC-PG) for the removal of Congo red was being investigated by Ghaedi *et al.*[12]. The experimental data fitted very well to the Freundlich isotherm for AC-MC and Langmuir isotherm for AC-PG. The interpretation of kinetic studies result showed a good compliance with pseudo-second-order with involvement of intraparticle diffusion model. The adsorption capacity of AC-PG and AC-MC for the removal of Congo red was found to be 19.231 and 10 mg/g, respectively. Based on the correlation coefficients values, Kumar *et al.*[13] concluded that the adsorption process of methylene blue onto activated carbon prepared from cashew nut shell fitted the isotherm models in the following order: Redlich Peterson > Toth > Sips > Koble-Corrigan > Langmuir > Temkin > Dubinin-Radushkevich > Freundlich. From the same study, it was revealed that that the adsorption process could be described by the pseudo-second-order equation. A thermochemically cracked shea nut shell activated carbon appeared to be a feasible low-cost adsorbent for textile dyestuff wastewater. Sorption energy values prove to be higher for biosorbent, SS/A/15 (1.364 kJ/mol), which also gave the corresponding higher adsorption capacity (4.169 mg/g) than the other three biosorbents in the series[14]. The adsorption of Rhodamine B (Basic dye) on *Leucaena leucocephala* seed shell waste carbon was investigated by Karthikeyan and Rajendaran[15]. The percentage removal of dye is observed to decrease with the increase in initial dye concentration. The adsorption isothermal data could be interpreted by both Langmuir and Freundlich equations. Thinakaran *et al.*[16] studied the removal of Acid Red 114 (AR114) from aqueous solution using activated carbons prepared from agricultural waste materials such as gingelly

(sesame) (Sp), cotton (Cp) and pongam (Pp) seed shells. Optimum conditions for AR 114 removal were found to be pH 3, adsorbent dosage = 3 g/L of solution and equilibrium time = 4 h. The adsorption isotherm data were fitted to Langmuir and Freundlich equation and the adsorption capacity of the studied adsorbents was in the order Sp > Cp > Pp.

Khaled *et al.*[17] stated that activated carbon developed from orange peel can be utilized as a low-cost adsorbent for the removal of Direct Navy Blue 106 (DNB-106). Based on the R^2 values, both Langmuir and Freundlich models fitted the adsorption data quite reasonably. The maximum adsorption capacity was 107.53 mg/g for 150 mg/L of DNB-106 concentration and 2 g/L carbon concentration. Meenakshisundaram *et al.*[18] studied the adsorption of Azure A dye onto commercial activated carbon (CAC) and activated carbon prepared from orange peel (OPC) and lemon peel (LPC). Kinetic of adsorption were found to be first order with regard to intra-particle diffusion rate. Nemr *et al.*[19] used the activated carbon developed from the orange peel to remove Direct Blue-86 from aqueous solution. The adsorption of Direct Blue-86 conform to pseudo-second-order rate equation and fitted better into Langmuir, Tempkin and Dubinin-Radushkevich (D-R) equations than Freundlich and Redlich-Peterson equations. The maximum adsorption capacity based on Langmuir equation was 33.78 mg/g and the intraparticle diffusion was found to be one of the rate determining steps. The conversion of orange peel into activated carbon in removing dyes from wastewater was being explored. The maximum removal was 96 % for 125 mg/L of DY-12 concentration on 5 g/L carbon concentration. The adsorption kinetics of DY-12 was studied and the rate of sorption fitted well to pseudo-second-order kinetics with correlation coefficients equal unity under all studied conditions. The maximum adsorption capacity calculated from the Langmuir isotherm model was 75.76 mg/g[20]. Thirumalisamy and Subbian[21] investigated the potential use of activated carbon prepared from the peel of *Cucumis sativa* fruit for the removal of methylene blue from simulated wastewater. The maximum adsorption capacity obtained from the Langmuir equation was 46.73 mg/g.

Santhi *et al.*[22] discussed the effects of different system variables in affecting the removal of malachite green (MG) by activated carbon prepared from the epicarp of Ricinus communis. The authors found that the adsorption process followed the pseudo-second-order rate equation and fits the Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Tempkin equations well. The maximum removal of malachite green was obtained at pH 7.

Revathi *et al.*[23] concluded that activated carbons developed from Jack fruit tree leaves (JTC) was as an ideal low-cost adsorbent to remove Direct Yellow 12 (DY-12) from wastewater. The experimental data fitted perfectly with Freundlich and Langmuir isotherms and the adsorption process followed pseudo-first-order kinetics with interactions occurs largely within the first hour. Batch experiments were conducted to assess the potential of Jack fruit carbon (JFC) as the adsorbent for methylene blue. In this study, Simi and Azeeza[24] observed that the equilibrium was attained around 0.5 h and the maximum adsorption capacity of Jack fruit carbon was found to be 0.1047 mg/g. The removal of mixture of textile basic dyes using

artocarpus heterophyllus seed carbon (AHSC) was performed by Meenakshi et al.[25]. The adsorption data were modeled using the Freundlich, Langmuir, Tempkin and Redlich-Paterson adsorption isotherms and pseudo-first and second-order-kinetic equations. The adsorption model shows the formation of monolayer coverage of the dye molecule, at the outer surface of the adsorbent.

Bouchemal and Addoun[26] found that a combination of chemical activation with $ZnCl_2$ and physical activation with CO_2, yielded a material that is capable in removing both methylene blue and Congo red dyes. From the scanning electron microscope results, it showed the conversion of the active carbon from the micropores into mesopores.

Areca nut pod was being investigated as a raw material to produce activated carbon that has an average surface area of 502 m/g. The results showed that as the amount of the adsorbent was increased, the percentage of direct blue removal increased accordingly[27].

The study conducted by Baccar et al.[28] indicated that activated carbon prepared from olive-waste cakes is a promising low-cost adsorbent for the removal of tannery dye from industrial wastewater. The maximum monolayer adsorption capacity was found to be 146.31 mg/g at 25 ºC and the activation energy, E_a = 9.50 kJ/mol. The adsorption mechanism of the dye is considered to be a complex process and the intra-particle diffusion step is not the only rate-controlling step. In a similar study, the adsorption of Lanaset Grey G, an industrial metal complex dye, on activated carbon derived from Tunisian olive-waste cakes was also being explored. The results indicated that the Langmuir model provides the best correlation of the experimental data and the adsorption capacity of the sorbent was found to be 108.7mg/g, which is better than the capacity of a commercial activated carbon[29].

Theivarasu et al.[30] studied the adsorption potential of theobroma caco shell activated carbon for methylene blue. The influence of various factors on the uptake of dye was carried out. The kinetic adsorption data fitted the pseudo-second order kinetic model well and also followed the intra-particle diffusion model.

Activated carbons from lignocellulosic waste materials were being tested as the adsorbents for water treatment. Altenor et al.[31] concluded that these waste materials can served as renewable resources for the preparation of activated carbon. Demirbas[32] evaluated the usage of different agricultural waste as the adsorbents for various types of dyes. The author stated that the dye adsorption capacities of agricultural waste adsorbents vary, depending on the characteristics of the individual adsorbent, the extent of surface modification and the initial concentration of adsorbate.

Shells/seeds: Jain and Jayaram discussed the adsorption of methylene blue and CV dyes onto wood apple shell (WAS). The results showed that Langmuir equation fits better than the Freundlich equation and the adsorption of dyes onto WAS proceeds according to a pseudo-second-order model. Higher adsorption capacity was observed for CV (130 mg/g) than methylene blue (95.2 mg/g). The fourier transform infrared (FTIR) studies indicated the interaction of dyes and WAS surface is *via* the nitrogen atoms of the adsorbate and oxygen groups of the adsorbent[33]. de Oliveira Brito et al.[34] found that

the removal of methylene blue and indigo carmine (IC) from solution by Brazil nut shells (BNS) was governed by: (i) polarization effects between the coloured ions and the surface sites, leading to physisorbed species due to weak electrostatic forces and (ii) diffusion limitations affecting the kinetic parameters. The adsorption followed the Langmuir model and the maximum uptakes were 7.81 mg/g, for methylene blue and 1.09 mg/ g for indigo carmine at room temperature. Dogan et al.[35] presented a study on the biosorption of methylene blue by hazelnut shells. The extent of the methylene blue removal increased with increasing in the solution pH, ionic strength and temperature but decreased with increase in the particle size. The maximum adsorption capacities for methylene blue were 2.14×10^{-4}, 2.17×10^{-4}, 2.20×10^{-4} and 2.31×10^{-4} mol/g at temperature of 25, 35, 45 and 55 ºC, respectively. Senthil Kumar et al.[36] concluded the sorption process of Congo red onto cashew nut shell was spontaneous and exothermic in nature. Besides, it was shown that the adsorption of Congo red could be described by the pseudo-second-order equation, suggesting that the adsorption process is a presumably chemisorptions.

Santhi et al.[17] studied the adsorption of malachite green and methylene blue from aqueous solutions on Annona squmosa seed (CAS). Results obtained indicate that the removal efficiency of malachite green and methylene blue at 27 ± 2 ºC exceeds 75.66 and 24.33 %, respectively. The adsorption process is highly pH-dependent and the optimum pH for dye removal occurred at pH 6[37]. In another similar study, Annona squmosa seed was tested as the adsorbent for methylene blue, malachite green and methylene red (MR). The isothermal data fitted the Langmuir model in the case of methylene blue sorption and the Freundlich model for the other dyes[38].

Fruits peels/Bagasse waste: Ong et al.[39] studied the ability of durian peel in removing Basic Blue 3 (BB3) and found that the maximum adsorption capacity was 49.50 mg/g. Various fruits peel was being tested for its adsorption properties towards methylene blue. The authors found that all the investigated sorbents were non-porous materials and the maximum adsorption capacity was in the range of 35-79 mg/g[40]. Saad et al. concluded the adsorption efficiency for the removal of methylene red from simulated wastewater was in the order commercial powdered activated carbon > sugarcane bagasse pretreated with phosphoric acid (SBC) > sugarcane bagasse (SB)[41]. The removal of basic dyes by sugarcane bagasse under continuous flow condition was being evaluated and the results showed that the theoretical breakthrough curves generated using Chu model agreed closely with the experimental data[42]. The removal of BB 3, methylene blue and Basic Yellow 11 (BY 11) were being evaluated using statistical approach. Plackett Burmann design was applied to identify the significant factors whereas optimization study was carried out using Response Surface Methodology. Under the optimum condition, the percentage of uptake can be greater than 90 % for methylene blue[43]. Liang et al.[44] discussed the adsorption of methylene blue by using shaddock peel and stated that the dye could be removed effectively when the initial pH ≥ 6. The authors found that adsorption data fitted very well with the Langmuir adsorption model and the maximum adsorption capacity was 305.81 mg/g at 303 K. Kinetics wise, it followed the pseudo-second-order kinetic model.

Husk/Hull/ Straw materials: Gupta *et al.*[45] evaluated the potential of coconut husk as a low cost adsorbent for Cyanosine and found that the sorption followed Langmuir and Freundlich adsorption isotherm models. In the determination of the role of different surface functional groups on ethylenediamine modified rice hull for the sorption of dyes, the authors concluded the carboxyl group was the major functional group responsible in the uptake of basic dye whereas for the binding or reactive dye, it occurs through the interaction with the amino groups[46]. Rehman *et al.*[47] investigated the removal of Murexide dye from aqueous media by adopting rice husk as the adsorbent. The rate of adsorption was investigated under various parameters and based on the results obtained, the authors concluded that rice husk can be effectively used for the elimination of Murexide from waste water. Ong *et al.*[48] used the statistical approach to study the effect of various operating parameters in the removal of basic and reactive dye. The empirical model developed from the interactive effects of the significant variables was being validated using ANOVA analysis.

Based on the results obtained from the study by Batzias *et al.*[49] the authors concluded that mild acid hydrolysis enhances significantly the adsorption properties of the original wheat straw in removing methylene blue and Red Basic 22 dyes. The enhancement can be attributed to the removal of the hemicelluloses during sulfuric acid treatment, resulting in the 'opening' of the pores of lignocellulosic matrix's structure and the increasing of the BET surface area[49]. Hassanein and Koumanova studied the potential usage of Flax shives for the removal of Basic Yellow 21 and found that the adsorption capacity was 76.92 mg/g. The adsorption kinetics fit very well in the second-order kinetic model and the isotherm data is better explained by Tempkin equation[50]. Cotton stalk and apricot seed were evaluated as low-cost biosorbents for the model pollutant Astrazone Black by Kahraman *et al.*[51]. The results indicated that the removal was adsorbent dosage and particle size dependent[51]. Moussavi and Khosravi[52] confirmed the efficiency of pistachio hull powder (PHP) for the elimination of methylene blue from aqueous solution. The dosage of PHP was found to be an important variable influencing the removal percentage of methylene blue. The maximum adsorption capacity increased from 389-602 mg/g when the temperature was increased from 20-50 ℃[52]. Safarik and Safarikova[53] found that ferrofluid modified biological waste (peanut husks) can be successfully used for the separation and removal of water soluble organic dyes. Apostol *et al.*[54] chosen pumpkin seeds hull (PSH) as the adsorbent for Acid Red 51 removal and they concluded that by using 20 g/L of PSH, the amount of dye uptake was around 3.5 mg/g. Zhou *et al.*[55] presented a study on the uptake of methylene blue by cottonseed hull substrate (SCHS) and discovered that the kinetics of dye removal by SCHS was rapid, with 90.0 % sorption within the first 5 min and equilibrium attained after 3 h. Biosorption kinetics and equilibrium followed the pseudo-second-order and Langmuir adsorption models. The maximum amount of methylene blue adsorbed on SCHS was 185.22 mg/g. Feng *et al.*[56] performed the study of methylene blue adsorption onto sesame hull and concluded that a wide range of pH (3.54-10.50) was favorable for the adsorption of methylene blue onto SH. The Langmuir model displayed the best fit for the isothermal data and the calculated maximum monolayer adsorption capacity (359.88 mg/g) was higher than most previously investigated low-cost bioadsorbents (*e.g.*, peanut hull, wheat straw, *etc.*)[56].

Sawdust/Wood waste/leaves: Jain *et al.*[57] concluded that formaldehyde pretreatment *Acacia nilotica* sawdust can be utilized as a low-cost biosorbent for removal of basic Swiss Blue dye from wastewater. Maximum dye removal was recorded as 97.5 % at the condition: pH 6, 50 mg/L dye concentration and 0.2 g/50 mL adsorbent dosage. Adsorption was endothermic and was accompanied by an increase in entropy and a decrease in Gibbs free energy for 288-333 K. Khattri and Singh[58] discussed the usage of Sagaun sawdust for the removal of CV from simulated wastewater and from the dimensionless factor, R_L, it revealed that the adsorption process is favorable in nature. Ouazena and Sahmoune[59] found that for the sorption process of Astrazon Yellow onto sawdust, the extent of dye removal decreased with increasing particle size and increased with increasing contact time, adsorbent dose and pH. Maximum adsorption capacity calculated at 293 K was 81.8 mg/g. The kinetics of adsorption of the basic dye followed both Elovich and pseudo-second-order kinetics and intraparticle diffusion was not the sole rate-controlling step.

In the study performed by Bajpai and Jain[60], the authors found that an increase in the pH value and temperature is beneficial to the CV uptake by spent tea leaves. The kinetic uptake data, obtained at different sorbate concentrations, is best interpreted by pseudo-second-order model and rate constants for adsorption are found to be 8.5×10^{-3}, 22.2×10^{-3} and 42.0×10^{-3} g/mg min for initial dye concentrations of 10, 20 and 30 mg/L, respectively. Santhi *et al.*[61] utilized the mixture of leafs, fruits and twigs of Muntingia calabura to adsorb cationic dyes and confirmed that the removal of the dyes was optimal at the pH value above 6. The biosorption processes followed pseudo-first-order rate kinetics. Fazaeli *et al.*[62] concluded that raw waste materials and activated carbon from plane tree yellow leaves can be utilized as the adsorbent for Direct Red 81. The influence from various factors and different adsorption isotherm models were employed to study the adsorption process. Ladhe *et al.*[63] studied the removal of Erichrome Balck T by activated Nilgiri leaves and found that this biosorbent could be employed as low cost alternative to commercial activated carbon in wastewater treatment for dye removal.

Azizi *et al.*[64] utilized wood waste (WW) to remove Reactive Blue 19 (RB 19) from synthetic dye solution and real textile wastewater. The authors found that the maximum dye removal efficiency (93.79 %) was observed at pH 2 and with 16 g/L of WW. Maximum value of Q for this waste was 30.92 mg/g. For the real textile wastewater containing RB 19, the dye removal efficiency was obtained at 73.84 %. Choy and McKay[65] conducted a study on the adsorption capabilities of several adsorbents such as bamboo, waste wood, bamboo char, waste wood char, bamboo activated carbon, wood activated carbon and active carbon F400. Based on a Langmuir analysis, the monolayer adsorption capacities were determined. The authors selected three of the adsorbents for binary layer adsorption to check the multilayer concept and the potential application for better adsorbent usage[65]. Srivastava and Rupainwar[66] compared the

adsorption capability of Neem bark and Mango bark for malachite green. The adsorption of malachite green followed the second-order kinetics in both the adsorbents. The results indicated that Langmuir adsorption isotherm fitted the data better than Freundlich isotherm. The negative values of free energy indicated the feasibility and spontaneous nature of the process and the positive heats of enthalpy suggest the endothermic nature of the process. In another similar study by the same authors, the removal of indigo carmine (IC) and methylene blue by Neem bark was tested. The maximum adsorption capacity obtained from Langmuir equation was 4.02×10^3 and 3.11×10^3 mol/g for IC and methylene blue, respectively. The rate of adsorption was found to conform to pseudo-second-order kinetics with a good correlation and intraparticle diffusion is one of the rate determining steps[67].

Industrial by-products/wastes: Fly ash: Kannan and Murugal[68] concluded factors such as initial dye concentration, particle size and contact time influence the removal of Rhodamine B, Congo red and acid violet by adsorption onto flyash. The kinetics of adsorption is found to be first-order with intraparticle diffusion as one of the rate determining steps. Purai and Rattan[69] tested the adsorption of Basic Green 4 onto biomass ash and found that the equilibrium adsorption data followed both Langmuir and Freundlich isotherms. Wang et al.[70] confirmed that the adsorption of methylene blue and humic acid by coal fly ash has a close relationship with surface area and pore volume, whereby a higher surface area and pore volume of fly ash resulted in higher adsorption for both model pollutants. Lin et al.[71] pretreated fly ash with H_2SO_4 to remove methylene blue. The experimental results showed that Freundlich isotherm and pseudo-second-order model are the appropriate equations to describe the adsorption process. Witek-Krowiak et al.[72] studied the removal of cationic dyes by adsorption onto flyash and suggested that this material can served as an appropriate adsorbent for the removal of basic dyes. The authors reported the maximum sorption capacity for methylene blue and malachite green was 36.05 and 40.65 mg/g, respectively. Zaharia et al.[73] performed a study on unconventional adsorptive materials for colour removal from textile effluents. They concluded that best colour removal option is obtained from combination of technologies or proposed treatment steps rather than from one single-stage process. Suteu et al.[74] reviewed on different industrial and agricultural waste materials for textile wastewater treatment and found that most of the sorption systems were well described by using Freundlich, Langmuir and Dubinin-Radushkevich isotherm models.

Sewage sludge: Cai et al.[75] concluded the anionic functional groups, phosphonate and carboxyl group were the binding sites for the cationic methylene blue whereas amine groups were identified to bind RR4. The main mechanism of the reactive dyestuffs adsorption occurred through electrostatic interaction. Meng et al.[76] discussed the usage of sewage sludge based activated carbon for the removal of chemical oxygen demand and colour. They found that pseudo-second-order model provided a better correlation for the kinetic adsorption data compared to pseudo-first-order. Moghaddam et al.[77] studied the adsorption of Acid Red 119 by mixtures of dried sewage sludge and sewage sludge ash. They suggested that the optimum condition under specified constraints (dye removal efficiency

> 95 % and turbidity < 50 NTU) occurred at a contact time of 1 h, 40 wt % DSS in the mixture, an initial pH of 6 and an initial dye concentration of 200 mg dye/L in distilled water. Under the optimal condition, dye removal efficiency of 94.98 % and effluent turbidity of 24.9 NTU was observed. Desorption studies revealed that AR119 dye could be well removed from dye-loaded adsorbent by 0.3 M NaOH solution.

Waste materials: Gupta et al.[78] found that the adsorption of Safranine-T dye onto deoiled-mustard followed Langmuir isotherm model better than Freundlich at 40, 50 and 60 °C. Desorption profile revealed that a significant portion (83 %) of the dye could be desorbed by using 12 % acetic acid solution as an eluting agent. Jain and Sikarwar[79] utilized deoiled mustard to remove Erythrosine dye and concluded that this is a spontaneous process at 203 K through the estimated negative values for ΔG°. Wu et al.[80] studied the potential of waste brewer's yeast to adsorb Basic Geen and found that the isothermal data of adsorption followed both Langmuir and Freundlich models. The functional groups that are responsible for the dye uptake are amino, amide, carboxyl and phosphate. Beer brewery waste appeared to be a potential adsorbent for methylene blue removal according to Tsai et al.[81]. The authors found that the pore properties of this waste were significantly larger than those of its raw material and suggested that the trapped organic matrices contained in the waste probably provided additional adsorption sites and/or adsorption area. The adsorption parameters obtained from the pseudo-second-order model were in accordance with their pore properties. Franca et al.[82] studied the adsorption of malachite green onto coffee press cake and revealed that pseudo-second-order kinetic model provided the best description of the adsorption process. Based on the results, the authors concluded that this adsorbent has a good potential to serve as an inexpensive and easily available alternative to remove cationic dyes from wastewater. Anandkumar and Mandal[83] employed various activation methods to investigate the potential use of tannery residual biomass in the removal of chromium(VI) and rhodamine B. The equilibrium data fitted satisfactorily with the Langmuir model and monolayer sorption capacity obtained as 177-217 and 213-250 mg/g for Cr(VI) and RB at 30-50 °C, respectively. The favorable uptake with increasing temperature indicates the endothermic nature of the adsorption process. The sorption kinetics was found to follow the pseudo-second-order kinetic model[83]. Atar and Olgun[84] tested the applicability of boron waste to remove basic and acid dyes. The sorption of both dyes was pH dependent whereby for basic dye, it increased at high pH values and the opposite was true for acidic dye. Zhang et al.[85] studied the usage of spent catalyst for the removal of methylene blue and concluded the best fitting for the kinetic data is corresponded to the pseudo-second-order. Attallah et al.[86] found that the maximum capacity of metal hydroxides sludge for Congo red and Naphthol Green B dyes at equilibrium (q_e) and percentage of removal at pH 6 are 40 mg/g, 93 % and 10 mg/g, 52 %, respectively.

Chitosan: Huang et al.[87] prepared crosslinked chitosan resin using inverse suspension polymerization with methanal and epichlorhydrin (ECH) to remove dyes and the authors included a comparison study to compare the adsorption ability of the prepared chitosan with the commercial activated carbon.

Feng *et al.*[88] characterized the modified flax shive (CFS) and found that the BET and Langmuir surface area of CFS were 1.772 and 3.057 m^2/g, respectively. Results showed that -NH$_2$ group on CFS is the main adsorption site for Reactive Red 88 sorption. The percentage removal were 100 % for dye concentrations of 10 and 20 mg/L, whilst 90 and 85 % removal for dye concentrations of 30 and 40 mg/L, respectively at pH 2.0. Zhu *et al.*[89] studied the adsorption of an anionic azo dye by chitosan/kalin/γ-Fe$_2$O$_3$ composites and concluded that 71 % of dye was adsorbed within 3 h from 20 mg/L dye solution at pH = 6 by 1 g/L adsorbent dosage. The surface characterization study showed that many pores and pleats were visible on the surface of the composites and provided a good condition for dye adsorption[89]. Azlan *et al.*[90] confirmed that cross-linked chitosan beads with ethylene glycol diglycidyl ether (EGDE) enhanced its chemical resistance and mechanical strength. Langmuir isotherm model showed the best conformity compared to Freundlich and BET. The desorption study revealed that the adsorbent still demonstrating good adsorption abilities though after three cycles of adsorption and desorption by NaOH and HCl.. FTIR analysis proved that the adsorption of acid dyes onto chitosan-based adsorbents was a physical adsorption[90].

Clay materials: Jovic-Jovicic *et al.*[91] proved that the adsorption isotherm data of Acid Orange 10 by organo-bentonite fitted well in Langmuir isotherm model. Based on the same study, the authors suggested that adjusting pH as an additional operation in wastewater treatment is not entirely necessary. Ma *et al.*[92] explored the possibility of using bentonite to remove anionic pollutant from water and reported that the adsorption capacities of the modified bentonite for fluoride, phosphate, Orange II and SDBS are 50.07, 29.1, 239.5 and 298.5 mg/g, respectively. Yao *et al.*[93] proposed that the self-assembly organobentonite can served as a potential super adsorbent for the removal of organic pollutant. The results indicated the adsorption capacity of self-assembled organo-bentonite was 50 % higher than that of traditional organo-bentonite. Based on the X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) analyses, it showed that the self-assembled organobentonite had a larger basal spacing than traditional organobentonite and CTMA + and dye were adsorbed on the external surface or intercalated into the interlayer of bentonite. Zhu and Zhu[94] confirmed that malachite green can be efficiently adsorbed by bentonite and the maximum adsorption is 430 mg/g. The authors noted that with the adsorption of malachite green, the interlayer spaces of bentonite changed from hydrophilic to hrophobic which enable the adsorption of 2-naphthol and naphthalene. Ongen *et al.*[95] studied the adsorption of Astrazon Blue FGRL onto sepiolite and found that the equilibrium time, optimum pH and temperature for this process were 90 min, pH: 7 and 293 K, respectively. Adsorption isotherm of Astrazon Blue FGRL on sepiolite (meerschaum) fitted better in the Freundlich model than the Langmuir model. Ugurlu[96] conducted the adsorption of Remazol Red B (RRB) from aqueous solution on thermal activated sepiolite (TAS) and acid activated sepiolite (AAS). For the adsorption involving AAS samples, the equilibrium time and optimum pH were found to be 2 h and pH: 2-3, respectively. Besides, the sorption capacity

of AAS samples was higher than that of TAS. The kinetic data for both sepiolite samples was highly supported by pseudo-second-order model and intra-particle model. Tekbas *et al.*[97] reported that the monolayer coverage capacities of sepiolite for basic dye were found to be in the range of 62.5-88.5 mg/g at different temperatures. Thermodynamic studies showed that the reaction for Basic Astrazon Yellow 7GL by sepiolite is endothermic in nature. Vimonses *et al.*[98] investigated the removal efficiencies of three Australian kaolins for Congo red and found that Ceram kaolin had the highest removal efficiency, followed by K15GR and Q38. The optimal dye uptake occurred at acidic pH and high dye concentration. The adsorption process obeyed the pseudo-second-order kinetic expression and was best described by the Langmuir isotherm. The adsorption mechanism was more likely to be governed by external mass transfer. Thermodynamic studies revealed that Congo red adsorption on all kaolins was exothermic and spontaneous in nature. In another study by Vimonses *et al.*[99], the authors tested the adsorption capability of bentonite, kaolin and zeolite for Congo red. The equilibrium data of kaolin was found to best describe by the Langmuir model, while bentonite and zeolite were better explained by the Freundlich model. Kinetic data followed the pseudo-second-order equation for the three adsorbents. Further study involving the mixture of natural clay materials with lime by Vimonses *et al.*[100] showed that this modification enhanced the efficiency and capacity of the adsorbent for Congo red. The effect of pH appeared to be a key parameter to govern the removal mechanisms, *i.e.,* adsorption/coagulation at acidic pH and precipitation at basic condition. Ca-dye precipitation contributed over 70 % total dye removal, followed by adsorption and ion-exchange. Vimonses *et al.*[101] also discovered that the mixed clay materials can be easily recovered by thermal treatment and the recovered mixtures demonstrated an enhanced removal capability after a few cycles of removal and regeneration. Khan *et al.*[102] studied the adsorption of kaolinite for Rhodamine B and found that the monolayer adsorption capacity was 46.08 mg/g. The optimized conditions for the adsorption process was reported as initial concentration of RhB (90 mg/L), agitation time (80 min), adsorbent dose (3 g/L), pH (7) and temperature (303K). Almeida *et al.*[103] investigated the removal of methylene blue by montmorillonite clay and suggested that the experimental data fitted the pseudo-second-order kinetic model, with an activation energy of +28.5 kJ/mol. Isotherm study revealed that the current adsorption process conform to Langmuir isotherm model. Wang and Zhang[104] utilized Cu(II)-loaded montmorillonite to adsorb CV and found that the maximum adsorption capacity was 114.3 mg/g. The kinetic study conforms to pseudo-second-order equation. Elass *et al.*[105] examined the suitability of ghassoul to remove methylene blue and concluded that the initial pH and temperature had a minimal effect on the dye uptake. Kinetic data and isotherm study are well expressed by pseudo-second-order equation and Langmuir isotherm model, respectively. Deniz and Saygideger[106] studied the adsorption of Basic Red 46 (BR 46) onto gypsum and concluded the equilibrium data fitted well with the Langmuir model (monolayer adsorption capacity = 39.17 mg/g). The adsorption kinetic was tested with different equations and it was found to be best described by the pseudo-

second-order model. Thermodynamic investigations indicated that BR 46 adsorption onto gypsum was spontaneous. Jalil et al.[107] used the calcined Lapindo volcanic mud (LVM) to remove methyl orange and reported that the maximum adsorption capacity was 333.3 mg/g. The thermodynamic parameters, such as the changes in enthalpy, entropy and Gibbs free energy, showed that the adsorption is endothermic, random and spontaneous at high temperature. Song and Yang[108] compared the adsorption properties of rectorite and attapulgite for methylene blue and concluded that the latter has a higher affinity towards the targeted dye. The analysis of the isotherm equilibrium data using the Langmuir and Freundlich equations showed that the data fitted better with Langmuir model. The experimental data conform to the pseudo-second-order kinetic model. Koyuncu[109] studied the removal of Tar-Chromium Green 3G dye by using natural diatomite and discovered that the reaction for the uptake by diatomite is exothermic in nature. The values of standard free energy (ΔG) and the values of standard enthalpy (ΔH) were negative and entropy (ΔS) was found to be positive. Wang et al.[110] compared the adsorption capability of activated carbon-attapulgite composite adsorbent (ACA) and zeolite-attapulgite composite adsorbent (ZA) for Congo red. The authors found that ACA had higher adsorption rate in the first 0.5 h contact time and ZA had higher removal percentage because of the difference on the pore size and total pore area. The effect of changing pH had a minimal impact on the removal percentage of Congo red. The removal efficiency of Congo red on ACA and ZA increased from 92-95 % with increase of temperature from 293-323 K. Alzaydien concluded that Jordanian tripoli, a low-cost clay can be utilized as a sorbent for the removal of methylene blue[111]. Bua et al.[112] reported that palygorskite possess excellent sorption properties for methylene blue because of its porous structure and fibrous morphology. The structure of palygorskite was destroyed gradually with increasing calcination temperature and the adsorption capacity of the palygorskite can be improved by thermal modification in appropriate temperature ranges. Rodriguez et al.[113] compared the adsorption of two dyes onto various inorganic materials. Bentonite, Fuller's earth and kaolinite presented higher adsorption capacity for methylene blue and hydrotalcite and Syntal HSA 696 were better for Orange II adsorption. Chen and Zhao[114] prepared the organo-attapulgite using hexadecyltrimethylammonium bromide (HTMAB) to be employed as adsorbent for the removal of Congo red dye from aqueous solution. The experimental results show that the amount of Congo red adsorbed on the organo-attapulgite increase with increasing dye concentration, temperature and by decreasing pH. The adsorption kinetics was evaluated and the authors concluded the adsorption followed pseudo-second-order kinetics with a significant contribution of film diffusion. The maximum adsorption capacity was 189.39 mg/g. The results from kinetic and desorption studies suggested that chemisorption should be the major mode of Congo red removal by the organo-attapulgite[114]. Based on the result from the study by Yuliani et al.[115], the authors confirmed that lignite can served as a potential adsorbent for the removal of colour, organics and total phosphorus from pulp and paper mill effluents. Table-1 summarized the adsorption capacities for different dyes by various low cost adsorbents.

TABLE-1
ADSORPTION CAPACITIES FOR DYES BY VARIOUS LOW COST ADSORBENTS

Adsorbent	Dye	Maximum* sorption capacity (mg/g)	Ref.
Myrtus communis	Congo red	19.23	12
Pomegranate	Congo red	10.00	12
Orange peel	Direct navy blue 106	107.53	17
Orange peel	Direct blue-86	33.78	19
Orange peel	Direct yellow 12	75.76	20
Cucumis sativa fruit peel	Methylene blue	46.73	21
Jack fruit	Direct yellow 12	0.1047	24
Tunisian olive-waste cakes	Lanaset grey G	108.7	29
Wood apple shell	Crystal violet	130	33
	Methylene blue	95.2	
Brazil nut shell	Methylene blue	7.81	34
	Indigo carmine	1.09	
Durian peel	Basic blue 3	49.50	39
Shaddock peel	Methylene blue	305.81	44
Flax shives	Basic yellow 21	76.92	50
Cottonseed hull substrate	Methylene blue	185.22	55
Sesame hull	Methylene blue	359.88	56
Sawdust	Astrazon yellow	81.8	59
Wood waste	Reactive blue 19	30.92	64
Fly ash	Methylene blue	36.05	72
	Malachite green	40.65	
Organobentonite	Orange II	239.5	92
Bentonite	Malachite green	430	94
Kaolinite	Rhodamine B	46.08	102
Montmorillonite	Crystal violet	114.3	104
Gypsum	Basic red 46	39.17	106
Lapindo volcanic mud	Methyl orange	333.3	107

Notes: *These reported adsorption capacities are values obtained under specific conditions. Readers are encouraged to refer to the original articles for information on experimental conditions.

Combination methods: The adsorption equilibrium data of methylene blue can be fitted well by the Langmuir adsorption isotherm model. The adsorption kinetics followed pseudo-second-order. The model pollutant could be catalysis oxidized by lava with the aids of H_2O_2 and ultrasound. The result showed that 95 % of the methylene blue could be decomposed in 100 min with the aid of ultrasound[116] at 85 W/cm². Ni et al.[117] considered the adsorption/ coagulation process for C.I. Reactive Red 120 was a cost-effective process. The authors studied the optimization process using response surface methodology (RSM) and they reported the optimal conditions as follows: magnesia dosage 2.5 g/L, PACl dosage 15 × 10⁻³ g/L and pH 12. The effect of aeration in the removal of colour from textile industry wastewater was being investigated. The results revealed that peanut hulls powder achieved the maximum colour removal percentage for both with and without aeration followed by coconut coir pith, orange peels and neem leaves powders[118]. Muthirulan et al.[119] investigated photocatalytic degradation for water soluble toxic Alizarin Cyanin Green (ACG) dye in aqueous suspension along with activated carbon as co-adsorbent. The pseudo-first-order kinetic equation was found to be applicable in the dye-catalyst systems. The authors reported that photocatalytic degradation by ZnO along with AC was a more effective and faster mode of removing ACG

from aqueous solutions than the ZnO alone. In a similar study, Patil *et al.*[120] reported that the removal of water soluble hazardous Ponceau-S dye by nanosized Nb_2O_5 along with commercial activated carbon (CAC) was a more effective, economic and faster mode of removing the dye from aqueous solutions. The maximum adsorption capacity was recorded as 41.05 mg/g. The optimum conditions for the degradation of the dye were initial concentration 40 ppm, pH 8 and catalyst concentration 5 g/L with CAC 1 g/L. The removal of Indigo Carmine through the coupling process involving electrocoagulation (EC)/ granular activated carbon (GAC) was being investigated. The authors found that F22 exhibited outstanding adsorption properties whereas Pica L27/EC coupling provided the best rate constants. Based on the significant decrease in electrical operating costs, the authors recommended the usage of EC/ GAC coupling method rather than the conventional simple EC[121]. Guendy[122] suggested that no single process is adequately capable to treat the textile effluents due to the complexity nature of the wastewater. The author proposed a combination of coagulation and adsorption processes for Acid Red removal. The results revealed that the percentage removal of dye is proportional to the shaking time, coagulants and adsorbent doses at pH 6-8 and indirectly proportional to the initial dye concentration.

Conclusion

Dyes removal in wastewater treatment is indeed a perplexing problem. However, various low cost adsorbents have demonstrated its potential and own suitability in removing different types of dyes. The utilization of these materials in wastewater treatment can be viewed as a sustainable one because most of it is abundant in nature, or is a by-product or waste material from another industry. Besides, these adsorbents often require little processing. In order to fully utilize its usefulness in wastewater treatment, materials that are found to possess the quality of efficient sorbents should be further studied and characterized. Attention should not be centralized on the maximum sorption capacity alone as the mechanism and modeling of the sorption pattern are of equally important. Besides, the possibilities of combining different treatment methods should be further explored as this would minimize or overcome the problem associated with a single treatment process.

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