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低成本吸附剂去除水体中亚甲基蓝的研究综述

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摘 要

本文综述了采用低成本吸附剂去除溶液中亚甲基蓝(MB)的方法。吸附法是去除水中染料最常用的方法，具有操作简单、对环境污染小、原料易得等优势。活性炭是目前用于去除水中染料的常规吸附材料，吸附速率快且吸附效果好，但由于活性炭的制备成本相对较高，使用范围受限，因此亟需寻找非常规、低成本的吸附剂。因此本综述的目的是探讨各种潜在低成本吸附剂用于去除MB的可行性，包括天然原料、农业废弃物、工业废弃物及其他低成本吸附剂。

关键词

低成本吸附剂，活性炭，亚甲基蓝，吸附机制

Research on the Removal of Methylene Blue from Water by Low-Cost Adsorbents: A Review

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Abstract

This article reviews the methods of removing methylene blue (MB) from solution with low-cost adsorbent. The adsorption method is the most commonly used method to remove dyes from water, and has the advantages of simple operation, low environmental pollution, and easy availability of raw materials. Activated carbon is currently a conventional adsorbent used to remove dyes in water. It has a fast adsorption rate and good adsorption effect. However, due to the relatively high preparation cost of activated carbon, its application range is limited. Therefore, it is urgent to find unconventional and low-cost adsorbents. Therefore, the purpose of this review is to explore the feasibility of various potential low-cost adsorbents for MB removal, including natural raw materials, agricultural waste, industrial waste and other low-cost adsorbents.

Keywords

Low-Cost Adsorbents, Activated Carbon, Methylene Blue, Adsorption Mechanism

1. 前言

染料被广泛用作许多行业的着色剂，例如纺织、印刷、皮革和油漆等[1] [2]。染料中含有痕量的有机染料和有毒化合物。如今，水体中染料正成为水污染的主要来源之一，并代表了一类主要的环境问题[3] [4]。亚甲基蓝(Methylene Blue, MB)是一种高色度、水溶性阳离子染料，广泛用于化学指示剂、染料、生物染色剂和药物等。MB 若接触到人或动物眼睛则会被灼伤，可能造成永久性伤害。吸入时，会引起短时间快速或呼吸困难，而通过口腔摄入会产生烧灼感，导致恶心、呕吐、大量出汗、精神错乱和高铁血红蛋白血症[5]。因此，对于如何修复 MB 污染水体受到科学家们的高度重视。

去除水中 MB 的方法主要包括光催化降解、阳离子交换、电化学降解、吸附等，其中吸附法在 MB 去除方面表面出很好的效率。目前活性炭被认为是最有前途的吸附剂，因为活性炭表面含有丰富的表面官能团(羟基、羧基、羰基等)和多孔结构，化学稳定性高，吸附过程不会产生有害物质[6] [7] [8]。但由于活性炭是在高温无氧环境下煅烧而得，其生产成本相对较高、制造工艺较复杂，因此亟需寻找环境中天然存在或简单易得的原料替代活性炭来修复 MB 污染水体。

本综述探讨了传统活性炭和非常规低成本吸附剂去除水体中 MB 的技术可行性，非常规低成本吸附剂包括农业废弃物、工业废弃物、粘土矿物和沸石等，供广大读者能够快速了解到最新的 MB 染料吸附剂信息。

2. 活性炭

活性炭的碳前驱体通常来源于天然材料，如生物质、褐煤或煤。煤是活性炭生产最常用的碳前驱体，它是由植物降解产生的碳质和矿物材料的混合物。每种煤的吸附特性取决于原始植被的性质和沉积后发生物理化学变化的程度。Qada 等人[9]研究发现使用蒸汽(浓度为 120 kg 蒸汽/kg 碳，温度 1050℃)活化新西兰煤制备的活性炭对 MB 染料的吸附能力最高为 588 mg/g。Karaca 等人[10]发现褐煤中的黄铁矿、有

机硫、碳酸盐和硅酸盐等成分对 MB 染料的吸附具有积极影响，吸附类型包括静电吸附和孔径吸附。

活性炭材料包括各类作物秸秆[11]、竹子[12]、稻壳、玉米芯[13]、藤木屑[14]、杏仁壳、核桃壳、榛子壳和杏核[15]等，活性炭的吸附能力取决于原料的来源、制备和处理条件，如热解温度和时间、活化剂的种类等。Hameed 等人[12]以竹子为原料，以氢氧化钾为活化剂，850℃下碳化 2 h，吸附动力学结果显示，活性炭对 MB 染料的吸附符合准二级动力学模型，吸附过程属于化学吸附，单层最大吸附容量为 454.2 mg/g。Aygun 等人[15]以农林废弃物(杏仁壳、核桃壳、榛子壳和杏核)为原料，氯化锌为活化剂，评估了活性炭的物理(磨损、堆积密度)、化学(元素组成、重量损失百分比)、表面(比表面积、表面化学)对 MB 染料的吸附特性，并得出活性炭生产原料的适宜顺序为：榛子壳 > 核桃壳 > 杏核 > 杏仁壳。

吸附剂对染料的具体吸附机制尚不清楚，这是因为吸附是一个复杂的过程，取决于多种相互作用，例如静电和/或非静电(疏水)相互作用。尽管在吸附特性和动力学方面已经取得了很大的成就，但仍需做大量工作来清楚地识别吸附机制[16]。

3. 低成本吸附剂

活性炭作为吸附剂用于去除废水中 MB 染料一直是常规操作方法，但其高成本带来了许多经济问题。因此，需要开发低成本、易获得的吸附剂，可以更经济大规模使用。针对上述问题，寻求低成本吸附材料替代昂贵的活性炭是近几年的研究重点。成本是比较和选择吸附剂的一个重要参数，如果吸附剂仅需要较少的加工且在自然界中含量丰富，那么可认定其为低成本吸附剂[17]。低成本的吸附剂主要包括天然材料、农业和工业废料物及副产品。

3.1. 天然材料

3.1.1. 粘土

黏土，是一种重要的矿物原料。是颗粒非常小的(<2 μm)可塑的硅酸铝盐。除了铝外，黏土还包含少量镁、铁、钠、钾和钙，一般由硅酸盐矿物在地球表面风化后形成。粘土表面存在的 Ca^{2+}、Mg^{2+}、H^{+}、K^{+}、NH^{4+}、Na^{+}和 SO_4^{2-}、Cl^{-}、PO_4^{3-}、NO^{3-}等离子可通过离子交换、吸附或两者兼有的方式富集阳离子和阴离子，可充当污染物的天然清除剂，从而在环境中发挥重要作用。这些离子可以很容易地与其他离子进行交换而不影响粘土矿物的结构[18]。天然粘土矿物成本低、资源丰富、吸附特性高和离子交换强，是一种天然低成本优势吸附材料。

粘土矿物，是组成粘土岩和土壤的主要矿物，包括高岭石族、伊利石族、蒙脱石族、蛭石族以及海泡石族。粘土矿物不仅可以吸附无机离子，还能吸附有机分子，如粘土矿物对 MB 的吸附已被广泛研究[19] [20] [21] [22]。Hong 等人[19]选用河南信阳非金属矿区的膨润土为原料，结果显示膨润土对 MB 染料的饱和吸附量为 175 mg/g，吸附过程为吸热反应。Almeida 等人[21]以蒙脱石粘土为吸附剂用于去除水中 MB 染料，结果显示吸附饱和量为 316 mg/g，动力学模型符合准二级动力学模型，即为化学吸附，活化能为+28.5 $kJ \cdot mol^{-1}$。结果表明，蒙脱石粘土可以有效吸附 MB 染料，可作为废水处理中阳离子染料的低成本吸附剂。

3.1.2. 沸石和其他硅质材料

二氧化硅、玻璃纤维、珍珠岩和沸石等硅质材料用作吸附剂去除水中 MB 染料的研究已有很多，这是由于它们的丰度高、易于获得且成本较低。Woolard 团队[22]以粉煤灰(其主要结晶成分为 $Na_6Al_6Si_6O_{24} \cdot 8H_2O$)为吸附剂，经 NaOH 水热改性后，对 MB 染料的吸附量提升 10 倍。粉煤灰孔径丰富、比表面积大、机械稳定性好，是一种优良的吸附材料。珍珠岩是一种火山喷发的酸性熔岩，经急剧冷却而成的玻璃质岩石，其二氧化硅含量约为 70%，珍珠岩价格低廉，分布广泛。Luo 等人[23]以腐殖酸改性

珍珠岩为去除 MB 染料的低成本吸附剂，最大吸附量为 78.2 mg/g，且受染料初始浓度、pH、离子强度和吸附时间的影响很大。吸附过程符合准二级动力学模型，吸附速率受初始阶段的外部扩散和随后的颗粒内部扩散所控制。因此珍珠岩是用于净化 MB 染料污染水体的良好吸附剂，但不同类型(膨胀和未膨胀)和不同产地的珍珠岩由于成分不同会具有不同的特性。

3.2. 农业和工业废弃物及副产品

农业和其他行业的废弃物和副产品同样被认为是低成本吸附剂，因为它们在自然界中很丰富，而且加工要求少。

3.2.1. 农业固体废物

农业固体废物种类繁多，如树叶、秸秆、果皮、种子、锯末、树皮等都已被用作吸附剂[24] [25] [26] [27] [28]。这些材料产量大，获取简单，成本低，结合其自身的物理化学特性可成为潜在的吸附剂。锯末是木材业丰富的副产品，可作为固体燃料或作为包装缓冲材料。它含有多种有机化合物(纤维素、半纤维素和木素)，具有多酚基团，可吸附水中 MB 染料。Ahmad 等人[24]以菲律宾桃花心木锯末为原料，对 MB 染料最大吸附量为 158.73 mg/g，热力学计算表明 MB 染料吸附过程是吸热和自发的行为，动力学研究表明吸附遵循准二级动力学模型。树皮是木材业另外一种高产量副产品，由于其低成本和高可用性，树皮作为吸附剂极具吸引力。大量实验验证了树皮中富含单宁，是一种有效的吸附剂。Demarchi [25]和 McKay [27]分别以 Jatoba 树皮和柚木树皮作为吸附剂去除水中 MB 染料，最大吸附量分别为 211.5 mg/g 和 914.59 mg/g，均表现出较好的吸附性能。

3.2.2. 工业固体废物

工业固体废物如污泥、粉煤灰和赤泥都属于低成本材料，这些材料如得不到合理的利用不仅会对环境造成一定的危害，还会造成资源的浪费。Rashed 等人[29]以饮用水处理厂明矾污泥和泥浆为原料，加入 0.25 M 硝酸在 700℃条件下活化获得污泥基吸附剂，MB 染料的饱和吸附量为 70.4 mg/g，符合 Langmuir 等温吸附模型，属于多孔物理吸附。粉煤灰是火力发电厂的废物/副产品，研究证明粉煤灰可用于 MB 染料的吸附。Nazari Moghaddam 等人[30]将粉煤灰用于 MB 染料吸附，吸附饱和容量为 7.87 mg/g。Lin [31]用硫酸处理后的粉煤灰作为低成本吸附材料，酸处理后的粉煤灰比表面积增加，吸附能力变强，吸附过程符合 Freundlich 等温线吸附模型和准二级动力学模型。热力学研究表明吸附属于吸热过程，焓值为 5.63 kJ/mol。

3.3. 其他吸附剂

除了上述几种原料外，还有一些材料可作为低成本 MB 染料吸附剂。例如 Uddin [32]和 McKay [33]分别研究了以废弃茶叶和头发为原料去除 MB 染料，饱和吸附量分别为 300.05 mg/g 和 120 mg/g，吸附效果很好。另外还有沙子[34]、牛粪灰[35]、蛋壳和蛋壳膜[36]等，但针对该类原料研究目前还较少。

4. 结论

本综述总结了多种低成本吸附材料去除水体中 MB 染料的可行性。低成本吸附剂种类繁多、来源广泛，研究较多的包括粘土、沸石、等天然材料，树叶、秸秆、果皮、种子、锯末等农业物体废弃物，污泥、粉煤灰、赤泥等工业废弃物，上述低成本材料可有效替代商业活性炭吸附 MB 染料。由于低成本吸附剂在去除 MB 染料效果良好，我们希望将其推广至大规模的工业领域，不仅可以最大限度减少成本，还可以提高盈利能力。毋庸置疑，低成本吸附剂为未来的商业用途提供了广阔前景。

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