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Review

Silver nanoparticles immobilised on the activated carbon as efficient adsorbent for removal of crystal violet dye from aqueous solutions. A kinetic study

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ABSTRACT

The focus of the present work is on exploiting the excellent structural properties of the nanomaterials. More specifically, it is demonstrated that Ag nanoparticles (AgNPLs) chemically immobilised onto activated carbon (AC-AgNPLs) can act as an effective solid sorbent for removal and/or minimisation of selected crystal violet (CV) dye from aqueous solutions by conducting experiments on water samples. Spectroscopic tools such as FTIR, SEM, TEM and XRD were used in the characterisation of the adsorbent before and after adsorption. The adsorbent dose, pH, contact time, rotation velocity, initial concentration of adsorbate and the temperature effects were examined to evaluate their role in the percentage elimination of crystal violet. Crystal violet uptake was favourable in alkaline media at $pH > 7.0$, while the Langmuir model revealed CV monolayer adsorption capacity of 87.2 mg/g. The pseudo second-order model fitted the data well and the thermodynamic parameters (ΔH, ΔS, and ΔG) of CV retention revealed that the uptake is endothermic and spontaneous in nature. When AC-AgNPLs was utilised, it removed a greater CV percentage from aqueous solution relative to AC. The mechanism of adsorption was explored using the intra-particle diffusion model and the liquid-film model. Desorption studies were made to elucidate recovery of the adsorbate and adsorbent for the economic competitiveness of the removal system. The AC-AgNPLs was successfully recycled for seven successive adsorption–desorption cycles indicating its high reusability.

Contents

1. Introduction . . . 834
2. Experimental. . . . 834
    2.1. Materials . . . 834
    2.2. Instruments . . . 834
    2.3. Chemical impregnation of silver nanoparticles on activated charcoal . . . 834
    2.4. Batching experiment . . . 835
    2.5. Isotherm models . . . 835
    2.6. Adsorption kinetic modeling . . . 835
    2.7. Thermodynamic activation parameters . . . 835
3. Results and discussion . . . 835
    3.1. Characterisation of activated charcoal and activated charcoal-loaded nanosilver . . . 836
    3.2. Adsorption of crystal violet onto AC-AgNPLs . . . 836
        3.2.1. Effect of pH . . . 836
        3.2.2. Effect of contact time. . . . 837
        3.2.3. Effect of the rotation velocity . . . 837

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3.2.4. Effect of adsorbent dose . . . 837
3.2.5. Effect of initial concentration on crystal violet adsorption . . . 837
3.3. Adsorption isotherm models . . . 838
3.3.1. Freundlich isotherm . . . 838
3.3.2. Langmuir isotherm . . . 838
3.4. Kinetic models for the adsorption of crystal violet on AC-AgNPLs . . . 838
3.5. Thermodynamic parameters for the CV removal by AC-AgNPLs . . . 839
3.6. Regeneration and reusability studies . . . 840
4. Conclusions . . . 840
. . . 840
References . . . 840

1. Introduction

Adequate supply of clean water is essential for sustenance and continuation of life. Water pollution results from agricultural, industrial and domestic activities, due to which dyes, phenols, detergents, pesticides, insecticides, heavy metals and other pollutants are released into the environment [1]. This process can exert acute effects on exposed organisms due to the toxicity of the dyes [2]. As most of organic dyes are carcinogenic and toxic compounds, they pose a serious threat to humans and environment [3]. Pollution by organic dyes is one of the most significant environmental issues due to their ability to form compounds characterised by high biological toxicity. Owing to the extent of their potential detrimental effects, dyes must be eliminated from industrial effluents prior to their discharge into the environment. Adsorption is the most efficient dye removal method when these are present in aqueous solutions [4]. This technique is based on dye uptake from the water effluent to a solid phase extractor, thereby keeping the effluent volume to a minimum. Activated carbon is the most commonly used sorbent for the removal of dye from wastewaters.

Adsorption is one of the most promising and most extensively used methods for the removal of both organic and inorganic pollutants from contaminated water [5]. While different techniques for removing organic pollutants from wastewaters presently exist, adsorption is the most common, as it is relatively easy and cost-effective to implement as a fast and effective water treatment [6,7]. Owing to its effectiveness and versatility, activated carbon (AC) is a popular adsorbent for use in adsorption methods. AC is obtained from C-rich material and possesses great adsorption capacities, high porosity and specific surface area. Removal of crystal violet (CV) by activated carbon extracted from some agricultural wastes, such as rice husk [8], golbasi lignite [9] and peanut shell kernels [10], have been extensively investigated.

Recently, nanoparticles loaded on activated carbon as adsorbents have attracted considerable interest in this field, due to their high surface area to volume ratio and short diffusion route [11–13]. The nanoparticles of Fe_2O_3 and CuS loading on activated carbon were used in the removal of mixture of organic dyes and these adsorbents have the higher adsorption capacity than free activated carbon [11–13]. The nanoparticles loaded onto activated carbon as most conventional and popular material lead to increase in reactive center and adsorption capacity. Nano-particles possess distinguished properties such as high number of reactive atoms and large number of vacant reactive metallic or semi-metallic centers are applicable for accumulation for various functional and reactive groups (atoms) Extant studies indicate that silver nanoparticles (AgNPLs) coated onto AC can effectively adsorb methyl orange (MO) dye [14]. Silver nano-particles dispersed on granular coal-based activated carbon to effectively remove formaldehyde from air. It was believed that silver nano-particles could improve the adsorption of formaldehyde on activated carbon through two reasons, i.e. oxidation potential and larger specific surface area. Silver also possesses high applicability for use of controlling indoor air due to its non-toxic feature [15].

Chemical methods are commonly used in the preparation of nanoparticles, due to their considerable advantages relative to physical methods. The preparation of silver nanoparticles by chemical reduction methods in aqueous micellar media has been previously investigated [16]. The use of capping molecules led to better shape and size control, as well as greater stability and assembly of silver nanoparticles. Several capping agents, ranging from simple ions to various biomolecules, have been employed in previous studies aimed at improving nanomaterial stability [17]. In these processes, ionic and non-ionic surfactants are used as stabilising agent in nanomaterial synthesis.

In this work, the effectiveness of Ag nanoparticles (AgNPLs) chemically immobilised onto activated carbon (AC-AgNPLs) as a solid phase extractor used in the removal of crystal violet from aqueous solutions was examined. Particular focus was given to the retention profile, kinetics, thermodynamic characteristics, and sorption isotherms. The present investigation thus represents significant advancement in solving environmental issues pertaining to dye toxicity and its effects on human health.

2. Experimental

2.1. Materials

All chemicals, solvents and reagents used in the present study were of analytical grade and were purchased from BDH and Merck. The solutions were prepared using double-distilled water. A solution of 0.01 mol/L $AgNO_3$, 0.1 mol/L maltose, and different CV solutions (10–50 mg/L) were prepared from stock solution (1000 mg/L) and were used throughout the adsorption experiments. To prevent oxidation, fresh aqueous solutions of maltose and $AgNO_3$ were prepared. The AgNPLs were prepared by the reduction of $AgNO_3$ solution using maltose in aqueous medium in presence of micelles [17]. The pH was adjusted by the addition of small amounts of 0.1 mol/L NaOH and 0.1 HCl mol/L.

2.2. Instruments

All UV–visible measurements were determined using LABOMED, INC UVD-2960 and PerkinElmer EZ-150 recording spectrophotometers, as this allowed the CV absorbance onto the AgNPLs to be observed. SEM and TEM images were used to determine the AgNPL size using a JEOL, JEM-1011 and LEO 440i instruments, respectively, while the FTIR spectra were recorded using a Bruker Equinox 55 spectrophotometer employing KBr pellets. The solution temperature was adjusted using automatic circulation thermostat (Julabo GmbH, ME-4 TopTech series). The pH measurements were performed using a pH-meter (ATC-G353).

2.3. Chemical impregnation of silver nanoparticles on activated charcoal

Activated carbon (AC) was modified by heat treatment. In this experiment, AC was heated up to 450 °C for four hours after previously being washed with double-distilled water. An accurate weight of AC (1.0 g) was added to the prepared silver nanoparticles by stirring for 24 h in the dark. The samples were subsequently filtered and washed with deionised water, before being dried at 120 °C for two hours. The