



Framboidal vaterite for selective adsorption of anionic dyes



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ABSTRACT

Framboidal vaterite has been used for the effective removal of anionic dyes over cationic dyes. Anionic dyes such as Eriochrome Black T (EBT) and Congo Red (CR) were found to adsorb more onto the vaterite polymorph of CaCO_3 . In a similar experimental condition, cationic dyes, Methylene Blue (MB) and Rhodamine 6G (R6G) adsorbed less compared to CR and EBT. Effects of contact time, temperature, pH and initial dye concentration on adsorption of these dyes onto vaterite surface were studied in detail. The adsorption kinetics was studied with the pseudo-first-order, pseudo-second-order and intra-particle diffusion models, and the rate constants were evaluated accordingly. The equilibrium data were evaluated using Langmuir and Freundlich isotherms and was found to follow preferably the earlier model. The thermodynamic calculations supported the spontaneity of the process. The desorption ability and reusability of these vaterite particles were also assessed. Overall, the vaterite surface was potentially explored and substantiated as a suitable dye loading container that could be effectively used for the removal of dyes from aqueous.

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Introduction

Water pollution is one of the major causes of concern in the present era. Various anthropogenic factors have led to the major depletion of the water system as a whole. Water bodies are being contaminated by the discharge of various dye-containing waste effluents generated by several sources such as textile, paper, printing, pulp mills, food, cosmetics and leather industries [1,2]. These contaminants then leak to the ground water system which mixes with the drinking water and brings a chief threat to human health due to either toxic or mutagenic and carcinogenic properties [3]. Another ecological impact of this coloured waste water is that it affects the aquatic environment by reducing the light penetration, which interferes with the natural photosynthesis process [4]. Therefore, the removal and remediation of this waste water are the most imperative environmental tasks for research and technology development on water management [5].

Numerous methodologies have been developed and implemented for the purpose of removing the dye contaminants from waste water; including adsorption, coagulation–flocculation [6], advanced oxidation processes [7], ozonation [8], membrane filtration [9] and biological treatment [10]. Most of these techniques have significant disadvantages including incomplete dye removal, high reagent and energy necessity, low selectivity, high capital and operational cost and generation of secondary wastes that is difficult to be removed or degrade. Amongst all the above mentioned methodologies adsorption seems

to be promising due to its ease of operation, ability to remove different types of dye and comparable low cost of application. Till date various solid surfaces have been explored for dye removal from aqueous solutions. For example activated carbon is used and is found to have a good adsorption capacity for the dyes but the high cost effectiveness of the compound makes it reluctant for application in large scale [11]. Many inorganic mineral surfaces have also been exploited for the same purpose. Silica was used as adsorbent for the removal of cationic dye by McKay et al. [12]. Perlite was used for the removal of Methylene Blue [13]. Natural phosphate [14], hydroxyapatite [15] and titania [16] were also applied for the removal study of waste water dyes. Clay minerals like bentonite, montmorillonite, smectite, kaolinite, sepiolite, and zeolite, etc. were also employed for removing the dyes from waste water [17]. Boujaady et al. reported the use of synthetic calcium phosphate for the removal of textile dyes [18]. Different inorganic mineral surfaces behave differently when introduced with different dyes. Negatively charged surfaces like clay minerals are favourable for cationic dye removal whereas apatitic tricalcium phosphate and apatitic octocalcium phosphate minerals are effective against removal of anionic dyes. It is therefore necessary to know the in-depth detail adsorption mechanism which is the outcome of the surface characteristics and the physio-chemical properties of the adsorbate and the adsorbent.

CaCO_3 is a mineral of great choice due to its vast applicability, low cost and biocompatibility. Out of three polymorphs of CaCO_3 (i.e., calcite, aragonite, and vaterite), calcite is the most and vaterite is the least thermodynamically stable. However, vaterite is a material of high potential application because of its high specific surface area, high solubility, high dispersion, and small specific gravity compared with calcite and aragonite [19]. The cost-effectiveness of these

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materials is better over other commonly used adsorbent. Moreover, vaterite is a highly bio-compatible and environmentally benign material. These properties of vaterite could be exploited for the dye removal study. Few uses of vaterite for adsorption studies are reported in the literature [20]. Sawada et al. have investigated the adsorption of phosphate on vaterite. The loading and releasing capacity of the sub-micron vaterite particles with Rhodamine 6G was investigated by Parakhonskiy et al. [21]. The adsorption of metallic ions (Cu^{2+} and Mn^{2+}) onto the vaterite and their subsequent entrapment by transformation into calcite have been elaborated by Aouad et al. [22].

This present study focuses the use of framboidal vaterite particles for the effective removal of dyes from aqueous medium. The as-synthesized vaterite particles are highly porous and have high surface area. Furthermore the point of zero charge (PZC) value for the vaterite was calculated to be pH 8.21. Therefore, this surface might prove to be a potential candidate for the anionic dye removal via electrostatic attraction. Keeping this in mind, we have considered to study the adsorption of anionic and cationic dyes onto vaterite and to see how the adsorption profile behaves. Eriochrome Black T (EBT) and Congo Red (CR) as anionic dyes, Methylene Blue (MB) and Rhodamine 6G (R6G) as cationic dyes were taken for the study. Batch experimental studies were carried out under various parameters such as pH, adsorbent dosage, contact time, initial dye concentration and temperature. The kinetic data obtained from experimental result were tested by the pseudo-first-order and the pseudo-second-order kinetic models. The equilibrium data were evaluated using Langmuir, Freundlich isotherm models and the thermodynamics of the adsorption was also calculated to get the details of the adsorption process.

Materials and methods

Materials

All the reagents used for the synthesis of the vaterite were of analytical grades. The dyes were obtained from Sigma-Aldrich and used as obtained. Calcium chloride was also obtained from Sigma-Aldrich and sodium carbonate was obtained from Merck, India.

Preparation of framboidal vaterite

The stable microspheres of vaterite were synthesized by a simple co-precipitation method as described in our earlier work [19]. In brief, 20 mM solution of CaCl_2 and 20 mM solution of Na_2CO_3 were allowed to mix in the presence of salicylic acid-aniline (10 mM) dye as the additive at a flow rate of 5 mL min^{-1} . The precipitate obtained was washed and dried and was characterized further by SEM, PXRD and FT-IR.

Adsorption studies

Batch mode experiments were conducted to procure the kinetics and equilibrium data. Dye stock solution of 500 mg L^{-1} was prepared and different desired concentration (10, 50, 100, 200) was done by proper dilution and a volume of 2 mL was taken for the study. After the addition of vaterite (1.5 mg mL^{-1}) to the dye of varied concentration, the vials were then kept under stirring until steady state was reached. Preliminary experiments were done to figure out the optimal conditions for various reaction parameters. The experiments were performed in duplicate for data consistency. The pH of was maintained using 0.1 M NaOH and 0.1 M HCL solution. The ionic strength was maintained constant using 0.05 M NaCl in all the cases otherwise mentioned. After the completion of each experiment, the samples were centrifuged at 10,000 rpm for 10 minutes to separate the solid phase from the liquid phase. The quantity of dye adsorbed per unit mass of adsorbent, i.e., the adsorption capacity (q_e , mg g^{-1})

and the adsorption efficiency can be calculated according to Eq. (1),

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

where C_o and C_e are the initial and steady state dye concentration (mg L^{-1}); V is the volume (L) of the solution and m is the amount (g) of adsorbent added. The pH in the range 5–9 was monitored to see the effect of pH on the adsorption process. Temperature oriented studies were performed with an increasing temperature range from 10 to $40 \text{ }^\circ\text{C}$ in an indigenous temperature controlled stirring unit coupled with a water cooler (Lauda).

Results and discussion

Characterization of framboidal vaterite

The vaterite micro-particles were synthesized using the methods described in our earlier work [19]. Fig. 1a represents the SEM micrograph of the vaterite particles. Framboidal vaterite spheres of size ranging $0.5\text{--}4 \text{ }\mu\text{m}$ were the major components in the precipitates. The FT-IR spectrum (Fig. 1b) shows the characteristic vaterite peak at 746 cm^{-1} along with the other peaks supporting the formation of vaterite. The PXRD spectra (Fig. 1c) also support the predominance of vaterite phase with almost absence of the other two phases. The BET surface area analysis of N_2 adsorption reveals that the vaterite has specific surface area of $12.266 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of 0.045 cc g^{-1} (Fig. 2a). The point of zero charge (PZC) value of vaterite was around pH 8.2 and given in Fig. 2b.

Effect of pH on adsorption

The pH of the medium highly influences the surface properties and the physio-chemical behaviour of the adsorbate which controls the adsorption capacity of any substrate in that medium. To study the effect of pH we have considered a pH range of 5–9. The dye concentration was taken 100 mg L^{-1} and the vaterite concentration was kept constant at 1.5 mg mL^{-1} . The temperature was also kept constant at $30 \text{ }^\circ\text{C}$. The adsorption profile was different for different dyes. The anionic dyes showed a higher adsorption in the acidic range and the cationic dyes were comparatively less adsorbed in the lower pH range. Fig. 3 gives the statistical overview of the q_e value with the pH of the medium. EBT and CR showed the highest adsorption value of 72.2% and 81% at pH 5 respectively. MB and R6G showed the lower adsorption value of 16% and 14% respectively, of the total value. With the increase in the pH the adsorption pattern of the anionic dyes showed a downhill curve. Above the PZC of vaterite at pH 9 the adsorption profile was found to be inverted.

Steady state and kinetic model of adsorption

The rate of uptake of the adsorbate onto the adsorbent surface controls the equilibrium time for the adsorption of the system. This rate of kinetics is required for selecting optimum operating conditions for the full-scale batch process [23]. The dye concentration was taken as 100 mg L^{-1} and the vaterite concentration was kept constant at 1.5 mg mL^{-1} at constant temperature of $30 \text{ }^\circ\text{C}$. Fig. 4 shows the plot of dye adsorption versus contact time. The plot indicates that the adsorption was rapid at the early phase of the process which then slowed with further increase in contact time until a steady state was achieved. The equilibrium time varied for different dyes. The steady state for EBT was achieved within 105 min while for CR, MB and R6G it took 120 min to achieve the steady state of the adsorption.

The kinetic data obtained were incorporated into Lagergren first order (Eq. (2a)) and second order kinetic models (Eq. (2b)) to deduce

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