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Review

Agricultural peels for dye adsorption: A review of recent literature

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ABSTRACT

This work summarizes the recently published literature (after 2010) regarding the use of agricultural peels for dye adsorption. The use of peels in decontamination technology is very promising given the near zero-cost for the synthesis of those adsorbents. Banana, orange, and potato peels are the most used types of biomass reported in literature. However, other peels such as pomegranate, citrus, grapefruit, yam, and garlic have been also investigated as potential dye adsorbents. The equilibrium data were analyzed and their fitting to known models (Langmuir, Freundlich, etc.) was discussed in details. Similarly, kinetic modeling applied in those studies was commented comparing the equations used (pseudo-first, -second order, etc.). Thermodynamic aspects also are discussed indicating that in many cases the process was spontaneous ($\Delta G < 0$) and endothermic ($\Delta H > 0$) or exothermic ($\Delta H < 0$).

Contents

1. Introduction

Water pollution is a plague in our modern society. Increased industrial and agricultural activities resulted in the generation of various types of toxic pollutants; the latter is believed to be the main cause of water pollution on a global scale. Polluted wastewater must be depurated and returned to water receptors or to land. Dyes are an important class of pollutants which came in large amounts from textile, dyeing, paper and pulp, tannery and paint industries [1]. The main use of dyes is to modify the color characteristics of different substrates such paper, fabric, leather and others [2,3]. It is already demonstrated that dyes largely affect the photosynthetic activity [4]. Moreover, many dyes are toxic and even carcinogenic thus affecting the aquatic biota and human health [4–6].

Various methods such as adsorption, coagulation, advanced oxidation, and membrane separation are used in the removal of dyes from wastewater. However, adsorption is one of the most effective processes of advanced wastewater treatment. Therefore, many industries use adsorption techniques (mainly in the tertiary stage of biological treatment) for reducing hazardous inorganic/organic pollutants present in

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Nomenclature

AR37	acid red 37
AY17	acid yellow 17
BB119	basic blue 119
BB159	basic blue 159
BG	brilliant green
CPO	color from palm oil mill effluent
CR	Congo red
CV	crystal violet
DBB	deazol black B
DR12B	direct red 12B
DR79	direct red 79
DY27	direct yellow 27
L	Langmuir isotherm equation
F-S	Fritz–Schlunder isotherm equation
F	Freundlich isotherm equation
L-F	Langmuir–Freundlich isotherm equation
MB	Methylene blue
MG	malachite green
ps1	pseudo-first order kinetic equation
ps2	pseudo-second order kinetic equation
RB	reactive blue
RB114	reactive blue 114
RB19	reactive blue 19
RB5	reactive black 5
RBB	remazol brilliant blue
RG	reactive gray BF-2R
RGY	remazol golden yellow RNL-150%
RNB	reactive navy blue
R-P	Redlich–Peterson isotherm equation
RR141	reactive red 141
RR198	reactive red 198
RR3B	reactive red 3B
RT	reactive turquoise Q-G125
T	Temkin isotherm equation
UB	ultramarine blue
V5R	violet 5R
VB	violet B

effluents [7]. Numerous works have been recently published with primary goal in the investigation of removal of different pollutants (either in gas or liquid medium) using adsorbent materials [8–23].

There are various adsorbent materials used for the removal of dyes from aqueous solutions: peanut hull [24], olive pomace [25], spent tea leaves [26], mango bark [27], rice husk [28], coffee husks [29], peanut husk [30] and eggshells [31]; agricultural peels present great interest. But after a detailed screening in literature, there is a lack of review articles focused only on using agricultural peels for dye removal.

The main goal of this work is to provide the recent progress regarding the use of agricultural peels as dye adsorbents. For this purpose, only recent studies (after 2010) were extensively discussed in terms of adsorption capacity, fitted isotherm and kinetic models and thermodynamic aspects.

2. Biosorption modeling

In order to develop an effective and accurate design model for the removal of pollutants from aqueous media, adsorption kinetics, thermodynamic and equilibrium data are required.

Adsorption isotherm model is a useful tool giving information about the theoretical maximum adsorption capacity and possible interactions between adsorbents and adsorbate [32]. Langmuir and Freundlich models have been widely known. Langmuir isotherm assumes that all binding sites have equal affinity for the sorbate, resulting in the formation of monolayer of adsorbed molecules [33]. On the other hand, Freundlich isotherm mainly describes adsorption onto heterogeneous surfaces that provide adsorption sites of varying affinities [34]. Linear and non-linear expressions of Langmuir and Freundlich isotherms are listed in Tables 1.

Kinetic studies are important for the prediction of optimum conditions in full-scale batch adsorption processes [38]. Kinetic modeling gives information about adsorption mechanisms and possible rate-controlling steps such as mass transport or chemical reaction processes [38–40]. Several kinetic models as pseudo-first and pseudo-second order, Weber–Moris, and Elovich are available. The most prevalent are the pseudo-first and the pseudo-second order kinetic equations. The linear and non-linear forms of pseudo-first and pseudo-second order kinetic models are presented in Table 2.

Thermodynamic studies are used to predict the adsorption spontaneity, the nature of adsorbent and adsorbate at equilibrium conditions. Also, thermodynamics provide information about the temperature range in which adsorption is favorable or unfavorable [41]. The main thermodynamic parameters are change of Gibbs energy (ΔG^0), adsorption enthalpy (ΔH^0) and entropy (ΔS^0). Those parameters can be calculated by fitting data obtained by adsorption experiments at different temperatures (Table 3).

A synopsis of best fitted isotherm and kinetic models, maximum adsorption capacities and thermodynamic results is tabulated in Table 4.

3. Agricultural peels for dye adsorption

3.1. Orange peels

Sayed Ahmed et al. [42] studied the removal of RB19 using raw orange, peel (OP) and chemically modified with NaOH orange peel (SOP). The same authors, in order to enhance the biosorption capacity, modified OP and SOP forms with cationic surfactant (CTAB: cetyltrimethylammonium bromide) to produce CTAB-OP and CTAB-SOP biosorbents. CTAB treatment provokes an increase in the dye uptake probably due to the formation of an ester linkage between CTAB and cellulosic hydroxyl groups of OP and introduction of $-CH_2-$ groups to the fiber. The equilibrium was attained after 30 and 60 min for OP, SOP and CTAB sorbents, respectively. The maximum dye removal was found at pH 4.

The ability of orange peel powder to adsorb Methylene blue was investigated by Khatod [43]. The first-order kinetic model was fitted to the kinetic data and equilibrium was achieved at 18 min using initial concentration of 2.5×10^{-5} mg/L dye. The dye adsorption decreased with increase of dye concentration due to the agglomeration of biosorbent as a result of less surface area involved in adsorption process.

Orange peels were also modified via calcination method for the removal of MB from water [44]. Calcination was carried out at 300, 400 and 550 °C for short or long duration (30 min to 2 h). Calcinations led to the preparation of a biosorbent with higher surface area (crude orange peel: 0.45 m^2/g, calcinated at 550 °C for 30 min 4.97 m^2/g) and change to the acid character (pH 4.65) of crude orange peel into basic, especially at high temperatures (pH = 6.51–9.96).

The ability of orange peel for the removal of MB was also tested by Boumediene et al. [45]. Batch experiments were performed (initial conditions: biosorbent mass = 1 g, V = 1 L of known dyeing solution; T = 25 ± 1 °C, 400 rpm agitation rate) in order to investigate kinetic, isotherms and thermodynamic studies.

Activated carbon was prepared from orange peels by carbonization at different temperatures (from 200 to 1200 °C) to investigate the adsorption behavior of 2-pic onto this biomass from aqueous solution [46]. The carbonization at 700 °C gives a biosorbent material with maximum pore structure (total pore volume 15 cm^3/g), higher internal surface area (248 m^2/g). The experimental findings showed that the

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