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Journal of Hazardous Materials



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Adsorption of methylene blue on low-cost adsorbents: A review

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ARTICLE INFO

Article history: Received 25 June 2009 Received in revised form 23 October 2009 Accepted 8 December 2009 Available online 14 December 2009

Keywords: Adsorption Methylene blue Low-cost adsorbents Agricultural wastes

ABSTRACT

In this article, the use of low-cost adsorbents for the removal of methylene blue (MB) from solution has been reviewed. Adsorption techniques are widely used to remove certain classes of pollutants from waters, especially those which are not easily biodegradable. The removal of MB, as a pollutant, from waste waters of textile, paper, printing and other industries has been addressed by the researchers. Currently, a combination of biological treatment and adsorption on activated carbon is becoming more common for removal of dyes from wastewater. Although commercial activated carbon is a preferred adsorbent for color removal, its widespread use is restricted due to its relatively high cost which led to the researches on alternative non-conventional and low-cost adsorbents. The purpose of this review article is to organize the scattered available information on various aspects on a wide range of potentially low-cost adsorbents for MB removal. These include agricultural wastes, industrial solid wastes, biomass, clays minerals and zeolites. Agricultural waste materials being highly efficient, low cost and renewable source of biomass can be exploited for MB remediation. It is evident from a literature survey of about 185 recently published papers that low-cost adsorbents have demonstrated outstanding removal capabilities for MB.

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1. Introduction

The presence of dyes in effluents is a major concern due to their adverse effects to many forms of life. The discharge of dyes in the environment is a matter of concern for both toxicological and esthetical reasons [1]. Industries such as textile, leather, paper, plastics, etc., use dyes in order to colour their products and also consume substantial volumes of water. As a result, they generate a considerable amount of coloured wastewater [2]. It is estimated that more than 100,000 commercially available dyes with over 7×10^5 tonnes of dyestuff produced annually [3–5]. It is recognized that public perception of water quality is greatly influenced by the colour. The colour is the first contaminant to be recognized in wastewater. The presence of even very small amounts of dyes in water – less than 1 ppm for some dyes – is highly visible and undesirable [6,7]. MB is the most commonly used substance for dying cotton, wood and silk. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. On inhalation, it can give rise to short periods of rapid or

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^{0304-3894/\$ -} see front matter © 2009 Elsevier B.V. All rights reserved. doi:10.1016/j.jhazmat.2009.12.047

difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia [8–10]. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving waters.

During the past three decades, several physical, chemical and biological decolorization methods have been reported; few, however, have been accepted by the paper and textile industries [11]. Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of coloring materials [12–14]. Recently, numerous approaches have been studied for the development of cheaper and effective adsorbents. Many non-conventional low-cost adsorbents, including natural materials, biosorbents, and waste materials from agriculture and industry, have been proposed by several workers. These materials could be used as adsorbents for the removal of dyes from solution.

Many treatment processes have been applied for the removal of dyes from wastewater such as: photocatalytic degradation [15,16], sonochemical degradation [17], micellar enhanced ultrafiltration [18], cation exchange membranes [19], electrochemical degradation [20], adsorption/precipitation processes [21], integrated chemical-biological degradation [22], integrated iron(III) photoassisted-biological treatment [23], solar photo-Fenton and biological processes [24], Fenton-biological treatment scheme [25] and adsorption on activated carbon [26,27]. As synthetic dyes in wastewater cannot be efficiently decolorized by traditional methods, the adsorption of synthetic dyes on inexpensive and efficient solid supports was considered as a simple and economical method for their removal from water and wastewater [28].

Methods of dye wastewater treatment have been reviewed by Pokhrel and Viraraghavan [29]; Robinson et al. [6]; Slokar and Majcen Le Marechal [30]; Delee et al. [31]; Banat et al. [7]; Cooper [32]; Crini [33] and Gupta and Suhas [34]. Fungal and bacterial decolorization methods have been reviewed by Aksu [35]; Wesenberg et al. [36]; Pearce et al. [4]; McMullan et al. [3]; Fu and Viraraghavan [37] and Stolz [38].

Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications [39–42]. 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. Adsorption also does not result in the formation of harmful substances.

The present review article deals the technical feasibility of various non-conventional low-cost adsorbents for MB removal from water and wastewater. The main aim of this review is to provide a summary of recent information concerning the use of low-cost materials as adsorbents. For this, an extensive list of adsorbents literature has been compiled. The authors recommend that the reported adsorption capacities be taken as specific set of conditions rather than as maximum adsorption capacities. The reader is strongly encouraged to refer to the original research papers for information on experimental conditions.

2. Adsorbent literature

2.1. Activated carbon

Though commercially available activated carbon (CAC) are usually derived from natural materials such as biomass, lignite or coal, but almost any carbonaceous materials may be used as precursor for the preparation of carbon adsorbents [43–52], because of its availability and cheapness, coal is the most commonly used precursor for activated carbon production. Coal is a mixture of car-

Table 1

Adsorption capacities for commercial activated carbon and coal.

Adsorbents	Adsorption capacity (mg/g)	Sources
Commercial activated carbon	980.3	[47]
Activated carbon produced from	588	[43]
New Zealand coal		
Filtrasorb 400	476	[43]
Activated carbon	400	[48]
Activated carbon produced from	380	[43]
Venezuelan bituminous coal		
Peat	324	[49]
Coal	323.68	[57]
Filtrasorb 400	299	[50]
Norit	276	[50]
Picacarb	246	[50]
Filtrasorb 300	240	[44]
Activated carbon	238	[52]
Coal	230	[56]
Commercial activated carbon	200	[45]
Bituminous coal	176	[54]
Charcoal	62.7	[55]
Activated carbon	9.81	[51]

bonaceous and mineral materials, resulting from the degradation of plants. The sorption properties of each individual coal are determined by the nature of the original vegetation and the extent of the physical-chemical changes occurring after deposition. Coal adsorption capacities are reported in Table 1. Coal based adsorbents have been used by Karaca et al. [53]; El Qada et al. [43]; Tamai et al. [54]; Banat et al. [55] and McKay et al. [56,57] with success for dye removal. However, since coal is not a pure material, it has a variety of surface properties and thus different sorption properties.

Biomass and other waste materials may also offer an inexpensive and renewable additional source of activated carbon. These waste 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 activated carbon 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. A wide variety of carbons have been prepared from biomass and other wastes, such as date pits [58], olive stones [59], furniture, sewage char and tyres [60,61], vermiculata plant [45], bamboo dust, coconut shell, groundnut shell, rice husk and straw [47,62], polyvilnyldienefluoride fibers [63], jute fiber [64], zeolite [65], coconut husk [9,54], oil palm fiber [66,67], waste apricot [68], corncob [69], coir pith [70], Pitch [54], olive-seed waste [44], fir wood [27], rattan sawdust [71], bio-plant of Euphorbia rigida [62], vetiver roots [73], durian shell [74], oil palm shell [10], sugars [75], wheat bran [76], Hevea brasiliensis seed coat [26], peach stones [77], almond shell, walnut shell, hazelnut shell and apricot stones [78] and Rosa canina seeds [79].

The excellent ability and economic promise of the activated carbons prepared from biomass exhibited high sorption properties as shown in Table 2. Kannan and Sundaram [47] reported the adsorption capacities of 472.10 mg/g of activated carbons made from straw. However, the adsorption capacities of carbons depend upon the sources of the raw materials used, the history of its preparation and treatment conditions such as pyrolysis temperature and activation time. Many other factors can also affect the adsorption capacity in the same sorption conditions such as surface chemistry (heteroatom content), surface charge and pore structure. A suitable carbon should possess not only a porous texture, but also high surface area. Recently, Guo et al. [80] showed that the adsorption does not always increase with surface area. Besides the physical structure, the adsorption capacity of a given carbon is strongly influenced by the chemical nature of the surface. The acid and

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Table 2

Adsorption capacities for activated carbons derived from agricultural and industrial wastes.

Adsorbents	Adsorption capacity (mg/g)	Sources
Polyvilnyldienefluoride activated carbon fibers	486	[63]
Straw activated carbon	472.10	[47]
Bamboo based activated carbon	454.20	[62]
Activated carbon (molasses/sulphuric acid)	435	[75]
Activated carbon prepared from coconut husk	434.78	[9]
Vetiver roots activated carbon-H ₂ O	423	[73]
Peach stones based activated carbon	412	[77]
Oil palm fiber-based activated carbon	400	[67]
Mesoporous carbons prepared by using alkaline-treated zeolite	380	[65]
Vetiver roots activated carbon-P1.5	375	[73]
Rice husk activated carbon	343.50	[47]
HCl-treated oil palm shell-based activated carbon	303.03	[10]
Rattan sawdust-activated carbon	294.12	[71]
Activated carbon prepared from durian shell	289.26	[74]
Coconut shell activated carbon	277.90	[47]
Oil palm fiber-based activated carbon	277.78	[66]
Olive-seed waste residue-based activated carbon	190–263	[44]
Activated carbon prepared from oil palm shell	243.90	[10]
Hevea brasiliensis seed coat-activated carbon	227.27	[26]
Activated tyre char	227	[61]
Jute fiber carbon	225.64	[64]
Mesoporous carbons prepared by using acid-treated zeolite	223	[65]
Activated furniture (850 °C)	200	[60]
Dehydrated wheat bran carbon	185.2	[76]
Groundnut shell activated carbon	164.90	[47]
Bamboo dust activated carbon	143.20	[47]
Activated tyres (850 °C)	130	[60]
Chemically activated Salsola vermiculata plant	130	[45]
Activated sewage char (800 °C)	120	[60]
Activated carbon prepared from a renewable bio-plant of <i>Euphorbia rigida</i>	109.98	[72]
Waste apricot-based activated carbon	102	[68]
Pyrolysed furniture	80	[60]
Coconut husk based activated carbon	66	[54]
Pyrolized Salsola vermiculata plant (PRSV)	53	[45]
Pitch/Y(OiPr) ₃	52	[54]
Pitch/Y(naphthoate) ₃	49	[54]
Activated Rosa canina seeds (500°C)	47.2	[79]
Activated olive stones with 40 wt.% ZnCl ₂ at	22.1	[54] [59]
Activated data pits (000 °C)	172	[59]
Activated olive stones with 40 wt.% ZnCl ₂ at	16.1	[59]
8/3K	12.0	[50]
Activated date pits (500 °C)	12.9	[58]
Hazemut snell-activated carbon /50°C	8.82	[78]
Apprised stopps, activated sorther, 750.00	5.8/	[70]
Apricol stones-activated carbon 750°C	4.11	[78]
Almond shell activated carbon 750°C	3.53	[78]
Fir wood based activated carbon 750°C	1.33	[78]
FIL WOUL DASELLACTIVALELL CATDON	1.21	[27]
Corneod based activated carbon	0.84	[69]

base character of a carbon also influences the nature of the dye isotherms. The adsorption capacity depends also on the accessibility of the pollutants to the inner surface of the adsorbent, which depends on their sizes. The specific sorption mechanisms through which the adsorption of dyes takes place on these adsorbents are still not clear. This is because adsorption is a complicated process and depends on several interactions such as electrostatic and/or non-electrostatic (hydrophobic) interactions. Although much has been accomplished in terms of sorption properties and kinetics, much work is still necessary to identify the sorption mechanisms clearly [33].

2.2. Non-conventional low-cost adsorbents

Activated carbon has been popular choice as an adsorbent for the removal of MB from wastewater but its high cost poses an economical problem. Therefore, there is a need for the development of low cost and easily available materials, which can be used more economically on large scale. Due to the problems mentioned above, research interest into the production of alternative adsorbents to replace the costly activated carbon has intensified in recent years. Attention has focused on various natural solid materials, which are able to remove MB from the contaminated wastewater at low cost. The cost is actually an important parameter for the comparison and selection of adsorbents. An adsorbent can be considered as low cost if it requires little processing and abundant in nature [81]. It may also be defined as a by-product or waste material from the industry and needs additional disposal cost. Certain waste products from industries and agricultural operations, natural materials and bioadsorbents represent potentially economical alternative adsorbents. Many of them have been tested and proposed for MB removal.

2.2.1. Natural materials

2.2.1.1. Clays. The clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fraction (<2 μ m) of soils, sediments, rocks and water [82] and may be composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides. The clays invariably contain exchangeable ions on their surface and play important role in the environment by acting as a natural scavenger of pollutants by taking up cations and/or anions either through ion exchange or adsorption or both. The prominent ions found on clay surface are Ca²⁺, Mg²⁺, H⁺, K⁺, NH₄⁺, Na⁺, and SO₄²⁻, Cl⁻, PO₄³⁻, NO₃⁻. These ions can be exchanged with other ions easily without affecting the structure of clay mineral [83].

Natural clay minerals are well known and familiar to mankind from the earliest days of civilization. Because of their low cost, abundance in most continents of the world, high sorption properties and potential for ion exchange, clay materials are strong adsorbents. They possess layered structure and are considered as host materials for the adsorbates and counter ions. Vermiculite clay has the largest surface area and the highest cation exchange capacity. Its current market price (about US\$ 0.04–0.12/kg) is considered to be about 20 times cheaper than that of activated carbon [84].

In recent years, there has been an increasing interest in utilizing clay minerals such as bentonite, kaolinite, diatomite and Fuller's earth for their capacity to adsorb not only inorganic ions but also organic molecules. In particular, interactions between MB and clay particles have been extensively studied [8,85–97]. The clay minerals exhibit a strong affinity for MB (Table 3). The adsorption of MB on clay minerals is mainly dominated by ion-exchange processes. This means that the sorption capacity can vary strongly with pH. Al-Ghouti et al. [95] showed that the mechanism of adsorption of dye onto diatomite is due to physiosorption (depending on the particle size) and the presence of electrostatic interactions (depending on the pH used).

Relatively good removal capabilities of clays to uptake MB has been demonstrated by many researchers. Bagane and Guiza [94] reported an adsorption capacity of 300 mg/g and suggested that clay is a good adsorbent for MB removal due to its high surface area. Almeida et al. [92] studied the removal of MB from synthetic wastewater by using as montmorillonite and described it as an efficient adsorbent where the equilibrium was attained in less than 30 min. The adsorption of dyes on kaolinite was also studied by Ghosh and Bhattacharyya [8] and reported that its adsorption capacity can be improved by purification and by treatment with

Table 3

Adsorption capacities for natural materials.

Adsorbents	Adsorption capacity (mg/g)	Sources
Clay	300	[94]
Montmorillonite clay	289.12	[92]
Bentonite	151-175	[87]
Diatomite	198	[95]
Perlite	162.3	[100]
Diatomite (Jordon)	156.6	[89]
Bentonite	150	[85]
Spent activated clay	127.5	[96]
Hexane-extracted spent bleaching earth	120.5	[97]
Carbonised spent bleaching earth	94.5	[97]
Fibrous clay minerals	85	[91]
Pyrophyllite	70.42	[90]
Zeolite	53.1	[100]
Palygorskite	50.8	[93]
Amorphous silica	22.66	[98]
NaOH-treated pure kaolin	20.49	[8]
NaOH-treated raw kaolin	16.34	[8]
Pure kaolin	15.55	[8]
Raw kaolin	13.99	[8]
Zeolite	10.82	[98]
Calcined pure kaolin	8.88	[8]
Calcined raw kaolin	7.59	[8]
Clay	6.3	[88]
Glass wool	2.24	[102]

NaOH solution. The removal performances of Fuller's earth and commercial activated carbon for MB were compared by Atun et al. [86]. They showed that the adsorption capacity is greater of Fuller's earth than that of CAC. Moreover, Fuller's earth is an interesting adsorbent since its average price is US\$ 0.04/kg whereas CAC costs US\$ 20/kg. Shawabkeh and Tutunji [89] studied the adsorption of MB onto diatomaceous earth (diatomite). They showed that this naturally occurring material could substitute for activated carbon as an adsorbent due to its easy availability, low cost, and good sorption properties. Further, its adsorption isotherms revealed that adsorption equilibrium was reached within 10 min. The feasibility of using diatomite for the removal of the problematic reactive dyes was also investigated by Al-Ghouti et al. [95]. The results presented above show that clay materials may be promising adsorbents from environmental and purification point of views.

2.2.1.2. Zeolites and other siliceous materials. The siliceous materials such as perlite, glass and zeolites have been proposed for MB dye removal (Table 3). The use of natural siliceous adsorbents such as silica, glass fibers and perlite for waste water is increasing because of their high abundance, easy availability and low cost. Among inorganic materials, amorphous silica deserves particular attention [98], considering chemical reactivity of their hydrophilic surface, resulting from the presence of silanol groups. Their porous texture, high surface area and mechanical stability also make them attractive as adsorbents for decontamination applications. However, due to their low resistance toward alkaline solutions their usage is limited to media of pH less than 8 [99]. Moreover, the surface of siliceous materials contains acidic silanol (among other surface groups) which causes a strong and often irreversible nonspecific adsorption. Perlite is a glassy volcanic rock and has high silica content, usually greater than 70%. It is inexpensive and easily available in many countries. The use of perlite as a low-cost adsorbent for the removal of MB has been investigated by Dogan et al. [100,101]. It was suggested that MB is physically adsorbed onto the perlite. Thus perlite is a good adsorbent for decontamination purposes. However, perlites of different types (expanded and unexpanded) and of different origins have different properties because of the differences in composition. Chakrabarti and Dutta [102] investigated the glass fiber for the adsorption of MB. They stated that a considerable amount of the dye is adsorbed on soft glass even at ambient temperature.

Zeolites are highly porous aluminosilicates with different cavity structures. They consist of a three dimensional framework, having a negatively charged lattice. The electro neutrality is maintained by exchangeable counter ions. The characteristics and applications of zeolites have been reviewed by Ghobarkar et al. [103]. High ion-exchange capacity and relatively high specific surface areas, and more importantly their relatively cheap prices, make zeolites more attractive adsorbents. Their price is about US\$ 0.03-0.12/kg, depending on the quality of the mineral [84]. Another advantage of zeolites over resins is their ion selectivities generated by their rigid porous structures. Woolard et al. [98], converted fly ash into zeolitic products by the hydrothermal treatment of raw ash with base. The product was found to bear significantly increased surface area and cation exchange capacity in comparison to the raw ash. This product also shows increased affinity for sorption of cationic dyes when compared to the raw ash. It is, however, that this increase in sorption capacity is merely the result of the increase in surface area, rather than a specific interaction. Although the removal efficiency of zeolites for dyes may not be as good as that of clay materials, their easy availability and low cost may compensate for the associated drawbacks.

2.2.2. Bioadsorbents

The accumulation and concentration of dyes from aqueous solutions by the use of biological materials is termed bioadsorption. In this instance, biomass used as an adsorbents in order to concentrate and to remove MB dye from solutions. The bioadsorbents are often much more selective than traditional ion-exchange resins and commercial activated carbons, and can reduce dye concentration to ppb levels. Bioadsorption is a novel approach, competitive, effective and cheap.

2.2.2.1. Biomass (dead and living). Removal of MB dye by biomass (dead or living), fungi, algae and other microbial cultures was the subject of many recent researches. It has been found that bioadsorbents derived from suitable algal biomass can be used for the effective removal of MB from aqueous solutions. The use of biomass for wastewater is increasing because of its availability in large quantities at low cost. Biomass has a high potential as an adsorbent due to its physico-chemical characteristics. Recent literature on the methods of removal of MB from wastewater focuses on MB adsorption [52,104-119]. Table 4 shows some of the adsorption capacities reported in the literature. Yu et al. [104] studied the poly (methacrylic acid) modified biomass of baker's yeast to improve the adsorption capacity of MB. He also studied the poly(amic acid)-modified biomass of baker's yeast to improve the adsorption capacities for removal of MB. Experimental results showed that pH and ionic strength had little effect on the capacity of the modified biomass, indicating that the modified biomass had good potential for practical use. According to the Langmuir equation, the maximum uptake capacities for MB were 869.6 mg/g for poly(methacrylic acid) modified biomass of baker's yeast and 680.3 mg/g for poly(amic acid)-modified biomass of baker's yeast respectively, which were 17 and 13 fold than that obtained on the unmodified biomass.

Fu and Viraraghavan [115], demonstrated that in comparison with commercial activated carbon dead fungal biomass of *Aspergillus niger* is a promising biosorbents for MB dye removal. Waranusantigul et al. [111] also reported the usefulness of biomass for the removal of MB. The biosorption capacity of fungal biomass could be increased by some pretreatment (by autoclaving or by reacting with chemicals). In spite of good sorption properties and high selectivity some problems might occur. The sorption process

Table 4

Adsorption capacities for bioadsorbents.

Adsorbents	Adsorption capacity (mg/g)	Sources
Poly(methacrylic acid) modified biomass of baker's yeast	869.6	[104]
Poly(amic acid) modified biomass of baker's yeast	680.3	[105]
Caulerpa lentillifera	417	[52]
Alga Sargassum muticum seaweed	279.2	[106]
Enteromorpha spp.	274	[117]
Activated sludge biomass	256.41	[107]
Dead macro fungi (Fomes fomentarius)	232.73	[112]
Dead macrofungi (Phellinus igniarius)	204.38	[112]
Hydrilla verticillata	198	[108]
Moss	185	[109]
Algae Gelidium	171	[110]
Duckweed (Spirodela polyrrhiza) (at pH 9)	144.93	[111]
Water hyacinth root	128.9	[109]
Duckweed (Spirodela polyrrhiza) (at pH 7)	119	[111]
Algal waste	104	[110]
Composite material	74	[110]
Unmodified biomass of baker's yeast	51.5	[104,105]
Green alga Ulva lactuca	40.2	[119]
The brown alga Cystoseira barbatula Kutzing	38.61	[113]
Dead Streptomyces rimosus	34.34	[114]
Dead fungus Aspergillus niger	18.54	[115]
Posidonia oceanica (L.) fibres	5.56	[117]
Caulerpa racemosa var. cylindracea	5.23	[118]
Living biomass	1.17	[115]

is slow and in case of biomass of Aspergillus niger the equilibrium was reached in 42 h. Another problem is that the initial pH of the dye solution strongly influenced the bioadsorption. Marungrueng and Pavasant [52] investigated the adsorption of MB onto green macro alga Caulerpa lentillifera. The results were compared to the sorption performance of a commercial activated carbon. The results revealed that the alga exhibited greater sorption capacities than activated carbon for the MB investigated in this work. For the sorption of MB, both alga and carbon seemed to have the same sorption rate. The sorption processes were initially controlled by both film and pore-diffusion, and only were limited by pore diffusion in the later stage. The isotherms followed Langmuir model which suggested that the sorption was monolayer coverage. Maximum sorption capacity obtained from the sorption of MB onto C. lentillifera was 417 mg/g which was relatively higher in comparison with the previous records as summarized in Table 4.

MB adsorption on Sargassum muticum, an invasive macro alga in Europe, has been investigated by Rubin et al. [106] using visible absorption spectroscopy. Different pre-treatments, protonation and chemical cross-linking with CaCl₂ or H₂CO, have been tested in order to improve the stability as well as the adsorption capacity of the algal biomass. The equilibrium binding has been described in terms of Langmuir and Freundlich isotherms, depending on the biomass pre-treatment. It is remarkable that the percentage of MB removed is up to 90%, which is higher than that found for other biosorbents and it could be even compared with that of activated carbon (99.8% uptake). Bioadsorption kinetics has been described by means of the first order Lagergren equation, from which the corresponding kinetics parameters were obtained. Nacera and Aicha [114] investigated the biosorption of basic dye, methylene blue onto dead Streptomyces rimosus. The results show the percentage of dye sorption increases with the increase in quantity of the dead bacterial biomass and reaches to highest value at 20 °C. The bioadsorption capacity decreased from 9.86 to 6.93 mg/g with an increase in temperature from 20 to 50 °C at the initial MB concentration of 50 mg/l. The kinetics of MB sorption by pre-treated dead S. rimosus were fast, reaching 86% ($C_0 = 50 \text{ mg/L}$) of the total adsorption capacity in 5 min. The mechanism follows a pseudo-second order reaction model. The activation energy of sorption was evaluated as $-7.18 \text{ kJ} \text{ mol}^{-1}$ and thus the process is exothermic. El-Khaiary [120] studied the adsorption characteristics of MB onto nitric-acid treated water-hyacinth (N-WH). The results showed that N-WH can remove MB effectively from aqueous solution. A complete removal of MB from solution was only achieved at the lower range of initial MB concentration (less than 286 mg/L). The amount of dye uptake (mg/g) was found to increase with the increase in contact time and initial MB concentration, but there is no linear relationship between the dye uptake and temperature. Laboratory investigations of the potential of the biomass of dried roots of water hyacinth (Eichhornia crassipes) to remove MB from aqueous solutions were studied by Low et al. [109]. Removal of MB by invasive marine seaweed: Caulerpa racemosa var. cylindracea was studied by Cengiz and Cavas [118]. The adsorption reached equilibrium at 90 min. for all studied concentrations (5–100 mg/L). Langmuir and Freundlich models were applied to the data related to adsorption isotherm. According to Langmuir model data, the observed maximum adsorption capacity was 5.23 mg/g at 18 °C. The enthalpy of adsorption was found to be 33 kJ/mol, which indicated a chemical adsorption between MB molecules and C. racemosa var. cylindracea functional groups.

Bio-adsorption processes are particularly suitable for the treatment of solutions containing dilute MB concentration. Biosorption is a promising potential alternative to conventional processes for the removal of MB [37,115]. However, these technologies are still in the developing stage and much more work is required.

2.2.3. Waste materials and by-product from agriculture and industry

The waste materials and by-products from the agriculture and other industries could be assumed to be the low-cost adsorbents due to their abundance in nature and less processing requirements.

2.2.3.1. Agricultural solid wastes. The raw agricultural solid wastes such as leaves, fibers, fruits peels, seeds etc. and waste materials from forest industries such as sawdust, bark etc. have been used as adsorbents. These materials are available in large quantities and may be potential adsorbents due to their physico-chemical characteristics and low cost. Sawdust is an abundant by-product of the wood industry that is either used as solid fuel for cooking or as packing material. Sawdust is easily available at the countryside at zero or negligible price [121]. It contains various organic compounds (lignin, cellulose and hemicellulose) with polyphenolic groups that might be useful for binding MB through different mechanisms. The role of sawdust materials in the removal of pollutants from aqueous solutions has been reviewed recently [122] and some valuable guidelines can be drawn from the review. Sawdust has proven to be a promising low-cost material for the removal of MB from wastewater

Hamdaoui [123] studied the removal of MB, from aqueous solution (40 mg/L) onto cedar sawdust in order to explore their potential use as low-cost adsorbents for wastewater dye removal. Adsorption isotherms were determined at 20 °C and the experimental data obtained were modelled with the Langmuir, Freundlich, Elovich and Temkin isotherm equations. By considering the experimental results and adsorption models applied in this study, it can be concluded that equilibrium data were represented well by a Langmuir isotherm equation with maximum adsorption capacity of 142.36 mg/g for cedar sawdust. The extent of the dye removal decreased with increase in the solution temperature and optimum pH value for dye adsorption was observed at pH 7 for both adsorbents. Ahmad et al. [124] investigated the scavenging behaviour of meranti sawdust in the removal of MB from aqueous solution. Batch studies were performed to evaluate and optimize the effects of various parameters such as contact time, pH, initial dye concentrations and adsorbent dosage. Langmuir, Freundlich and Temkin isotherms were used to analyze the equilibrium data at different temperatures. Equilibrium data fitted very well in the Langmuir isotherm equation, confirming the monolayer adsorption (120.48 mg/g) of MB onto meranti sawdust.

Most of the studies showed that sawdust is natural form or modified form is highly efficient for the removal of MB [125–129]. The summary of these research works is given in Table 5. Chemical pretreatment of sawdust has been shown to improve the adsorption capacity and to enhance the efficiency of sawdust adsorption [121,130-132]. Batzias and Sidiras [130] studied that beech saw dust as low-cost adsorbent for the removal of MB. Further, in order to know the effect of chemical treatment and to improve its efficiency the authors also tested the potential of the adsorbent by treating it with CaCl₂ [130], using mild acid hydrolysis [131] and found it to increase the adsorption capacity. Besides this, the simulation studies for effect of pH were also carried out by Batzias and Sidiras [132]. The authors determined the point of zero charge (pHzpc = 5.2) of the sawdust and suggested that increase of the pH enhances the adsorption behaviour. The low adsorption of MB at acidic pH was suggested to be due to the presence of excess H⁺ ions that compete with the dye cation for adsorption sites. With the increase of the pH of the system, the number of positively charged sites decreases while the number of the negatively charged sites increases that favour the adsorption of MB due to electrostatic attraction

Another waste product from the timber industry is bark, a polyphenol-rich material. Bark is an abundant forest residue which has been found to be effective in removing dyes from water solutions. Because of its low cost and high availability, bark is very attractive as an adsorbent. Like sawdust, the cost of forest wastes is only associated with the transport cost from the storage place to the site where they will be utilized. Bark is an effective adsorbent because of its high tannin content. Mckay et al. [57] used the teak wood bark as an adsorbent to remove the MB from aqueous solutions. Equilibrium isotherms were studied at 20 °C using sealed flasks in a temperature controlled, agitated shaker bath. A constant fixed mass of adsorbent was shaken with 0.050 dm³ dye solution using solutions varying in dye concentration from 10 to 1000 ppm. Dynamic flow studies were performed using glass columns, 0.010 m diameter and 0.150 m packed bed height, were used to determine the adsorption breakthrough curves. The dye solution flow rates through the columns were maintained at 0.120 dm³ h⁻¹ and 0.005 dm³ samples were collected for analysis out of every 0.100 dm³ of solution treated. The monolayer saturation capacity for MB onto teak wood bark is 914.59 mg g^{-1} .

Rice husk is an agricultural waste and a by-product of the rice milling industry to be about more than 100 million tonnes, 96% of which is generated in the developing countries. The utilization of this source of agricultural waste would solve both a disposal problem as well as access to a cheaper material for adsorption in water pollutants control system [133]. The maximum cost of commercially available rice husk is approximately US\$ 0.025/kg. Since, the main components of rice husk are carbon and silica (15-22% SiO₂ in hydrated amorphous form like silica gel), it has the potential to be used as an adsorbent. Mckay et al. [56,57] studied the use of rice husk in the removal of MB from aqueous solutions then after Vadivelan and Kumar [134] used the rice husk for the adsorption of MB. The operating variables studied were initial solution pH, initial dye concentration, adsorbent concentration, and contact time. The amount of dye adsorbed was found to vary with initial solution pH, adsorbent dose, and contact time. The monolayer sorption capacity of rice husks for MB sorption was found to be 40.58 mg/g at room temperature (32 °C). The dye uptake process was found to be controlled by external mass transfer initially followed by intraparticle diffusion.

Table 5

Adsorption capacities for agricultural solid wastes.

Adsorbents	Adsorption	Sources
	capacity	
	capacity	
	(mg/g)	
Tools wood bark	014 50	[57]
	914.59	[57]
Papaya seeds	555.55	[135]
Grass waste	457.64	[136]
Pomelo (Citrus grandis) peel	344.83	1381
Dies hush	212.20	[[50]
RICE HUSK	312.20	[57]
Untreated guava leaves	295	[139]
lackfruit peel	285.71	[142]
Cotton waste	777 77	[57]
Cotton waste	2/1.//	[57]
Banana stalk waste	243.90	[143]
Palm kernel fiber	217.95	[145]
Modified rice straw	208.33	[146]
Prood boon peols	102 72	[1/7]
bioau bean peers	192.72	[147]
Gulmohar (Delonix regia) plant leaf	186.22	[141]
powder		
Castor seed shell	158 73	[149]
Codar cauduct	142.26	[100]
Ceual sawuust	142.50	[125]
Pumpkin seed hull	141.92	[150]
Saw dust	133.87	[125]
Chemically treated guaya leaves	133 33	[140]
Manuati and ant	133.35	[1]
Meranti sawdust	120.48	[124]
Pineapple stem	119.05	[151]
Dehydrated peanut hull	108.6	[152]
Cocoput busk	00	[152]
	55	[155]
Coffee husks	90.1	[154]
Phosphoric acid treated Parthenium	88.49	[155]
hysterophorus		
Tools wood bark	0.4	[56]
Teak wood bark	04	[20]
Garlic peel	82.64	[156]
Rubber seed shell	82.64	[148]
Fallen nhoeniy tree's leaves	80.9	[157]
Pauv data pite	80.2	[[57]]
Raw date pits	80.3	[36]
Ground hazelnut shells	76.9	[126]
Coconut bunch waste	70.92	[160]
Peanut hull	68.03	[161]
	50.15	[101]
Walnut sawdust	59.17	[126]
Luffa cylindrica fibers	47	[162]
Yellow passion fruit waste	44 70	[163]
Olive pomaça	12.2	[55]
Onve poinace	42.3	[33]
Rice husk	40.59	[134]
Cherry sawdust	39.84	[126]
Sulphuric acid treated Parthenium	39.68	[155]
hustoronhorus	30100	[100]
nysterophorus		(
Hazelnut shell	38.22	[158]
Mansonia wood sawdust	33.44	[127]
Modified sawdust	32.3	[128]
December notatum (gardon grace)	20.4	[127]
Fuspulum notucum (garden grass)	30.4	[137]
Oak sawdust	29.94	[126]
Rice husk	28	[56]
Pitch-nine sawdust	27 78	[126]
Cotto a succest	21.10	[120]
Cotton waste	24	[56]
Salsola vermiculata leaves	23	[45]
lute processing waste	22.47	[164]
Banana neel	20.8	[1//]
	20.0	[144]
Cereal chaff	20.3	[165]
Orange peel	18.6	[144]
Spruce wood shavings from Picea abies	17.91	[129]
Wheat shalls	16.56	[166]
which shells	10.30	[100]
Beech sawdust pretreated with 20%	16.05	[130–132]
(w/v) CaCl ₂ for 1 h at 100 °C		
Beech sawdust pretreated with 20%	13.02	[130]
(w/w) CoCl for 1 h at 22 of	13.02	[150]
(wy/v) CaCl ₂ IOI 111 at 23°C		1.0.1
Indian Rosewood sawdust	11.8	[121]
Raw beech sawdust	9.78	[130]
Coarse grinded wheat straw	3.87	[167]
Noom (Agadirachta indian) loof norod	2.02	[107]
Neem (Azaairachia maica) lear powder	3.07	[108]
Fine grinded wheat straw	2.23	11671

Table 6

Adsorption capacities for industrial solid wastes.

Adsorbents	Adsorption capacity (mg/g)	Sources
Activated sludge biomass	256.41	[107]
Baggase bottom ash	142.54	[181]
Sewage sludge from an urban wastewater	114.9	[169]
Sewage sludge from an agrifood industry	87	[169]
Coal fly ash (0.01 NaCl)	16.6	[172]
Coal fly ash	12.7	[172]
HNO3 Fly ash	7.99	[171]
Fly ash (bagasse)	6.46	[173]
Fly ash (CFA)	6.04	[175]
Fly ash	5.57	[176]
Fly ash	4.60	[174]
Fly ash	4.47	[171]
Fly ash	3.07	[51]
Fly ash	2.85	[181]
Red mud	2.49	[171]
Fly ash (SFA)	1.47	[175]
Fly ash	1.10	[98]
Chrome sludge	0.51	[170]

Other agricultural solid wastes from cheap and readily available resources such as papaya seeds [135], grass waste [136,137], pomelo (Citrus grandis) peel [138], guava leaves [139,140], gulmohar (Delonix regia) plant leaf powder [141], jackfruit peel [142], cotton waste [56,57], banana waste [143,144], palm kernel fiber [145], rice straw [146], broad bean peels [147], rubber seed shell [148], castor seed shell [149], pumpkin seed hull [150], pineapple stem [151], dehydrated peanut hull [152], coconut husk [153], coffee husks [154], Parthenium hysterophorus [155], garlic peel [156], fallen phoenix tree's leaves [157], raw date pits [58], ground hazelnut shells [126,158,159], coconut bunch waste [160], peanut hull [161], Luffa cylindrica fibers [162], yellow passion fruit waste [163], olive pomace [55], Salsola vermiculata (SV) leaves [45], jute waste [164], cereal chaff [165], orange peel [144], wheat shells [166], wheat straw [167], neem (Azadirachta indica) leaf powder [168] have also been successfully employed for the removal of MB from aqueous solutions (Table 5).

2.2.3.2. Industrial solid wastes. Industrial solid wastes such as sludge, fly ash and red mud are classified as low-cost materials because of their low cost and local availability and can be used as adsorbents for MB dye removal [107,169–176].

The activated sludge biomass collected from electroplating industry of Adana Organize Sanayi, Turkey was used as an adsorbent for MB by Gulnaz et al. [107]. It contains insoluble metal hydroxides and other salts and showed the highest dye uptake capacity, having the monolayer adsorption capacity 256.41 mg/g for MB, at pH value of 7.0 and 20 °C. Otero et al. [169] investigated the use of dried sewage sludges, pyrolysed sewage sludges and both chemically activated and pyrolysed sewage sludges as adsorbents material in single batch liquid-phase adsorption tests. The adsorption equilibriums of MB by these materials have been described in terms of both Langmuir and Freundlich equations.

Among the various adsorbents used for removal of MB dye the fly ash was found to be an effective adsorbent. Table 6 summarizes the adsorption capacity of MB onto the fly ash. It is a waste/byproduct of thermal power plants and generally available free of cost that may be used in construction of roads, bricks and cement etc. Owing to its high availability and problem of disposal, a number of workers have attempted to use it as an adsorbent in pollution control. Although it may contain some hazardous substances, such as heavy metals, it is widely utilized in industry in many countries [175].

[a]	ble	7
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Adsorption capacities for miscellaneous type of adsorbents.

Adsorbents	Adsorption capacity (mg/g)	Sources
Spent tea leaves	300.05	[178]
Hair	120	[56]
Crushed brick	96.61	[123]
Tea waste	85.16	[177]
Carbinized press mud	50	[181]
Fe(III)/Cr(III) hydroxide	22.8	[182]
Melamine-formaldehyde-urea resin	15	[183]
Cow dung ash	5.31	[181]
Eggshell and eggshell membrane polyacrylic	0.80	[184]
acid-bound iron oxide magnetic nanoparticles	0.199	[185]

However, bagasse fly ash generated in the sugar industry does not contain large amounts of toxic metals and has been widely used for adsorption of dyes [173]. Fly ash has a surface area of $15.6 \text{ m}^2/\text{g}$ [171]. Its properties are extremely variable and depend strongly on its origin [171,175]. Wang et al. [171] used fly ash as adsorbent for the removal of MB from aqueous solutions and the adsorption capacity for raw fly ash was reported to be 4.47 mg/g. The effect of physical (heat) and chemical treatment was also studied on as-received fly ash and the heat treatment was reported to have adverse effect on the adsorption capacity of fly ash but acid treatment (by nitric acid) resulted in an increase of adsorption capacity of fly ash (7.99 mg/g). Coal fly ash was used successfully as low-cost adsorbents for removal of MB from aqueous solution by Wang et al. [172]. Viraraghavan and Ramakrishna [174] investigated the use of coal fly ash from the Shand power plant in Canada for removal of dyes from wastewater. The negative values of free energies indicate the feasibility and spontaneous nature of the process, and the positive heats of enthalpy suggest the endothermic nature of the process.

Another abundant industrial by-product/waste material is red mud. Waste red mud is a bauxite processing residue discarded in alumina production. Red mud, an aluminum industry waste was converted into a low-cost potential adsorbent and the final material has been used for the removal of MB by Wang et al. [171] who showed that physical and chemical treatment can significantly change its adsorption capacity.

2.2.4. Miscellaneous adsorbents

Various other materials have also been put to use for preparing alternative adsorbents. An attempt to remove MB by using waste tea leaves was studied by Uddin et al. [177] and Hameed [178], so as to develop a low-cost methodology while having low impact on environment. Besides this various other materials have also been studied less extensively as low-cost adsorbents, such as sand [179], stainless steel [180], hair [56], crushed brick [123], carbinized press mud [181], Fe(III)/Cr(III) hydroxide [182], melamine–formaldehyde–urea resin [183], cow dung ash [181], eggshell and eggshell membrane [184] and polyacrylic acid-bound iron oxide magnetic nanoparticles [185] have also been explored as an adsorbents. The adsorption capacities of these materials are given in Table 7.

3. Conclusions

This review has attempted to cover a wide range of nonconventional low-cost adsorbents so that the reader can get an idea about the various types of low-cost materials used for the removal of MB from the wastewater. Inexpensive, locally available and effective materials could be used in place of commercial activated carbon for the removal of MB from aqueous solution. Little efforts seem to have been made to carry out a cost comparison between activated carbon and various non-conventional adsorbents. This aspect needs to be investigated further in order to promote largescale use of non-conventional adsorbents. In spite of the scarcity of consistent cost information, the widespread uses of low-cost adsorbents in industries for wastewater treatment applications today are strongly recommended due to their local availability, technical feasibility, engineering applicability, and cost effectiveness. If lowcost adsorbents perform well in removing MB at low cost, they can be adopted and widely used in industries not only to minimize cost inefficiency, but also improve profitability. Undoubtedly lowcost adsorbents offer a lot of promising benefits for commercial purposes in the future.

Literature also reveals that in some cases the modification of the adsorbent increased the removal efficiency. However, very less work has been carried out in this direction especially to understand the mechanism of adsorption. We speculate the possibility of the ion exchange mechanism to play an important role in MB uptake being a cationic dye. The following observations of different authors hint toward this mechanism:

- 1. Increase of adsorption capacity of CaCl₂ treated adsorbents.
- 2. In crease of adsorption capacity in basic medium.
- 3. Decrease of adsorption capacity in acidic medium.

In all these cases the ion exchange sites on the surface of adsorbents are converted to cationic form and cations are exchanged with MB, being a cationic dye, in the equilibrating solution. However, release of H⁺ ions (in the 3rd case) decreases pH of the solution and the condition becomes unfavourable for dye uptake by ion exchange and ultimately apparent total adsorption capacity decreases. Thus uptake of MB is accompanied by dual mechanism of ion exchange as well as adsorption.

The process of bioadsorption requires further investigation in the direction of modeling, regeneration of bioadsorbents and recovery of MB and immobilization of the waste material for enhanced efficiency and recovery. Most of the reported studies are performed in the batch process; this gives a platform for the designing of the continuous flow systems with industrial applications at the commercial level also. Further research is to be carried out to make the process economically viable at industrial scale with focus on MB recovery and regeneration of agricultural waste.

Finally we wish to comment of zero waste strategy of adsorption process in treatment of water waste waters. There is a bigger scope of research of utilization of used adsorbents for further treatment processes. For example MB adsorbed adsorbents can further be explored for their application in second stage adsorption which is completely an unexplored area of research. Another possibility of exploration is the recovery cum reuse of adsorbed substances. All future researches might be accompanied by adsorption/desorption and/or adsorption/readsorption process so that there is no net sludge generation and, if any, it should be minimum. Such a strategy will fulfill the goal of zero waste.

Acknowledgement

One of the authors (M. Rafatullah) is grateful to the University Sains Malaysia, for providing assistance under the post doctoral scheme for this work.

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