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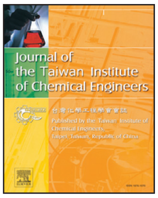

Removal of Congo red, methylene blue and Cr(VI) ions from water using natural serpentine

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ABSTRACT

Natural layered magnesium silicate mineral (serpentine) was investigated as an adsorbent material for three common water pollutants (methylene blue dye, Congo red dye, and Cr(VI) metal ions). The adsorption properties of serpentine were explored as a function of contact time, serpentine dosage, initial concentrations and the initial pH value. The kinetic studies uncovered that the equilibrium time for the adsorption of Congo dye, methylene blue dye, and Cr(VI) ions was acquired after 180 min, 240 min, and 480 min, respectively. The uptake process of all the examined pollutants is chemical adsorption and represented by pseudo-second-order kinetic model instead of by Intra-particle diffusion and Elovich kinetic models. The adsorption equilibrium modeling of methylene blue and Cr(VI) was described as a monolayer adsorption and fitted well with Langmuir model rather than with Freundlich or Temkin isotherm models. The adsorption of Congo red dye occurred in a multilayer form and fitted well with Freundlich isotherm than the other studied models. The adsorption of the three pollutants controlled for the most part by the pH value. The basic media is promising for the removal of methylene blue, while the acidic conditions are favored for the adsorption of Congo red dye and Cr(VI) metal ions. The thermodynamic parameters revealed that the adsorption of methylene blue dye is endothermic reaction while the adsorption of Congo red dye and Cr(VI) metal ions is an exothermic reaction. Modifying the serpentine surface through acid and thermal activation improve the removal of the contemplated pollutants to a high degree. Acid leached serpentine utilizing HCl acid of 15%concentration and thermally activated serpentine at 200 °C are the best- modified products for maximum removal of Congo red dye, methylene blue dye, and Cr(VI) metal ions. Fixed bed Colum study gives the best results at bed thickness 3 cm, flow rate 5 mL/min and initial concentration 25 mg/L

1. Introduction

In the most recent decade, the quick urbanization, industrialization, and financial advancement prompt a continuous release of toxic pollutants from heavy metals, dyes, synthetic manure and organic compounds into the encompassed water bodies which oftentimes cause water pollution. Heavy metals were characterized as elements which have atomic weights from 63.5 to 200.6, and a specific gravity above 5 [22]. Heavy metals are toxic non-biodegradable pollutants and tend to accumulate in the organisms tissue and human bodies which cause significant disorders as damage of the blood composition and damage of central nervous system [35,43,52]. There are several areas in the world suffering from pollution of water resources with high levels of heavy metals. This impairs the water quality, and their toxicity affects the safety of the living system [44,45]. Thus the removal of such water pollutants is critical demand.

Chromium element is one of the regular heavy metals that present in the aquatic environment in two fundamental structures; trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) [11]. The trivalent chromium is generally of low toxicity quality and ends up plainly toxic just at high concentrations. The hexava-

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lent chromium is extraordinarily harmful and cancer-causing element [7]. Hexavalent chromium is usually delivered as waste material from a few enterprises, for example, electroplating, pigment, chrome plating, leather tanning and metal finishing [10]. Hexavalent chromium show in two main forms of chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$); and both forms are highly toxic in nature [11,64]. Presences of (Cr(VI)) in high concentration cause several diseases as anuria, cancer, gastrointestinal ulceration and nephritis [42]. Moreover, Cr(VI) exhibits high affinity to bind to DNA causing damaging of the cellular components in addition to its carcinogenic effect [20,46]. 0.05 mg/L has been set by US regulations as the maximum limit for hexavalent chromium in water [11]. USEPA Drinking Water regulations limited total chromium in water to be under than 0.1 mg/L [51].

Around 100,000 types of dyes are produced with a yearly production rate of over 7×10^5 to 1×10^6 tons and utilized as a part of a few businesses, for example, material, textile, leather, paper, printing, paint, pigments, rubber and plastic [15]. Around 10 to 15% from the used dyes released into the encompassing condition and water bodies which cause sensitivity, dermatitis, cancer, skin irritation, dysfunction of kidneys, liver and reproductive system in people [4].

Adsorption by minimal effort and powerful materials gave off an impression of being all the more encouraging methodology and prescribed for the removal of heavy metals and dyes from water [23,66]. The adsorption process is simple, cheap, and easy to handle, less maintenance; and the amount of produced sludge is smaller than the other methods [23]. A few materials have been examined as adsorbents for such water pollutants as natural zeolite [19,63], activated carbon [58], fly ash [48], activated carbon and carbon nanotubes [25], ZnO nanorod-loaded activated carbon [24], bentonite [3], silica (Tran et al., 1999), clay [59], synthetic zeolite Y [33], natural and modified kaolinite (Bhattacharyya et al., 2008, [20]) .

Adsorption by clay minerals pulled in consideration of several authors for its low cost, high adsorption capacity, high cation exchange capacity, and high surface area [40,54]. Clay minerals are a class of layered silicate minerals that framed as secondary minerals during change or chemical weathering of silicate minerals [39,77]. The clay minerals were characterized into seven groups: (a) kaolinite-serpentinite, (b) pyrophyllite-talc, (c) smectite, (d) vermiculite, (e) mica, (f) chlorite, (g) interstratified clay minerals [41]. Be that as it may, the adsorption conduct of kaolinite, montmorillonite, and muscovite was seriously contemplated for this objective, the adsorption by other layered clay minerals including serpentine and chlorite have not been considered in detail [68].

Serpentinite is ultramafic rock made mainly of serpentine minerals that formed as an altered product for olivine and pyroxene minerals [49] Serpentine is a 2:1 clay mineral with hydrated magnesium silicate chemical composition and happen in three polymorphic types (antigorite, chrysotile, and lizardite) with chemical formula $Mg_3Si_2O_5\ (OH)_4$ [70,76]. Basically serpentine is worked from octahedral brucite-like layer $[MgO_2\ (OH)_4]$ between two layers of silicate tetrahedrons [49]. Serpentine is characterized by the abundance of several OH functional groups in addition to amounts of water molecules that bound to its surface [49]. Such functional groups are responsible for pH based surface charge and expected good adsorption properties, which has not been assessed in details until this point. As of late, the adsorption of Cd^{2+} and anionic textile dyes using serpentinite was considered by Momcilovic et al., [49] without referring to kinetic studies, isotherm modeling or the possible modification process.

Here we explore for the first time the adsorption of hexavalent chromium, Congo red acidic dye and methylene blue basic dye utilizing Egyptian serpentine. The adsorption study was performed as a function of pH, contact time, initial concentrations, adsorbent masses, temperature, and reusability of serpentine for several runs of adsorption. Several kinetic and isotherm models were addressed to explore the adsorption systems. Additionally, the improvement of the adsorption limit of serpentine through thermal and acid treatment process was examined. Extra, fixed bed column study for the adsorption of the studied pollutants using serpentine was evaluated in this study.

2. Experimental work

2.1. Material and methods

Serpentine samples were collected from El-Sid-Fawakhir quarry for crushed serpentinite, Quseir city, Eastern Desert, Egypt at the intersection of longitude 33 °32′–33°40′E and latitude 25°55′–26°05′N. The present mineral phases were distinguished from X-ray powder diffraction pattern using a Philips APD-3720 diffractometer with Cu Kα radiation, worked at 20 mA, 40 kV, and 2θ range 5–70° at a scanning speed of 5°/min. The Fourier Transform Infrared spectrometer (FTIR - 8400 S Shimadzu, Japan) was used to determine the chemical structural groups of serpentinite sample. The entire chemical analysis of the serpentine sample was performed by Analytical Axios Advanced XRF technique at Central Metallurgical Research and Development, Egypt.

Petrographic examinations are connected utilizing the Nikon transmitted polarized microscope instrument joined with PC program analysis to identify the occurrence of different mineral phases. The morphological properties of synthetic and natural zeolite were investigated using scanning electron microscopy (SEM) using a scanning electron microscope (JSM-6510, JEOL, and Tokyo, Japan). Particle size analyses, the size distribution of serpentine sample were determined using BT–2001 (wet) laser particle size analyzer technique. The specific surface area was estimated using Nova 2000 analyzer after degassing the samples at 100 °C for 2 h.

2.2. Adsorption experiments

Methylene blue and Congo red dye stock solutions were set up by dilution of pre-prepared standard dye solution (1000 ppm) the used dyes were obtained from the Lab-scan company, Poland. Chromium stock solutions were prepared by dilution of standard chromium solution (1000 mg/L) delivered from Sigma-Aldrich Company, Egypt. The pH value was adjusted using sodium hydroxide solution (0.1 N) and nitric acid solution (0.1 N) to be fixed at pH4. The used sodium hydroxide pellets and nitric acid were purchased from El Nasr pharmaceutical company, Egypt. All chemicals were of reagent grade and were used without purification.

2.2.1. Kinetic study

The adsorption kinetic experiments were completed by shaking 0.2 g of serpentine with100 mL (100 mg/L) of methylene blue, Congo red dye and chromium solutions for various time interims (from 30 min to 720 min) as separated experiments. The samples were centrifuged to separate the dye solution from the adsorbent, and the concentrations of dye were determined by UV–visible spectrophotometer, while the rest chromium concentration was distinguished utilizing inductively coupled plasma mass spectrometry (ICP-MS).

2.2.2. Effect of adsorbent dose

Effect of serpentine dose on the uptake capacity of the different water pollutants (methylene blue, Congo red dye and hexavalent chromium) was assessed by shaking different amounts of serpentine (0.02, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35 g) with 100 mL(100 mg/L) of methylene blue, Congo red and chromium solutions as separated experiments for 120 min. At that point, treated solutions

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