Chemical Engineering Journal 290 (2016) 371–380

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Adsolubilization phenomenon perceived in chitosan beads leading to a fast and enhanced malachite green removal

Dipshika Das, Anjali Pal *

Civil Engineering Department, Indian Institute of Technology, Kharagpur 721302, India

HIGHLIGHTS

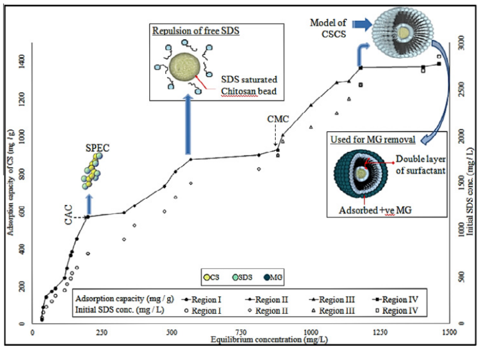
- Chitosan beads are modified with sodium dodecyl sulfate, an anionic surfactant.
- Modification of chitosan beads are done at various concentration levels of SDS.
- Malachite green, a cationic dye is removed by SDS-modified chitosan beads.
- Adsolubilization of malachite green within modified beads is perceived.

ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form 19 January 2016
Accepted 20 January 2016
Available online 25 January 2016

Keywords:
Chitosan beads
SDS-modified chitosan beads
Malachite green removal
Adsolubilization
Kinetic and thermodynamic studies

GRAPHICAL ABSTRACT



ABSTRACT

Chitosan (CS) is a well recognized cationic polyelectrolyte, widely used as an adsorbent. However, CS hydrogel bead lacks its ability to adsorb cationic dyes because of the obvious repulsion between cationic CS and the dye of same charge. In this work CS hydrogel beads are modified by sodium dodecyl sulfate (SDS), an anionic surfactant, under various conditions to improve its efficiency for the adsorption of malachite green (MG), a cationic dye. In the first part, the complex forming ability of surfactant (at <<CMC) with counter ion polyelectrolyte is utilized to fabricate modified chitosan beads, which are designated as surfactant–polyelectrolyte-complex (SPEC). In the second part of the adsorbent preparation, micelle aggregation behavior of surfactant (at >>CMC) is used to modify the surface charges and solubilization properties of the modified adsorbent. These beads are called as chitosan–surfactant–core–shell (CSCS). The mechanism of formation for both is discussed. Besides these modified beads, the CS–SDS composite material (CSC) is also prepared. The adsorptive removal of MG by all the prepared beads has been evaluated. The CSCS beads are found to be the best (adsorption capacity: 360 mg/g) for MG removal. Such an enhanced adsorption is believed to be due to 'adsolubilization' of MG on surfactant bilayer, which has been realized for the first time in CS bead support. The kinetics of removal also is much faster compared to CS beads. The efficiency of CSC for MG removal is higher compared to that of CS beads. The adsorption behavior of CS beads in binary mixture of MG and SDS has also been examined.

1. Introduction

Discharge of colored effluent from industries like dye industry itself, textile, paper, food processing and many others, is one of the potential threat against the aquatic environments in recent

---

* Corresponding author. Tel.: +91 (0)3222 281920; fax: +91 (0)3222 282254.
E-mail address: anjalipal@civil.iitkgp.ernet.in (A. Pal).

http://dx.doi.org/10.1016/j.cej.2016.01.062
1385-8947/© 2016 Elsevier B.V. All rights reserved.

years. Because of the high tinctorial value, presence of dye even in very less concentration often raises the aesthetic issues. The high COD and BOD, suspended solids and toxic compound contents in dye-containing effluents make those difficult to be treated through available conventional methods [1]. Malachite green (MG), which is classified as a triphenylmethane dye (Fig. S1) is a popular one to be used extensively since the early 1930s as a biocide to exert a controlling effect against protozoal and fungal infection in aquatic species. In dye industry MG is used directly to color silk, wool, jute and leather. But later it has been found to be toxic and tumor promoter [2]. Werth and Boiteux while working with isolated rat liver mitochondria, observed a rapid effect of MG to destroy mitochondria [3]. Since it is resistant to aerobic digestion because of its oxidizing power and stability in light, further refinement of MG-bearing wastewater is required even after treating it through existing conventional processes [4].

A wide range of methods like coagulation, chemical precipitation, ion-exchange, ozonation, and adsorption have been developed to mitigate the impact of dye on aquatic environment. Among the aforementioned methods, adsorption through bioadsorbent has been exploited as the most effective one in terms of efficiency, cost and environment friendly approach [5]. Chitosan (CS), a commercially available by-product of chitin, has drawn the attention of researchers in this field since last few decades. Chitosan, chemically known as poly (β-1,4)-2-amino-2-deoxy-D-glucopyranose (Fig. S1) has been prepared through deacetylation of chitin that has been found in large quantity in the exoskeleton of crustaceans, cuticles of insects, cell walls of fungi etc. The presence of number of functional groups in CS offers it some of the outstanding properties like metal chelation, poly-functionality, bioadhesivity etc. [6]. Because of these intrinsic characters it has been already proved as a bioadsorbent to capture dissolved dyes from aqueous solutions.

The widespread use of surfactant in the form of large variety of products like soap, detergents, pharmaceuticals and personal care products has triggered the concern of many research groups. The world surfactant production was 1.7, 1.8 and 9.3 million tons in the years of 1984, 1987 and 1995 respectively [7]. It can alter the quality of the receiving water bodies in short-term as well as long-term basis. Besides this it is harmful to human beings, aquatic species and vegetation because of its xenobiotic property. Hence to mitigate the threat of the surfactant on the aquatic environment its removal is very important.

During the last three decades in number of papers the efficiency of CS as an excellent bioadsorbent has been discussed. The adsorption capacities as high as 3 mmol Cu/g of CS, 1–2 mmol metal/g for Pt and Pd and up to 7–10 mmol of Mo and V/g of CS could be achieved [8]. Its efficiency to capture dissolved dyes from aqueous solutions has also been investigated by many researchers. Maximum uptake of acid orange 12 and acid red 73 per g of CS has been found respectively as 973.3 mg and 728.2 mg [9]. Its dye adsorption efficiency has been tried to be improved by chemical modification using bentonite, activated clay. Chitosan/bentonite adsorbent exhibited adsorption capacity as high as 294.1 mg/g and 345 mg/g of tartrazine and MG respectively [10]. Compared to commercially available adsorbents, CS is advantageous in terms of adsorption capacity.

Because of the environmental regulations enforced, the concern to reduce even the surfactant concentration in the effluent system has been raised. Nowadays, anionic surfactants (AS) are the main ingredients of detergent formulation. Linear alkyl sulfate is the major group of anionic surfactants (AS); sodium dodecyl sulfate (SDS) (Fig. S1) being the most common. The toxic interaction of SDS with skin induces irritant dermatitis reactions which lead to structural changes in the epidermal surfaces [11]. Removal of AS has been performed by numerous adsorbents like activated carbon [12], silica gel [13], clay [14] and once again CS [15]. Surfactants are often used to modify the hydrophobic/hydrophilic property of adsorbents to enhance its uptake efficiency. However, it is very difficult to predict its exact effect in the adsorption process because of the occurrence of the number of competitive and simultaneous operating mechanisms during sorption [16].

A fundamental property of surfactants is their ability to form micelles in solution, provided their concentration is sufficiently high. With micelle formation at critical micelle concentration (CMC), many physico-chemical properties of surfactant like surface tension, electrical conductivity, fluorescence scattering get changed. Spheroidal micelles are the simplest among these aggregations. The concept of hemi-micelle or admicelle formation has concluded the aggregation of surfactant monomers on solid surface while getting adsorbed on to it [17]. These hemimicelles or admicelles are well capable to increase the solubility of poorly soluble molecules by several orders. Hydrophobic solutes may get incorporated in that adsorbed surfactant micelle. This unique phenomenon is known as 'adsolubilisation' that has been already used to improve the adsorption behavior of some known adsorbents of solid state [18]. Another interesting property of surfactant is its association with counter-ion polyelectrolyte to form surfactant–polyelectrolyte-complex (SPEC) at a specific concentration known as critical aggregation concentration (CAC) that is manifold lower than the CMC. In previous studies the effect of AS has been discussed frequently on the sorption of the basic dye whereas the impact of nonionic or cationic surfactant on the adsorption of oppositely charged dye is found insignificant [16]. The SPEC formation between anionic SDS and cationic polyelectrolyte CS has been investigated recently. Even in very low concentration of SDS, the binding isotherm between these two indicates strong electrostatic and highly co-operative interaction [19]. The interaction between them boosts to produce properties that neither the surfactant nor the polymer possess when used alone. The upgraded qualities offer potential to the duo system to be applicable in numerous fields like drug delivery, surface conditioning, rheology control etc.

The risk possessed by MG in water environment, has alarmed already to the concerned researchers to conduct a number of adsorption studies on MG by low-cost adsorbents. But all these low-cost adsorbents like khejri tree sawdust [20], bagasse fly ash [21] has not been found very efficient like activated carbon, for higher dye concentration. But granular activated carbon and other derived adsorbents from the same are non-regenerative and expensive in terms of energy requirement. But the alarming effects of MG, like cell transformation and lipid peroxidation that may cause endogenous DNA damage, teratogenecity, mutagenecity [22] leave no choice but to find out a very efficient adsorbent of low cost.

In the present study, hydrogel bead prepared from CS, the commercially available product with ease has been modified in different ways with SDS, a representative AS, through adsorption process. The efficiency of those modified beads to remove MG, which has been selected as a model cationic dye, from its aqueous solution has been compared with that of CS hydrogel beads. To our knowledge extent this is the first attempt to introduce the adsolubilization property of the surfactant into hydrogel phase of any adsorbent to improve its efficiency.

2. Materials and method

2.1. Chemicals

SDS, MG oxalate, methyl orange (MO) were purchased from MERCK and used without further purification. Sodium hydroxide from EMPLURA, acetic acid from BDH and methanol from SISCO were used as received. CS of low molecular weight (50–190 kDa)