



## Review

# A review on waste-derived adsorbents from sugar industry for pollutant removal in water and wastewater

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## ABSTRACT

Sugar industry generates a significant amount of by-products (such as sugar beet pulp (SBP), sugarcane bagasse (SCB)) and their handling and management is a matter of great concern. Among their uses such as fuel and fertilizer, the valorization of biowastes from sugar industry as adsorbents for the removal of various aquatic pollutants presents promising features in terms of cost reduction for waste disposal and environmental protection. This review article deals with the use of sugar waste based materials used as adsorbents in water treatment. For this purpose, isotherms, kinetics, desorption and thermodynamic information are thoroughly presented. Moreover, many parameters which control the adsorption process, such as the effect of initial concentration, initial solution pH, contact time, temperature and adsorbent's dosage, are also discussed in detailed. The performance of the adsorbents largely depends on the type of pollutants and experimental conditions. Surface modification with chemicals greatly enhance the removal efficiency with favorable kinetics and adsorption mechanism.

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**Abbreviation:** MB, methylene blue; EB, erythrosin B; MG, malachite green; AO7, acid orange 7; CPBr, cetylpyridinium bromide; OR2, orange II; CR, congo red; MR, methyl red; RBB, remazol black B; BB3, basic blue 3; RO16, reactive orange 16; CRR195, chemazol reactive red 195; BV16, basic violet 16; RR2, Reactive red 2; AR1, acid red 1; SA, safranin; DW, distilled water; SBP, sugar beet pulp; SCB, sugarcane bagasse; COD, chemical oxygen demand; FTIR, fourier transform infrared spectroscopy; BET, Brunauer, Emmett and Teller;  $E_a$ , activation energy; C-SCB, carbonaceous bagasse; CPBr, cetylpyridinium bromide; F-SCB, formaldehyde-sugarcane bagasse; S-SCB, sulphuric acid-SCB; PAC, commercial activated carbon; QSCB, quarterized sugarcane bagasse; DSBPC, dehydrated sugar beet pulp carbon;  $\Delta G^0$ , Gibbs free energy;  $\Delta H^0$ , enthalpy change;  $\Delta S^0$ , entropy change; L, Langmuir; F, Freundlich; Ps1, pseudo-first-order; Ps2, pseudo-second-order.

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## 1. Introduction

Water pollution due to industrial, agricultural and domestic activities has caused a significant threat to human as well as surrounding environment [1]. Various water treatment technologies have been developed during the last few decades [2]. Among them, adsorption still remains the most favorable process for removing pollutants from water and wastewater due to its simplicity to design, easiness to operate and low cost [3].

Activated carbon has been used for this purpose since long, but focus has been shifted towards developing low-cost adsorbents using agro-industrial wastes such as rice husk, wheat straw, coffee waste, coconut wastes, peanut hull, fruits and vegetable peels, sludges, steel slag, red mud, sugarcane bagasse etc. [4–13].

Various industries produce huge amounts of wastes which create disposal problems as well as environmental pollution in many ways (air, soil and water). Sugar industry is one such industries generating large amounts of wastes [14,15]. Around 160 million tons of sugar are produced annually from >123 sugar-producing countries with Brazil, India, China, Thailand and Pakistan as top five producers. A significant amount of wastes is generated during the production of sugar which consists elevated levels of suspended solids, organic matter, effluent, sludge, press mud, and bagasse [16].

Bagasse and filter cake are two main types of solid wastes generated by sugarcane industry [17,18]. The solid residual material, left after the juice is extracted from the sugarcane, is termed as bagasse. It is estimated that bagasse contributes to 33% residue of the total cane crushed [17, 18]. It has a calorific value of about 1920 kcal kg<sup>-1</sup> [17,18] and is mainly used as fuel in boilers for steam generation. For each 10 tons of sugarcane crushed, a sugar factory produces nearly 3 tons of wet bagasse. Bagasse fly ash is produced when bagasse is burned to generate energy and steam for power. The precipitate in the form of sludge slurry after filtration is termed as filter cake or press mud cake.

Press mud is a residue of sugarcane juice filtration process [19]. It contains all non-sucrose impurities along with CaCO<sub>3</sub> precipitate and sulphate. Press mud from double sulphitation process contains valuable nutrients such as nitrogen, phosphorous, potassium, etc., and therefore used as a fertilizer. The press mud from double carbonation process is used for land filling [20]. Molasses is a by-product left over from the process of crystallization of sugar from the sugarcane juice [21].

Sugar mills significantly contribute towards environmental pollution by generating wastewater, emissions and solid wastes. The massive quantities of plant matter and sludge washed from mills are decomposed in freshwater bodies, absorbing available oxygen and leading to massive fish kills [22]. In addition, mills release flue gases, soot, ash, ammonia and other substances during processing. If all the by-products of sugar industry can be used for converting into value-added products, it will minimize the pollution load to a large extent. Sugar industry wastes are, therefore, a promising resource for environmental technology if applied in the treatment of water and wastewater. This paper presents the recent advances in the utilization of sugar industry wastes as adsorbents and their performance in the removal of different aquatic pollutants.

## 2. Sugar waste for heavy metals removal

Heavy metals are recognized as one of the most toxic groups which reach in food chain through the disposal of wastes to water receptors or land. Heavy metals are taxed in causing toxic effects, cancer and diseases because they cannot be degraded [23–25]. The most important factors which affect their mobility are pH, sorbent nature, presence and concentration of organic and inorganic ligands [26]. The maximum adsorption monolayer capacity, best isotherm and kinetic models are tabulated in Table 1.

### 2.1. Raw sugar wastes

The adsorption of Mn<sup>2+</sup> by sugar beet pulp (SBP) and sugarcane bagasse (SCB) from aqueous solution was examined by Ahmed et al. [27]. Optimum adsorption conditions for SCB was obtained at pH 6, 1.5 g and equilibrium was reached after 150 min, while for SBP optimum adsorption conditions were recorded at pH 6 and 1 g and the equilibrium time was attained after 90 min. FTIR spectra before and after Mn<sup>2+</sup> adsorption were used to determine the functional groups which participated in adsorption process. For both SCB and SBP, it was found that oxygen containing functional groups vis, methoxy –OCH<sub>3</sub>, carboxy–COOH and phenolic –OH groups were affected after removal process. Intra particle diffusion was found to involve in uptake process but it was not the only rate limiting step.

Moubarik et al. [28] examined the use of SCB for the uptake of Cd<sup>2+</sup>. Highest removal was noticed at pH 7 and at 25 °C and the equilibrium was reached in 25 min. Arrhenius activation energy (*E<sub>A</sub>*) was estimated to be 4.6 kJ mol<sup>-1</sup> suggested physisorption. The adsorption percentage was found to increase from 87 to 96% as the concentration increase from 10 to 30 mg L<sup>-1</sup>.

SCB was also used as adsorbent for the removal of Cd<sup>2+</sup> from aqueous solutions [29]. Maximum adsorption was achieved at 150 rpm of agitation rate and at pH 5–7. Adsorption was noticed to be fast and equilibrium was reached after about 90 min of contact time. Kinetic studies showed that pore diffusion was not the only rate-limiting step. Rosmi et al. [30] also concluded that maximum adsorption percentage (55%) of Cd<sup>2+</sup> by SCB was achieved at pH 7, with 120 min of contact time and 1 g of adsorbent dosage.

Pehlivan et al. [31] studied the adsorption of Pb<sup>2+</sup> and Cd<sup>2+</sup> by SBP. The pH was found to control the uptake process and maximum adsorption was found at pH 5.3 and 5, for Cd<sup>2+</sup> and Pb<sup>2+</sup>, respectively. Equilibrium time was attained after 70 min for both metals and the increase of adsorbent dosage from 0.1 g to 1 g caused an increment of removal efficiency from 57 to 72% for Cd<sup>2+</sup> and from 65 to 71% for Pb<sup>2+</sup>, respectively. The presence of 0.1 M NaNO<sub>3</sub> had no significant effect on Pb<sup>2+</sup> and Cd<sup>2+</sup> removal, while increasing the ionic strength over 0.1 M NaNO<sub>3</sub>, a reduction in the adsorbed amount for both metals was noticed.

Batch equilibrium studies were carried out in order to test the uptake of Cu<sup>2+</sup> by dried SBP [32]. The increase in pH from 2 to 4 was found to positively affect the adsorption process and the removal efficiency was raised from 10.8 to 24.6 mg g<sup>-1</sup>. At higher pH values such as 4.5 and 5, a significant decrease of Cu<sup>2+</sup> uptake was noticed due to the plausible precipitation of Cu<sup>2+</sup> as insoluble Cu(OH)<sub>2</sub>. The increase in temperature from 25 to 45 °C had negative effect on Cu<sup>2+</sup> adsorption that resulted in the decrease of the amount adsorbed from 24.6 to 12.3 mg g<sup>-1</sup>. The external mass transfer, intra particle diffusion and sorption process were potential rate controlling-steps indicated the complexity of the adsorption mechanism. The activation energy of adsorption (*E<sub>A</sub>*) was estimated to be –58.47 kJ mol<sup>-1</sup> and thermodynamic studies suggested that the adsorption was spontaneous, exothermic with a decrease in the randomness at the solid/solution interface.

SCB and its modified forms (NaOH-SCB and HCl-SCB) were used as promising adsorbents for the removal of Hg<sup>1+</sup> from aqueous solution [33]. Raw biomass appeared to have higher maximum adsorption capacity than modified adsorbents. The highest removal of 97.58% was noticed at pH 4, while for pH values higher than 4, a decrease was observed due to the potential precipitation of mercury ions. The raise of temperature from 30 to 50 °C caused an increment of the uptake efficiency in the first minutes but at equilibrium time negligible changes were performed.

### 2.2. Chemically modified sugar wastes

SCB was treated with 0.1 M oxalic acid in order to use as adsorbent for the removal of Cu<sup>2+</sup> from water [34]. Optimum adsorption

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