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Adsorptive potential of agricultural wastes for removal of dyes from aqueous solutions

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ABSTRACT

Present work aims to investigate the adsorptive characteristics of agricultural wastes (*Citrus Limetta* Peel and *Zea Mays* Cob) for effective removal of dyes from aqueous solutions. Batch adsorption experiments were carried out in order to analyse sorption behaviour of dye-adsorbent systems at different adsorbent dosage and initial dye concentration. Possibility of mass transfer resistance was investigated to improve the diffusion rate, whereas kinetic aspects were examined to achieve thermodynamic equilibrium for the proposed adsorption process. Solution pH was observed to significantly affect the adsorption efficiency by regulating degree of ionization of the adsorbate's functional groups. More than 90% removal of dyes was attained for all dye-adsorbent systems under optimum reaction conditions. Characterization studies were performed to examine the changes in morphology and functional groups of the adsorbents before and after adsorption process. Kinetic study suggested the pseudo-secondorder kinetic model with normalized standard deviation Δq_t (%) <5% and regression coefficient >0.999 as being able to better describe kinetic data than pseudo first order and elovich kinetic models. Adsorbate-adsorbent interaction was investigated by looking into the applicability of Langmuir, Freundlich and Dubinin-Radushkevich isotherms for the proposed adsorption process. Maximum adsorption capacity Q° was observed to be highest for malachite green dye (8.733 mg/g and 16.72 mg/g) using CLP and ZMC respectively. Findings obtained from thermodynamic studies indicated endothermic and spontaneous nature of the proposed process. This work offers an economic incentive to the industrial practice for waste management and eofriendly approach for removal of toxic dyes from textile waste water.

1. Introduction

Unprecedented growth of industries, in spite of playing an important role in mankind welfare, has left a significant negative impression on the ecosystem. Many industries such as textile, paint, leather etc. use dyes for colouring their products and large volume of effluents containing several dye organics is heedlessly discharged into the surface water bodies without any prior treatment. Presence of dyes, even at small amounts (<1 mg/L) in the industrial effluent, is a sincere matter of concern for both toxicological and esthetical reasons [1]. Dyes can affect the biological metabolism process by interfering the transmission of sunlight through water [2]. Also dyes have tendency to sequester metal ions and thus may engender toxicity to aquatic life. Mutagenic and carcinogenic nature of dyes may impart hazardous health effects such as dysfunction of kidneys, central nervous system and reproductive system.

Several biological, physicochemical and electrochemical treatment methods have been reported in literature [3–6] however high process cost, secondary pollution possibilities, use of toxic reagents and long process time confine the use of these conventional methods at industrial scale. Therefore, a strong need is felt to develop an effective eco-friendly process for the removal of dyes from industrial wastewater. Adsorption process has been found to be superior among the existing processes for water treatment due to high efficiency, flexibility, ease of operation, insensitivity towards toxic pollutants and economic feasibility [1,7,8]. Activated carbon (AC) has shown considerable good dye removal efficiency [9,10] though practical application of AC is limited due to problems associated with its regeneration or disposal, sludge production and economic feasibility [11,12]. Recently, agricultural and industrial wastes [13–17] have dictated the researcher's interest owing to their wide availability, low cost, less commercial value and biodegradable properties. Babalola et al. [18] investigated the adsorption efficiency of a plant waste Cedrela odorata Seed Chaff

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(COSC) for the adsorption of industrial dyes from aqueous solutions. Microstructures of COSC indicated presence of various organic moieties which are responsible for efficient adsorption of toxic dyes. Unuabonah et al. [19] performed continuous adsorption studies in a fixed bed reactor using a novel hybrid adsorbent (a combination of Carica papaya seeds and Kaolinite clay) and reported breakthrough adsorption capacity of 35.46 mg/g for the adsorption of methylene blue dye. Regeneration possibilities, significant adsorption capacity and economical feasibility make this proposed hybrid adsorbent as a promising alternative. Tree waste Pentaclethramacrophylla tree bark and Malacanthaalnifolia tree bark were employed as low-cost adsorbent for the removal of toxic dyes and heavy metals (Cd^{2+}, Pb^{2+}) from aqueous solutions [20]. Adsorption efficiency of the adsorbents was optimized by varying various process parameters such as pH, biomass dose, initial solute ion concentration, agitation time and temperature [20]. Biosorption potential of abundantly available waste biomass Zea mays seed chaff was investigated for the removal of heavy metals (Cr^{3+},Cd^{2+} and Pb^{2+}) from aqueous solutions. Authors suggested endothermic nature of the biosorption of these metals with large positive entropy values [21]. Adsorption potential of lignocellulosic material (native and modified form) was investigated for the effective removal of Direct Yellow 50 dye from aqueous solution under batch and continuous mode [22]. Modified biosorbents demonstrated the enhanced biosorption capacity than native and immobilized forms. Polyethylenimine treated peanut-husk biomass was also illustrated as an efficient biosorbent for the removal of Indosol Black NF and Indosol Orange RSN dyes from aqueous solutions and desorption study were conducted to look into the possibility of regeneration of bioadsorbent [23]. Maximum dye removal (58.01 mg/g) was achieved at 200 mg/L initial dye concentration, pH 2.0, and 0.17 g peanut husk adsorbent dose by optimizing the process parameters using response surface methodology [24].

Present study explores the adsorptive potential of *Citrus Limetta* Peel (CLP) and *Zea Mays* Cobs (ZMC) for the removal of three different textile dyes (Malachite Green (MG), Methylene Blue (MB), Congo Red (CR)) from synthetic samples. *Citrus Limetta* (Sweet Lemon) and *Zea Mays* (Corn) are considered important fruit and cereal crops respectively across the globe and are produced in more than 100 countries. Nearly 115 million ton production of citrus across the globe was reported in year 2012 which is predominantly contributed by China, Brazil, USA and India [25]. Zea Mays is currently the second most abundant crop globally [26,27] and is predicted to surpass both wheat and rice to become the number one grain at global scale by 2020 [28]. Nearly 968 million tons of corn production is reported globally in year 2015–16 in which USA contributes to more than 35% of total production [29]. Consequently, large amount of sweet lemon peels and corn-cobs are produced every year from these crops. These agricultural by-products are structurally composed of cellulose, hemicellulose, lignin and protein content, therefore their direct disposal in ecosystem may increase the biological oxygen demand of water and putrefaction of biomass [30].

To the best of our knowledge, removal of MB, MG and CR textile dyes has not been examined yet using CLP and ZMC as green adsorbents. The focus of the study was to investigate mass transfer limitations, equilibrium and kinetic aspects in order to optimize the dye adsorption efficiency of the proposed novel low-cost adsorbents. Various characterization techniques were employed to investigate the changes in physico-chemical properties of fresh and dye-loaded adsorbents.

2. Material and methods

2.1. Synthetic dyes

Methylene blue (MB), also known as tetramethylthionine chloride is a cationic thiazine dye which consists of dark green crystals or crystalline powder and has a bronze-like luster. It is one of the most commonly used dyes in textile industry for dying cotton, wool and silk. Exposure to MB has been reported to cause increased heart rate, cyanosis, nausea, jaundice, quadriplegia, Heinz body formation and tissue necrosis in humans. Iris epithelium, corneal and conjunctival injury [31], neurotoxic effects on central nervous system [32], serotonin toxicity [33] and teratogenic effects [34] have also been reported widely due to acute exposure to MB dye. Table 1 describes the main characteristics of each dye employed in present study.

Malachite Green (MG), a cationic N-methylated diaminotriphenylmethane dye, exists as a mixture of chromatic malachite green cation and its carbinol base in solution [35]. It is extensively used in dyeing of textile material and in distilleries. Applicability of MG as a therapeutic agent in aquaculture has also been reported widely. However, excessive exposure of MG may cause teratogenicity, respiratory toxicity carcinogenesis, mutagenesis and chromosomal fractures [36,37].

Congo Red (1- Naphthalenesulfonic acid, 3, 3′-(4, 4′ biphenylene bis (azo) bis 4-amino) di sodium salt) is known to metabolize to a human carcinogen benzedene. Acute exposure of this dye may cause an allergic reaction and anaphylactic shock. Therefore, the treatment of effluent containing toxic dyes is of sincere concern these days.

2.2. Preparation and characterization of low-Cost adsorbents

CLP and ZMC samples were collected from local vendor, New Delhi (INDIA) and washed thoroughly using distilled water in order to remove the impurities present on the surface. The samples were dried in presence of sunlight for 5–7 days. Completely dried material was grinded to powder and then sieved using 40 mesh screen in order to obtain the desired particle size. The powdered sample was finally dried in a hot air oven at 100 °C for 2 h and was stored in an airtight vessel. It was used directly for batch adsorption experiments without any further treatment. Fig. 1 demonstrates raw material and the grinded form (150 μm particle size) of the prepared adsorbents.

Proximate analysis was performed in order to estimate the moisture, ash, volatile matter and carbon content in fresh samples of CLP and ZMC adsorbents. Fourier Transform Infrared (FTIR) spectroscopic analysis was performed for the determination of functional groups on the adsorbent surface. Samples for FTIR

Table 1
Characteristics and Structure of the dyes MB, MG and CR.

Characteristics	Methylene Blue	Malachite Green Oxalate	Congo Red
Manufactures	Qualikems India Pvt. Ltd.	Fisher Scientific	CDH
Class	cationic thiazine dye	cationic N-methylated diamino triphenyl methane dye	anionic benzedene dye
Molecular Formula	$C_{16}H_{18}N_3SCl{\cdot}xH_2O$	$C_{52}H_{54}N_4O_{12}$	$C_{32}H_{22}N_6Na_2O_6S_2$
Molecular Weight	319.85	927.02	696.67
Wavelength (λ_{max})	662 nm	616 nm	499 nm