

Abstract

The present work explores, for the first time, the adsorptive removal of methylene blue (MB) dye from aqueous solution at very high dye concentrations using different parts of abundantly available agricultural waste, namely overripe *Abelmoschus esculentus* (lady's finger) seedpods, with the processed seed powder (designated as AESP) being the most effective. The as-prepared materials were then used to remove acridine orange (AO) and Nile blue A (NB) dyes from single-component liquid wastes. This study also looked into the production of environmentally friendly and cost-effective biosorbents from as-prepared AESP materials using thermodynamically-controlled esterification in the presence of oxalic, citric and tartaric acids, which are referred to as OA-AESP, CA-AESP and TA-AESP, respectively. These AESP materials with di- and tri-carboxylic acid modifications were used to remove hazardous gentian violet (GV) dye from single-component liquid wastes. The pristine and modified biosorbents were characterized using field emission scanning electron microscopy (FESEM), Fourier transform infrared (FTIR) spectroscopy, X-ray powder diffraction (XRD), particle size distribution, diffuse reflectance spectroscopy (DRS), thermogravimetric analysis (TGA), Brunauer-Emmett-Teller (BET) surface area analysis, structural and elemental composition, and point of zero charge (pH_{ZPC}) analyses. Batch studies were used to evaluate adsorption performance at a predetermined temperature under varying operating conditions such as solution pH, biosorbent dose, initial dye concentration and contact time. In case of MB dye removal, the obtained results were used to determine the applicability of two-parameter adsorption isotherms, namely the Freundlich and Langmuir models. However, the applicability of multi-parameter adsorption isotherms was performed in the removal of AO, NB and GV dyes. For each isotherm model, the experimental and calculated q_e values were compared. The higher degree of R^2 and lower percentage non-linear error values indicated that the MB dye followed the Langmuir and Temkin isotherms better, whereas the AO, NB and GV dyes followed the Fritz-Schlunder-V isotherm, Sips isotherm and Redlich-Peterson isotherm, respectively. Similarly, kinetic studies revealed that the adsorption of MB and AO dyes followed the pseudo-second-order kinetic model, whereas the time-dependent experimental data for NB and GV dyes were simulated in higher-order parametric equations, indicating that the adsorption processes here followed the fractal-like pseudo-first-order kinetic model. All adsorption processes were found to be governed by both film and intra-particle diffusions. Thermodynamic properties (ΔG , ΔH and ΔS) were calculated, and all processes were found to be endothermic, favourable and spontaneous. Following that, MB desorption from MB-adsorbed AESP could be accomplished with 0.5 M HCl solution, whereas AO and NB desorption from AO- and NB-adsorbed AESP, respectively, could be accomplished with 0.1 M HCl solution. On the other hand, desorption of GV dye from exhausted carboxylic acid-modified AESPs by 0.1 M HCl solution was advantageous, making them promising sorbent materials for real-field applications because they retain their high adsorption efficiency even after three adsorption-desorption cycles. The problems associated with the use of

old kinetic models were also addressed, and a novel three-parametric kinetic model called the normalized Gudermannian kinetic equation was proposed, which predicted the equilibrium adsorption time very accurately at different initial dye concentrations and could be used to configure large-scale industrial reactors. The multi-variate optimization of the adsorption process variables targeting maximum sorption capacity for the predefined dye eradication by the prepared biosorbents and the analysis of variance (ANOVA) results of the proposed quadratic equations through central composite design (CCD) of response surface methodology (RSM) revealed their interactive effects among the significant independent process variables on the performance of the biosorbents as well as the overall optima of the adsorption process. In addition, the adsorption process was performed with multi-variate optimization by employing the artificial neural network technique and then modifying it to obtain the optimized ANN architecture. The present study also included the simultaneous removal of GV and NB dyes from binary-component liquid wastes at high dye concentrations using AESP, which simulated one of the most important conditions found in real textile effluent. The adsorption potentiality of GV and NB dyes in the binary mixture was determined using the first-order derivative spectrophotometric method. Here, a CCD matrix was used to configure experiments for this complex binary mixture, and the RSM method was used to analyze the significance of important parameters and potential interactions. The results demonstrated that the presence of GV and NB dyes in the binary solution created a competition for the biosorbent sites; consequently, the interaction of dyes was one of the most important factors to be investigated in order to simulate the real effluent. With $R^2 > 0.97$, the predicted values for the removal efficiencies of GV and NB dyes from the binary mixture using the AESP biosorbent, were in excellent agreement with the remarkable removal efficiencies of both dyes observed in the experiment.

Keywords: Dye adsorption, Overripe *Abelmoschus esculentus* seeds, Carboxylic acid modification, Normalized Gudermannian model, Multi-variate optimization, Response surface methodology, Artificial neural network, Derivative spectrophotometric method