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Radiation grafting: A voyage from bio-waste corn husk to an efficient thermostable adsorbent

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ABSTRACT

The initiator free environmentally benign gamma radiation is employed to graft poly-acrylic acid (PAA) onto the widely produced bio-waste corn husk to develop promising, cheap, efficient and reusable adsorbent (AAc-g-husk) having specific adsorption capacity of 1682.7 mg g^{-1} of methylene blue (MB) at pH 9.0 and 320 K. The most suitable grafting yield is found by optimizing absorbed dose, dose rate and concentrations of monomer, Mohr's salt and inorganic acid. The inter-planar hydrogen bonding among (002) planes of cellulose in the husk decreases after diversifying grafting of PAA on ad-axial, ribs and micro-fibrils surfaces of the corn husks. The chemically and structurally modified AAc-g-husk shows superior thermal stability. The mechanism of MB dye adsorption by AAc-g-husk has been discussed through six two-parameters adsorption isotherm and ten three-parameters adsorption isotherm models at three different temperatures (300, 310 and 320 K), seven kinetic models at room temperature, FT-IR and desorption studies in different solvent compositions.

1. Introduction

Rapid urbanization and industrialization generates voluminous waste water containing mixture of hazardous organic pollutants all over the world. The mixing of the untreated waste water with main water bodies causes surface and ground water pollution. Synthetic complex structured organic dyes belong to one of the major groups of pollutants which are being highly used in textile industries (Riu, Schönsee, Barceló, & Ràfols, 1997). These synthetic dyes are manufactured intending to remain stable under sunlight, temperature and microbial attack and thus, those are more persistent in the environment (Paska, Pacurariu, & Muntean, 2014). Further, the intense colour of the dyes absorbs a good fraction of sunlight and disturbs the photosynthetic activity of the aquatic plants. As a result, the concentration of the dissolved oxygen in the aquatic ecosystem decreases (Paska et al., 2014). Therefore, to maintain an ecological balance, proper management of the textile and industrial waste water is highly necessary to make water recyclable and reusable for various applications.

Various conventional methods such as coagulation-flocculation, chemical oxidation, ozonation and biological degradation are currently being followed in the effluent treatment plants (Akar, Ozcan, Tunali, & Ozcan, 2008). These processes either show inadequate removal of pollutants or possess several limitations. The major problems in these conventional treatments are associated with the production and disposal of huge amount of secondary sludge, formation of toxic by-products, and requirement of intensive energy, high operational cost, long operation time (Pandey, Singh, & Iyengar, 2007). Therefore, these associated problems limit the utilization of the conventional treatment processes as efficient technologies for the treatment of waste water (Kara, Aydiner, Demirbas, Kobya, & Dizge, 2007). On the other hand, adsorption process is being explored as a promising alternative method for the removal of pollutants due to its simple operational design and higher efficiency (Oladoja, Aboluwoye, Oladimeji, Ashogbon, & Otemuyiwa, 2008). Moreover, this process minimizes the production of toxic by-products and shows the possibility to recycle the used adsorbent as well as dye after recovering the adsorbed dye molecules from the adsorbent as per the need. Although having high treatment cost and difficulties in regenerating the adsorbent, the activated carbon is the most widely used adsorbent for water treatment (Hameed, Mahmoud, & Ahmad, 2008). Therefore, there is a real need to find out low cost alternate adsorbents which are renewable, abundant, easily available, environment friendly as well as efficient.

The bio-adsorbents such as bacterial cellulose, polysaccharides, starch and their composites are emerging as potential adsorbents for inorganic ions and organic pollutants (Crini, 2006; Foresti, Vázquez, & Boury, 2017; Kushwaha, Avadhani, & Singh, 2015; Lv et al., 2013; Ragavan & Rastogi, 2017). On the other hand, agricultural waste materials (i.e. bio-waste) such as bagasse, rice husks, ginger husks, orange peels, banana peels, coconut husks have been investigated as adsorbents for effective removal of the textile dyes (Annadurai, Juang, &

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Lee, 2002; Kumar & Ahmad, 2011; Vadivelan & Kumar, 2005; Fiorentin et al., 2010; Hameed et al., 2008). The corn husk, which is the outer collective layers over the corn cob, is significantly considered as bio-waste as it is the non-consumable part of the corn, which is the second largest produced crop after sugarcane among all the agricultural crops worldwide (Reddy & Yang, 2005; Zhou, Yang, & Zhang, 2014). As per the report, 640 million ton of corn production is associated with the generation of 45 million tons of corn husks (El-Torky, Mostafa, El-Masry, & Mahdi, 2015). Surprisingly, only few attempts have been made to utilize corn husk for dye adsorption (Paska et al., 2014; Solanki & Kohli, 2016). The ligno-cellulosic matrix of the bio-waste has different functional groups such as hydroxyl, methoxy, phenols, etc., which can physically adsorb the dye molecules through hydrogen bonding and/or weak van der Waals interaction. Due to the absence of any strong ionic functional groups in bio-waste, the maximum adsorption capacities of the corn husk for the ionic dyes fall in the range 18–102 mg g^{-1} depending on the pretreatments (Paska et al., 2014; Solanki & Kohli, 2016). The adsorption capacity of corn husk is expected to be improved upon surface modification with the ionic functional groups. Graft polymerisation is a well known surface modification process, in which, the polymer chains containing ionic functional groups are covalently bonded to the surface of polymer backbone to form a grafted matrix. Among many grafting methods, owing to an additive- and initiator-free process, the ionizing radiation, has evolved as a green technique to perform grafting reactions (Cruz, García-Uriostegui, Ortega, Isoshima, & Burillo, 2017).

Therefore, in the present study, we have strategically prepared an anionic poly-acrylic acid grafted corn husks by following radiation grafting method to improve the dye adsorption capacity of the bio-waste (corn husks) for the adsorption of methylene blue (MB) dye, which is generally used for coloring papers, hairs, cottons and wools. Although, this model cationic dye is not the most dangerous pollutant, but acute exposure of this dye can cause difficulty in breathing, increase heart rate, nausea, vomiting, diarrhea, shock, jaundice, quadriplegia, and tissue necrosis in humans (Ahmad, Rafatullah, Sulaiman, Ibrahim, & Hashim, 2009). To the best of our knowledge, no attempt has been made till date to synthesize poly-AAc-grafted corn husks (AAc-g-husks) by utilizing gamma radiation grafting method with this objective. In this paper, we have optimised the absorbed dose, dose rates, concentrations of the monomer and other additives used in the grafting solution to obtain the best possible AAc grafting yield on the corn husks. The changes in the chemical structures, thermal stability, crystallinity and surface topography of husk after surface grafting process have been discussed to understand the mechanism of gamma radiation grafting of AAc on to corn husk. AAc-g-husks have showed significant improvement in the specific dye adsorption capacity for MB. The mechanism of MB dye adsorption by AAc-g-husk has been thoroughly discussed through six two-parameters adsorption isotherm models such as Langmuir (L), Freundlich (F), Temkin (T), Dubinin-Radushkevich (DR), Jovanovic (J), Halsey (H); ten three-parameters adsorption isotherm models such as Redlich-Peterson (RP), Radke-Prausnitz (RPr), Sips (S), Toth (t), Hill (h), Koble-Corrigan (KC), Khan (Kh), Vieth-Sladek (VS), Brouers-Sotolongo (BS), Brunauer-Emmett-Teller (BET) at three different temperatures (300, 310 and 320 K); seven kinetic models such as pseudo first order (non-linear and linear), pseudo second order (non-linear and linear), intraparticle diffusion, film diffusion and Elovich at room temperature; FT-IR and desorption studies.

2. Experimental

2.1. Materials

The collected corn husks from a local vegetable vendor in Mumbai, India have been thoroughly washed with the flowing tap water to remove dusts and water soluble substances. Then those are soaked in aqueous ethanol (50% v/v) solution for an hour to remove the soluble organic impurities. Finally the husks are washed with double distilled water and dried at 60 °C in an oven for 8 h followed by further drying in air for a week. AAc monomer (purity > 97%), Mohr's salt, MB and acid red 1 (AR1) are purchased from Sigma Aldrich and are used as received. The analytical grade reagents such as sulfuric acid (H_2SO_4), methanol (CH_3OH), ethanol (C_2H_5OH), sodium chloride (NaCl) and acetic acid (CH_3COOH) are used in this study.

2.2. Instrumentations

GC–5000 gamma chamber having ^{60}Co gamma source with known dose rate is used for the grafting reaction on corn husk. The dose rate is determined by Fricke dosimetry [G(Fe^{3+} = 15.6/100 eV]. All other instrumental details are given in the Section **SM 1**.

2.3. Methods

2.3.1. Synthesis of grafted corn husk and determination of grafting yield of the grafted husks

The detailed procedures for synthesis of grafted corn husks and determination of grafting yield are given in the Section **SM 2**.

2.3.2. Equilibrium adsorption of MB dye

The procedure for studying the equilibrium adsorption of MB dye onto AAc-g-husk is given in the Section **SM 3**. The equilibrium adsorption isotherm of MB on AAc-g-husk at each temperature is studied by comparing with six two-parameters adsorption isotherm models such as L, F, T, DR, J, H and ten three-parameters adsorption isotherm models such as RP, RPr, S, t, h, KC, Kh, VS, BS, BET as shown in **Table S1**.

2.3.3. Statistical error analysis to measure the goodness-of-fit

The experimental data is fitted with each specific non-linear model by Origin 2015 software and the statistical parameters such as reduced χ^2, residual sum of squares (RSS), coefficient of determination (R^2), Akaike information criterion (AIC), Bayesian information criterion (BIC) have been evaluated to understand the goodness-of-fit of a model in our experiment (**Table S2**). Higher the value of R^2 towards 1 and lower the values of reduced χ^2, RSS, AIC and BIC indicate better fitting.

2.3.4. Thermodynamics of dye adsorption

The equilibrium adsorption isotherm parameters representing the equilibrium adsorption of MB dyes onto AAc-g-husks at 300, 310 and 320 K are used to determine the thermodynamic parameters such as change in standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) in the dye adsorption process (Eqs. (1)–(4)):

$$k_e = \frac{q_e}{C_e} \quad (1)$$

$$\Delta G^0 = -RT \ln k_e \quad (2)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (3)$$

$$lnk_e = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (4)$$

where, k_e is the equilibrium constant at temperature T. Then, ΔH^0 and ΔS^0 are calculated from the slope ($\Delta H^0/R$) and intercept ($\Delta S^0/R$) of the linear van't Hoff plot of ln(k_e) versus 1/T, respectively.

2.3.5. Kinetics of dye adsorption

The procedure for studying kinetics of MB adsorption onto AAc-g-husks is given the Section **SM 4**. The experimental kinetic data is compared with seven kinetic models such as pseudo first order (non-linear and linear), pseudo second order (non-linear and linear), intraparticle diffusion, film diffusion and Elovich as presented in **Table S3**.