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Removal of methylene blue dye from artificially contaminated water using citrus limetta peel waste as a very low cost adsorbent

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ABSTRACT

In the present work, the potential of *citrus limetta* peel (CLP) as a low cost adsorbent for the removal of Methylene blue (MB) dye was investigated. Batch adsorption studies were conducted to find out how adsorption was affected by various factors like contact time, initial dye concentration, adsorbent dosage, pH and temperature. The experimental data was analysed in the light of Langmuir, Freundlich and Temkin isotherm models. The data was found to be best represented by Langmuir adsorption isotherm with maximum adsorption capacity for monolayer coverage was found to be 227.3 mg/g. The data were analysed in the light of different available kinetic models and was observed to be best followed pseudo-second order kinetics.

Desorption of MB-loaded CLP was studied with various desorbing agents and HCl was found to be most effective desorbing agent among HCl, NaOH, NaCl, CH_3COOH and deionised doubly distilled water (DDDW). Results suggest that CLP is a very effective low cost adsorbent for the removal of dyes from wastewater.

1. Introduction

Water is essential for the survival of all living organisms. Today contamination of freshwater systems with a wide variety of pollutants is a subject of great concern. Out of all the contaminants present in industrial effluents, dyes are an important class of pollutants and can be identified by even human eye. Dyes are used as colouring agents in a variety of industries such as textiles, food, paper, rubber, plastics, cosmetics, leather, *etc*. The discharge of wastewater from these industries to water resources causes unavoidable problems due to the toxic and unpleasant nature of dyes. The presence of dyes in water in trace amount is undesirable because most of them are toxic, mutagenic and carcinogenic [1]. Dyes also prevent light penetration and thereby reduce photosynthetic activities of water streams and disturb the aquatic equilibrium. Thus, removal of dyes from wastewater before discharge is a challenging task.

Methylene blue (MB), a cationic dye, is most commonly used as the colouring agent for cotton, wool and silk. It is also used as a staining agent to make certain body fluids and tissues easier to view during surgery and diagnostic examinations. The medical applications of MB also include the treatment of methaemoglobinemia and cyanide poisoning. In spite of several applications, this dye has a number of negative impacts on human beings and animals; such as irritation of mouth, throat, oesophagus and stomach with symptoms of nausea, abdominal discomfort, vomiting and diarrhoea. Skin contact may cause mechanical irritation resulting in redness and itching. Thus, removal of MB dye from wastewater is of great concern from human and environmental point of view as well.

Several techniques like flocculation, adsorption, oxidation, electrolysis, biodegradation, ion-exchange, photo catalysis have been employed for the removal of dyes from wastewater [2]. Amongst the various techniques, adsorption has received considerable attention due to its several advantages in terms of cost, ease of operation, flexibility and simplicity of design and insensitivity to toxic pollutants [3,4]. Among the variety of adsorbents, activated carbon may be logically the most preferred adsorbent for the removal of dyes because of its excellent adsorption ability [5]. However, widespread use of activated carbon is restricted because of its high cost [6]. Thus, attention has shifted to find cheaper and efficient alternatives of activated carbon. Natural materials, agricultural and industrial wastes and bio-sorbents represent potential alternatives. A number of non-conventional and low cost adsorbents have been proposed by many workers for the removal of dyes [7–10]. These include agricultural waste products (saw dust [11], bark [12], orange peel [13]), industrial waste products (metal hydroxide sludge [14], red mud [15], fly ash [16]), clay materials (bentonite [17], diatomite [18]), zeolites [19,20], siliceous materials (silica beads [21],

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alunite [22], dolomite [23]), biosorbents (chitosan [24], peat [25], biomass [26,27]) and others (cyclodextrin [28,29], starch [30], cotton [31]) *etc*.

Many low cost adsorbents such as jack fruit peel [32], garlic peel [33], hazelnut shell [34], pine apple stem [35], longan shell [36], spent tea leaves [37] zeolite [38], corn cobs [39] have been reported in literature for the adsorption of methylene blue dye. However, literature survey reveals that so far no considerable effort has been made to study the treatment of MB dye by *citrus limetta* peels. *Citrus limetta* is a species of citrus, commonly known as sweet lime, sweet lemon or mousambi. It is a native to south and south-east Asia and cultivated in the Mediterranean Basin. In India, it is available throughout the year and abundantly during the months of July and August and also from November to March. It is generally taken as a fresh fruit or consumed as juice. Its juice is commonly sold by roadside stalls and mobile vendors. The peels of *citrus limetta* are discarded as waste. In view of the above facts, the present investigation was undertaken with the prime objective to explore the feasibility and utilization of CLP for the adsorptive removal of MB dye. It has also been decided to optimize, wherever possible, the important variables which affect the adsorption capacity.

2. Materials and methods

2.1. Materials

Analytical reagent grade each MB dye (Loba Chemie, India), HCl (Merck, Germany), NaOH (CDH, India), NaCl (CDH, India), KNO_3 (CDH, India) and CH_3COOH (SD Fine, India) were used in the present investigation. The water used was purified by deionisation followed by double distillation. This doubly distilled deionised water (DDDW) was used throughout the experiment.

2.2. Preparation and characterization of CLP adsorbent

CLP waste was collected from local fruit stall, washed thoroughly by DDDW to remove dust and water soluble impurities from its surface and dried in the sunlight for about 4 days and then in an air oven at 90 °C for 24 h until the peels become crisp. The dried mass was pulverised into the fine powder by a mechanical grinder and then sieved to pass through 80 BSS mesh. It was then washed with DDDW till the colour and turbidity of washings were completely removed. The washed adsorbent was finally dried in an air oven at 105 °C for about 4 h. After drying, the mass was crushed again, screened through a set of sieves to get different fractions, namely, 80–150, 150–200 and > 200 BSS scales and stored in air tight containers.

The surface morphology of CLP before and after adsorption was analysed by Scanning electron microscopy (JEOL, JSM6510LV, Japan). Fourier Transform Infrared spectrometer (FTIR) was used to analyse the functional groups on the surface of CLP in the spectral range of 4000 to 400 cm^{-1}.

2.3. Batch equilibrium studies

The batch equilibrium experiments were planned to determine the efficiency of CLP for the removal of MB from aqueous solution. The adsorption experiments were carried out by taking 25 mL of adsorbate solutions with varying initial concentrations (25–250 mg/L) in different conical flasks of borosilicate glass. The fixed quantity of adsorbent (0.05 g) was added to each flask kept on a shaker and equilibrated for 3 h. After filtration, the residual concentration of MB was measured by a UV–vis spectrophotometer at a pre-optimised λ_{max} of 665 nm. The amount of MB dye adsorbed at equilibrium is expressed by a factor q_e (mg/g) given as:

$$q_e = \frac{C_o - C_e}{m} V \quad (1)$$

where, C_o and C_e are the initial and equilibrium concentrations (mg/L) of MB, respectively, V is the volume of solution (L) and m is the mass of adsorbent (g).

The percentage removal of MB (%R) was calculated using the equation:

$$\%\,R = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

The equilibrium data so obtained have been made to analyse in the light of different available isotherm models. The Langmuir isotherm [40] has been commonly used to discuss various adsorbate–adsorbent combinations for both liquid and gas phase adsorptions. This isotherm may be represented as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where, q_m is the maximum adsorption capacity (mg/g) to form a complete monolayer coverage on the surface bound at high equilibrium adsorbate concentration (C_e) (mg/L) and K_L (L/mg) is Langmuir constant related to affinity between the adsorbate and adsorbent.

The Langmuir equation can be arranged to following linearised form:

$$\frac{1}{q_e} = \frac{1}{q_m K_L C_e} + \frac{1}{q_m} \quad (4)$$

The essential characteristics of Langmuir isotherm can be expressed by dimensionless parameter known as separation factor, R_L, which is defined as:

$$R_L = \frac{1}{1 + K_L C_o} \quad (5)$$

where, C_o (mg/L) is the initial concentration of MB dye. The value of R_L throws light on the nature of adsorption to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

Freundlich model is an empirical isotherm commonly used to describe heterogeneous system. The model is represented in linear form as:

$$\ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (6)$$

where, K_F ($mg^{1-1/n}L^{1/n}/g$) and n are Freundlich constants related with the adsorption capacity and adsorption intensity, respectively [41].

Another model, Temkin is also used to fit the experimental data. This model assumes that heat of adsorption on the surface decreases linearly with the coverage adsorbate–adsorbent interaction [42]. The linear form of the Temkin adsorption isotherm is given as:

$$q_e = B \ln C_e + B \ln K_T \quad (7)$$

where, $B = RT/b$, b is Temkin isotherm constant related with heat of adsorption (J/mol) and K_T is the equilibrium binding constant (L/g).

2.4. Adsorption kinetics

In order to understand the kinetics behind the MB removal process, the extent of adsorption was monitored as function of time. The method was similar to that employed for the equilibrium studies. The samples from the reaction flasks were withdrawn at the pre-planned time intervals and the residual concentrations of MB