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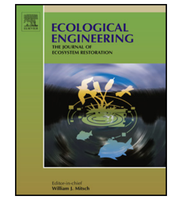

Cerastoderma lamarcki shell as a natural, low cost and new adsorbent to removal of dye pollutant from aqueous solutions: Equilibrium and kinetic studies

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ABSTRACT

The readily available, highly efficient and relatively inexpensive adsorbents of *Cerastoderma lamarcki* shell (CLS) was applied for removal of dye as pollutant using the Taguchi design as an optimization strategy. The Taguchi design was utilized to find out the influencing optimization conditions. As expected, the *C. lamarcki* waste shell is mainly composed of mineral component, so powdered CLS applied for removal of dye pollutant. The pH of solution, CLS particle size, adsorbent dose, contact time, temperature and initial dye concentration were studied as the affecting factors on the adsorption process. The experimental results showed that maximum adsorption occurs in pH about 5. The equilibrium was attained for dyes in 60 min. Adsorption isotherm well fitted to the Freundlich and kinetics of the adsorption reaction followed the pseudo second-order. The maximum adsorption capacity for malachite green was 35.84 mg/g at 303 K. The morphology of the surface of adsorbent was studied before and after the adsorption by SEM micrograph. It was concluded that CLS powder has a great potential to be applied as an adsorbent for removal of malachite green.

1. Introduction

It is clear that environmental pollution is a global issue. Dyes are of the most harmful chemical compounds present in industrial sewages causing decrease in light penetration and perturbation in photosynthesis process in water sources. Dyes can pollute drinking water (Royer et al., 2010), cause allergy, irritation (Brookstein, 2009), cancer disease (Lima et al., 2007) and mutations (Carneiro et al., 2010), thus removal of dyes as a pollutant is an interesting subject (Royer et al., 2009; Lima et al., 2008). There are many approaches for water purifying such as: oxidation (Karatas et al., 2012), reverse osmosis, membrane filtration (Wu et al., 1998), chemical precipitation (Zhu et al., 2007), ion exchange electrolysis (Raghu and Basha, 2007) and adsorption (Eren and Acar, 2006). Most of these techniques, however, suffer from several drawbacks, including the requirement of high operational cost, high energy and reagent, insufficient selectivity and incomplete dye removal, but adsorbing technique is effective due to its simplicity and reproducibility (Tsai et al., 2009). There is, therefore, considerable interest in developing the use of low-cost adsorbents for the removal of dyes from wastewater such as agricultural residues (Nigam et al., 2000), dolomitic (Walker et al., 2003), fly ash(Eren and Acar, 2007) zeolite (Wu et al., 2006), chlorella (Tsai and Chen, 2010), sewage sludge ash (Pan et al., 2003). The successful use of marine adsorbents such as: Sea shells (Chowdhury and Saha, 2010), oyster shells (Liu et al., 2010), mussel shells (Haddad et al., 2014) and scallop (Siboni et al., 2014) have also been reported. Since, marine adsorbents are available and inexpensive can potentially be applied to remove dye pollutants from queues solution.

These materials are utilized in many processes including sulfur adsorbing (Jung et al., 2000), removal of phosphate (Namasivayam et al., 2005), metallic ion trapping (Blais et al., 2003), material synthesis (Yoon et al., 2004), sludge removal (Lee et al., 2001) and food preservatives (Kim et al., 2007). *Cerastoderma lamarcki* shell (CLS) is selected as a suitable material for water pollutants removing. *C. lamarcki* is a type of marine organism, which is a part of the *Cerastoderma Genus* (Subfamily of Lymno cardiinae). *C. Genus* is in the Cardiidae Family and Cardioidea Superfamily, the Veneroida Order (Birshtain et al., 1968). When the animal died, Shells are washed up onto a beach empty and clean. Shells are made up of three separate layers: cuticle, prismatic and nacreous. The prismatic layer has a large number of micropores (Namasivayam et al., 2005; Hsu, 2009) which are the rich source of calcium carbonate. Reusability

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Fig. 1. The images of *Cerastoderma lamarcki* samples.

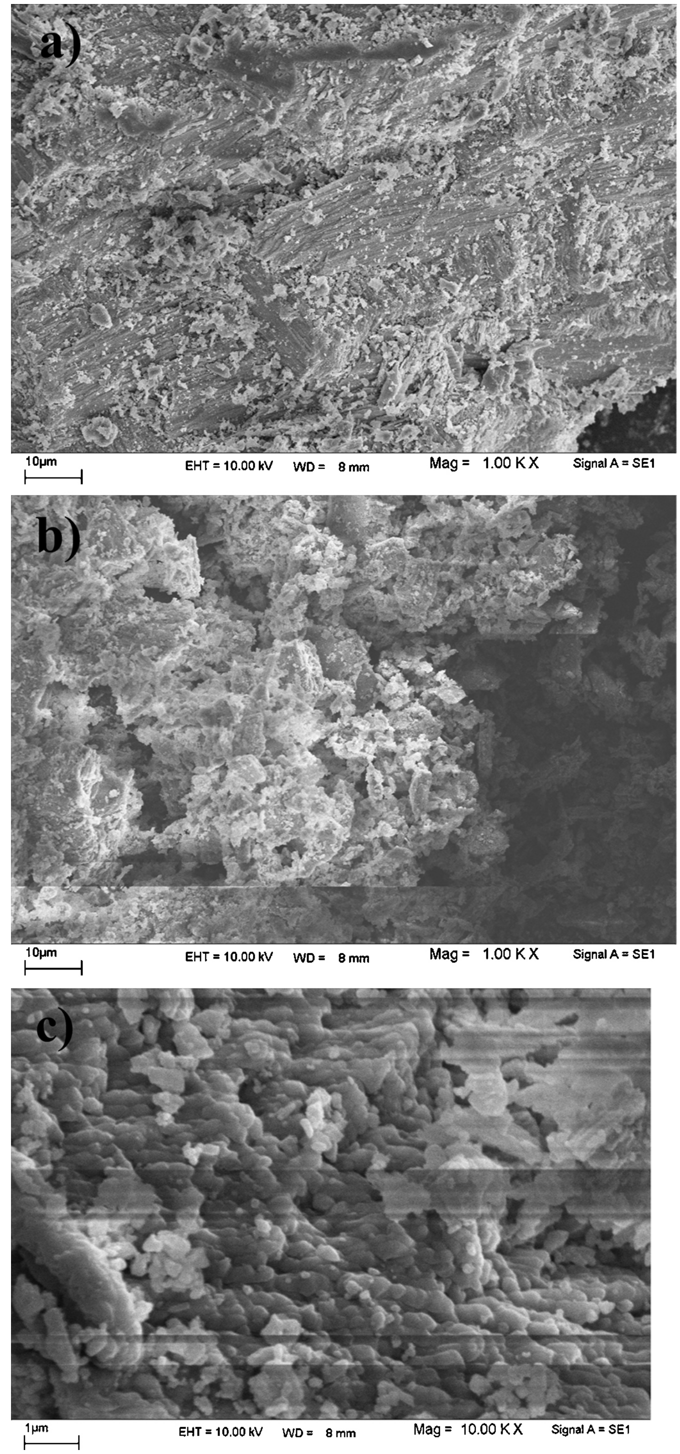

Fig. 2. (a) Natural form of CLS SEM without contact with dye solution, (b) SEM (image size 10 μm) of CLS after contact with dye solution, and (c) SEM (image size 1 μm) of CLS after contact with dye solution.

and abundance of *C. lamarcki* compared to other adsorbents is its main advantages.

The selection of a suitable adsorption condition is crucial for the removal of the pollutant, so it is important to determine the variables influencing the removal percent. The conventional method for medium optimization is "one_at_a_time" approach that is time consuming, expensive and unmanageable (Kazemi et al., 2010, 2014; Zolgharnein et al., 2008). A large number of variables have to be investigated in designing a new adsorption condition and measurement conditions such as pH, temperature, reaction time, amount and the size of adsorbent on the dye adsorption. Multivariate optimization through experimental design has several advantages rather than traditional method not only for having fewer experiments but also to present more information about the whole process under consideration. The information would be summarized on the recognition of effective variables interaction, and finding a mathematical model. Owing to this, the relation of percent removal of dye to variables and their interactions and finding optimum conditions for best performance of removal would be achievable as well (Kazemi et al., 2010, 2014; Zolgharnein et al., 2008).

In this study we investigated the potential of CLS to remove malachite green (MG) from aqueous solution. The influence of pH, temperature, reaction time, amount and size of adsorbent on the dye adsorption was investigated. The Taguchi design was utilized to find out the influencing optimization conditions. Also adsorption isotherm and kinetic studies were performed to find the adsorption mechanism and efficiency of CLS.

2. Materials and methods

2.1. *Cerastoderma lamarcki* shell sample

Cerastoderma lamarcki were collected from the Caspian Sea beach in Sari, Iran (Fig. 1).CLS were washed twice with double deionized water and then dried at 85 °C for 12 h in oven to remove moisture. CLS were crushed, powdered to small grains using a hammer mill into small particles of different sizes in the range of 74–425 μm. The morphology of the adsorbent was investigated using scanning electron microcopies LEO 1455 VP (Zeiss, Oberkochen, Germany). The SEM image of the adsorbent before contact with dye solution is presented in Fig. 2a; and the SEM images after contact with dye solution are shown in Fig. 2b and c.

2.2. *Chemical and reagent*

All chemicals were analytical grades and solutions were prepared with double deionized water from a hydroservice reverse