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Study of competitive adsorption of malachite green and sunset yellow dyes on cadmium hydroxide nanowires loaded on activated carbon

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ABSTRACT

Cadmium hydroxide nanowires loaded on activated carbon ($Cd(OH)_2$-NW-AC) was applied for removal of malachite green (MG) and sunset yellow (SY) in single and binary component systems. This novel material was characterized and identified by different techniques such as Brunauer, Emmett and Teller (BET), scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis. Unique properties such as high surface area (>1271 $m^2\ g^{-1}$) and low pore size (<35 Å) and average particle size lower than 50 Å in addition to high reactive atom and presence of various functional groups make it possible for efficient removal of these two dyes. In the single component system in this study, maximum adsorption capacity of 80.6 for SY and 19.0 mg g^{-1} for MG at 25 °C was reported. The Langmuir model had very well fit with the experimental data ($R^2 > 0.996$). A better agreement between the adsorption equilibrium data and mono-component Langmuir isotherm model was found. The kinetics of adsorption for single and binary mixture solutions at different initial dye concentrations were evaluated by the nonlinear first-order and second-order models. The second-order kinetic model had very well fit with the dynamical adsorption behavior of a single dye for lower and higher initial dye concentrations. SY and MG without spectra overlapping were chosen and analyzed with high accuracy in binary solutions. The effect of multi-solute systems on the adsorption capacity was investigated. The isotherm constants for SY and MG were also calculated in binary component systems at concentrations within moderate ranges, the Langmuir isotherm model satisfactorily predicted multi-component adsorption equilibrium data. The competitive adsorption favored the SY in the A mixture solution (both SY and MG concentration at 10 mg L^{-1}) and B mixture solution (25 mg L^{-1} of SY and 10 mg L^{-1} of MG). Also, in both cases, kinetic data was fairly described by two-step diffusion model. An endothermic and spontaneous nature for the adsorption of the dyes studied were shown from thermodynamic parameters in single and binary component systems.

1. Introduction

Effluent comes from the textile industry particularly generates problem for human and other environment that is due to the presence of color in the final effluent. The color and dyes following, entering to the water systems are dark enough and undesirable. Conventional treatment procedures are unable to remove certain forms of color (particularly reactive dyes) due to their high solubility and low biodegradability. The failure of conventional physiochemical technique for treating reactive dye waste could be overcome by adsorption, especially based on high adsorption capacity nano scale based adsorbent. The advantages such as low cost, high adsorption of regenerable adsorbent make adsorption as recommended viable means for reactive dye removal [1–6]. Azo and triphenylmethane dyes are the largest classes of commercially produced colorants. Azo dyes are famous to the presence of chromophoric azo group and triphenylmethane dyes contain chromophore based on three phenyl groups bound to the central carbon. They are used for coloring paper, food, cosmetics, textiles, leather, medical treatment and analysis [7–11]. The reduction in dyes concentration may be achieved by physicochemical and biological processes. The conventional physicochemical methods of dyes removal include flocculation, flotation, oxidation, reduction, ozonation, coagulation and membrane separation [12–15]. Among various dye removal processes, adsorption is superior because of its simplicity and low cost in addition of reusability of nontoxic adsorbent; one of the most important properties of the adsorbent which significantly increases the efficiency of the removal process is its surface area and functional atom or group. Nano scale material benefit from advantages such as high surface

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Nomenclatures

C_t	dye concentration (mg L^{-1}) at time t
Q_e	equilibrium adsorption capacity (mg g^{-1})
C_e	dye concentration (mg L^{-1}) at equilibrium
V	volume of solution (L)
W	weight of adsorbent (g)
k_1	rate constant of pseudofirst order adsorption (min^{-1})
k_2	second-order rate constant of adsorption (mg g^{-1} min^{-1})
H	second-order rate constants (mg g^{-1} min^{-1})
α	initial adsorption rate (mg g^{-1} min^{-1})
β	desorption constant (mg g^{-1})
C	intercept of intraparticle diffusion (related to the thickness of the boundary layer)
K_{dif}	rate constant of intraparticle diffusion (mg g^{-1} $min^{-1/2}$)
F	fraction of solute adsorbed at any time t (mg g^{-1})
D_i	effective diffusion coefficient of adsorbate in adsorbent phase
r^2	radius of adsorbent particles (m)
Q_m	maximum adsorption capacity reflected a complete monolayer (mg g^{-1}) in Langmuir isotherm model
K_a	Langmuir constant or adsorption equilibrium constant (L mg^{-1}) that is related to the apparent energy of sorption
RL	Dimensionless equilibrium parameter (separation factor)
K_F	isotherm constant indicate the capacity parameter (mg g^{-1}) related to the intensity of the adsorption
N	isotherm constant indicate the empirical parameter (g L^{-1}) related to the intensity of the adsorption
T	absolute temperature in Kelvin
R	universal gas constant (8.314 J K^{-1} mol^{-1})
B_1	related to the heat of adsorption (B1 = RT/b)
b_T	constant related to the heat of adsorption
K_T	equilibrium binding constant
K	constant related to the adsorption energy at the D-R isotherm (mol^2 kJ^{-2})
Q_m	theoretical saturation capacity at the D-R isotherm
ε	Polanyi potential at the D-R isotherm
E	mean free energy of adsorption
A	isotherm constants in the Harkins_Jura adsorption isotherm
X^2	chi-squared test statistic
$q_{e,exp}$	experimental data of the equilibrium capacity (mg g^{-1})
$q_{e,calc}$	equilibrium capacity obtained by calculating from the isotherm model (mg g^{-1})
R^2	correlation coefficient

reactive atom, large surface area with porous structure. These advantages improve the dye adsorption efficiency. Cadmium hydroxide nanowire due to its ordered structure, high aspect ratio, ultra-light weight, high mechanical strength and high surface area is suitable for adsorption [16,17]. Such adsorbents can bind to dye molecules through general mode via AC and soft–soft or hard–hard interaction via their metallic center or hydroxide group at nanoscale.

In the last few years, various adsorbents were applied for various dyes removal from aqueous solutions. In these studies, mainly, single component systems have been investigated [18–23]. Most industrial wastewaters contain more than one pollutant and require strong effort to treat them. An investigation into the effects of multi-solute systems on the adsorption capacity is practically important. Therefore, in the present work, ($Cd(OH)_2$-NW-AC) was used for the competitive adsorption of sunset yellow (SY) and malachite green(MG) dye from aqueous solution [24–30].

2. Experimental

2.1. Materials and instruments

Applied reagents such as NaOH, HCl, KCl with the analytical reagent grade were purchased from Merck (Darmstadt, Germany). Reactive SY and MG dyes (Scheme 1) were supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia. The dyes stock solutions were prepared from corresponding pure dried solid materials. The wavelengths for the measurement and quantification of dyes concentration were 412 and 627 nm for sunset yellow and malachite green, respectively. The concentration of the dyes was determined at these wavelengths using Jusco UV-Visible spectrophotometer model V-530 from Japan according to calibration curve obtained at the same conditions, pH/Ion meter model-686 (Metrohm, Switzerland), thermometer Metrohm, international ASTM sieves and Stirrer model UKA are also used in this study. The field emission scanning electron microscopy (FESEM) was performed on Hitachi, model S-4160, Japan. A BET surface analyzer (Quantachrome NOVA 2000, USA) was used to measure nitrogen adsorption–desorption isotherm at 77 K. Before each study, the samples were degassed via helium purging at 553 K for 3 h. The BET experiments give useful information on the adsorbent properties such as surface area, total pore volume and micro pore area. The $Cd(OH)_2$-NW-AC was synthesized according to previous publication [31].

2.2. Adsorption test

Stock solution of dyes in aqueous were prepared by dissolving accurately weighed amount of solid dye in distilled water to the required concentration. The batch sorption experiments were carried out in 100 mL Erlenmeyer flasks, where 0.005–0.06 g of the $Cd(OH)_2$-NW-AC and 50 ml of the MG solutions(5–15 mg L^{-1}) and the SY solutions (10–25 mg L^{-1}) were added following pH adjustment. Experimental solutions were obtained by successive dilutions. The pH of the dye solutions was adjusted by applied reagents of NaOH/HCl (0.1 M). The Erlenmeyer flasks were subsequently capped and agitated for up to 30–35 min at 400 rpm in an isothermal shaker at room temperature to achieve equilibrium. At the end of the equilibrium period, the solutions were filtered to separate the $Cd(OH)_2$-NW-AC and the residual concentration of SY or MG in the filtrate quantified by UV/Visible spectrophotometer. The data obtained from adsorption tests was used to calculate the adsorption capacity, q_t (mg g^{-1}) of the adsorbent by mass-balance relationship according to below equation:

$$q_t = \frac{v(C_{0-}C_e)}{w} \quad (1)$$

where C_0 is the initial dye concentration (mg L^{-1}) in the solution; C_e is the residual dye concentration (mg L^{-1}) at equilibrium; V is the volume (L) of the solution; and W is the weight (g) of the adsorbent used.