Efficient Removal of Crystal Violet and Orange G Dyes Using Modified Chlorella Vulgaris:

Optimization, Kinetics, and Thermodynamics

by

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Abstract

The rapid increase in population led to a massive escalation in different industries, one of which

is dye-based industries and the rise in the use of textiles, leather, and paper. In this work, the

Chlorella vulgaris algae has grown and used as a reliable adsorbent to remove dyes from aqueous

solutions.

The algae growth process was conducted in the 250 ml flask, transparent photobioreactor, and

airlift bioreactor. The 1L Airlift bioreactor is transparent and its dimensions are 34 cm in length

and 7 cm in internal diameter, split in the middle into two sections riser and downcomer with air

sparger in riser section. Chlorella vulgaris was cultivated from medium every 16 days, then after

the growth step the algae was dried, washed and treated with Hydrochloric acid (HCl).

The dried algae was then modified using Ferric Chloride ($FeCl_3$). The algae was mixed in a (2M)

Ferric Chloride solution for 24 hours, washed several times to remove excess, and dried.

The dried algae was used to remove the Crystal Violet (cationic dye) and the modified algae was

used to remove the Orange G (anionic dye) from the aqueous solution. The experimental work was

conducted in two sections batch and semi-batch. The batch section was performed in 250 ml

Erlenmeyer flasks and the semi-batch was conducted in an Airlift Bioreactor. Several factors were

changed to study their effect on the removal process, algae dosage (0.3- 1.8 g/L) for dried algae

and (0.2-1.4 g/L) for modified algae, initial dye concentration (10-40 ppm), pH (3-10), time (5-60

min), airflow (5-40 ml/min), and temperature (20-40 OC).

Several tests were conducted in this work. The dye concentration was measured using a Visible

Spectrophotometer, Fourier transform infrared spectroscopy (FTIR), The Scanning Electron Microscope

(SEM), and Energy-Dispersive X-ray spectroscopy (EDS) was performed on algae particles before and

after the Ferric-Chloride modified process and after the adsorption of two dyes, The X-ray

Diffraction (XRD), Thermogravimetric analysis, The Point of Zero Charge (PZC), and BET surface area

were performed on algae particles before and after the Ferric-Chloride modified process.

The experimental results show that the Crystal violet removal by dried algae and Orange G dye

removal by Ferric-Chloride modified algae were both high, reaching 96.1% and 93.5% respectively.

The highest absorption capacity was 108.01 mg/g and 63.4 mg/g for Crystal violet and Orange G

removal respectively, at the condition of (0.3 g/L dried algae, 0.2 g/L Ferric- modified algae in

Batch experiments) at 40 ppm initial dye concentration, pH 7, temperature 20 OC, shaking at 350

rpm, and 60 min contact time.

The thermodynamics parameters (ΔHO, ΔSO, ΔGO) studied showed that the Crystal violet removal was

exothermic and spontaneous, and Orange G removal was endothermic and spontaneous. The kinetic model

was investigated, and the two kinetics pseudo-first-order (PFO) and pseudo- second-order (PSO) were

studied using the experimental data. The results reveal that the pseudo-second-order was best

fitted for the two dyes removal with the highest correlation coefficient R^2 of 0.999 for the two.

The Isotherm model study was investigated using the Freundlich, Langmuir and Temkin models. The

result of the data was best fitted with the Langmuir model with the highest R^2 of 0.9974 for

Crystal Violet and 0.9564 for Orange G fitting the data very well.

Finally, study mass transfer adsorption models were examined using the Weber and Morris model and

Liquid film diffusion. the Liquid diffusion model was best fitted for both two dyes removal with

the highest R^2. Of 0.9815 for Crystal Violet and 0.9482 for Orange G.

The Design Expert with a 3-level factorial was used to get the mathematical model that describes

the process. The optimum condition for Crystal Violet removal gives a maximum removal of 97.938% of

initial concentration of 37.64 ppm, a pH of 6.43, at a temperature of 25.73 OC, and a time of 20.68

min, and for Orange G removal that gives a maximum removal of 93.5% was the initial concentration

of 30 ppm, pH of 3, the temperature of 40 OC, and time of 30 min.