Selective adsorption of multi-dye ions by Citrus Peel: Characterization, Performance, Regeneration

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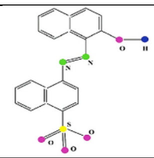
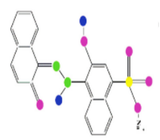
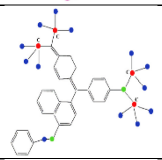
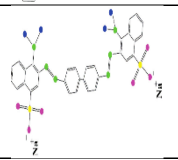
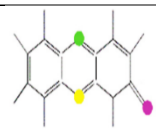
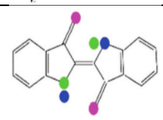
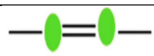
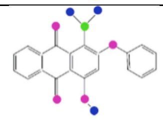
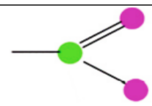
Abstract The irrefutable harmful components of wastewater originating from the textile industry are dyes. For this reason, it is accepted as an important environmental and health problem. A large number of natural adsorbents have been used for the efficient removal of industry-sourced dyes. In this study, removability was investigated of methylene blue (MB) and reactive black-5 (RB-5) which are used as dyestuffs in many industries by using Citrus Peel (CP), which is an environmentally friendly, economical, and easily accessible adsorbent with high removal potential. For this purpose, the batch adsorption method was applied to remove dyes from industrial synthetic wastewater. The main parameters affecting the adsorption process such as initial dye doses, citrus peel amount, pH, and contact time were studied in single, double, and triple combinations. Scanning Electron Microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FTIR) were used to determine the properties of the Citrus Peel surface before and after adsorption. Citrus Peel was regenerated after loading with dyestuffs and its reusability was investigated. The results obtained show that the removal efficiency of raw Citrus Peel is highly dependent on the dye types and reveals that it can be an effective adsorbent to remove these dyes.

Keywords: Adsorption, Citrus Peel, Dyestuff, Color removal

1. Introduction

Water is of vital importance among the sine qua non of human beings. Pollution of water has a synergetic structure that also affects other ecosystems. Therefore, it is important to remove the wastewater generated after use in a healthy and reliable (Dutta et al., 2021). The reasons such as rapid population growth, excessive consumption, and increase in energy and food needs in recent years constitute environmental problems. What has been done to solve these problems has accelerated industrialization. Industries that include dyes with different properties in their wastewater are the leading industrial organizations that increase environmental pollution and play an important role in the deterioration of the ecological balance (Chikri et al., 2020; Rápó & Tonk, 2021). Methylene blue (MB) and Reactive Black-5 (RB-5) are among the most consumed and polluting dyestuffs in the paint industry (Ben Mbarek et al., 2023; Danso-Boateng et al., 2023). These dyestuffs originating from different industries such as textile, cosmetics, leather, food, medicine, paint and varnish, and pulp production are among the most important sources of industrial pollutants (Table 1) (Ishak et al., 2020; Yeow et al., 2020).

Table 1. Classification and chemical structure of dyestuffs (Dutta et al., 2021).

Class	Chemical Structure	Class	Chemical Structure
Acid		**Mordan**	
Basic		**Reactive**	
Direct		**Sulfur**	
Vat		**Azo**	
Disperse		**Nitro**	

Dyes and dyestuffs are soluble and used as colorants, especially in the textile industry (Benkhaya et al., 2020; Donkadokula et al., 2020). In the structure of dyes and dyestuffs, chromophore, autochrome and matrix design can be realized (Slama et al., 2021; Umar et al., 2021). Binding affinity groups can be listed as $-NHX_2$, -OH, -COOH, -CHO, $-SO_3H$ (Dutta et al., 2021; Rápó & Tonk, 2021). Some functional radicals such as -N=N-; =C=O; =C=C=C=; >C=NH/-CH=N-; -NO/N-OH; -NO/=NO-OH; and >C=S in the structural properties of dyes can be advantageous in removal by adsorption (Berradi et al., 2019). The main source of dye waste given to the receiving environment is the textile (54%) and dye (21%) industries, and many industries also contribute to waste generation (Benkhaya et al., 2020). Wastewater containing dyes is very dangerous in terms of pollution load (biological/chemical oxygen demand, suspended solids etc.) and is difficult to treat (Al-Tohamy et al., 2022).

Processes related to dyestuff treatment can be separated into 3 basic classes: physical (adsorption, membrane separation, reverse osmosis, ion exchange, etc.), chemical (catalytic reduction, coagulation/flocculation, electrochemical and photochemical reduction, advanced oxidation processes, etc.) and biological methods (bacterial, algae, fungi, mycoremediation, enzyme degradation, phytoremediation, etc.) (Choi & Lee, 2022; Kishor et al., 2021). Most of these methods have various limitations such as high investment and operating costs, disposal of the formed sludge and inability to be applied to small-scale industries. Therefore, low-cost designs are required to remove dyestuffs from wastewater. In this regard, the use of adsorbents, which are easily available and can remove dyestuffs in wastewater, is a suitable option. Adsorption is currently accepted as an effective and economical method for dye removal from wastewater. The adsorption process is a more advantageous process than other methods due to its simple design, cheap, fast, high efficiency, and eco-friendly.

Nowadays, natural materials (agricultural/food wastes, clay, pumice stone, zeolite, etc.) are preferred instead of commercial adsorbent use in the adsorption method (Kumar et al., 2022; Rathi & Kumar, 2021; Selvaraj et al., 2021). Especially it is preferred to remove waste with the waste these days. The most important reasons why adsorbents obtained from wastes are preferred are that they are easily available and low cost. Fruits have a great place in the daily nutrition of people. The citrus group is a fruit also grown in many countries and consumed worldwide (Çelebi et al., 2023). In this study, orange, tangerine, and grapefruit peels mixed as citrus peels (CP) were evaluated together. Within the scope of the study, batch experiments were carried out based on the basic operating parameters of adsorption. Singular (MB, RB-5) and multiple (MB and RB-5 together) removals were investigated using CP at different pH, time, and dose values. The surface structure and functional groups and elemental distribution of CP are given as the preliminary findings of the study.

2. Material and Methods

CP selected as adsorbent was obtained from orange, tangerine, and grapefruit fruits are grown in the Mediterranean region. Firstly, the orange, tangerine, and grapefruit peels that generated the CP were weighed in equal proportions. In order to remove dirt, dust, and different contaminations that may be on the surface of these peels, washing was done with distilled water at 20 ^{0}C obtained from a pure water device Millipore Elix Advantage brand. After the washing process, it was dried in a Memmert oven at 100 °C for 24 hours. In the last step, the dried CP material was ground into powder form. Model dyes MB and RB-5 were provided by Sigma-Aldrich. Typical properties and chemical structures of these dyes are shown in Figure 1. A dye solution was prepared separately in 1 L of distilled water by weighing 0.5 g of MB and RB-5 in powder form. λ_{max} values were measured with a Shimadzu UV-1200 brand UV/VIS spectrometer and peaks were obtained at 663 nm for MB and 597 nm for RB-5. The surface morphology and element distribution of CP were examined by scanning electron microscopy (SEM/EDX) (Hitachi-SU 1510). The functional groups of the material were carried out with Perkin Elmer brand Fourier Transform Infrared Spectroscopy (FTIR) device in the range of 400-4000cm^{-1}. Adsorption studies were carried out in batch mode. Erlenmeyer flasks with constant dye concentration were processed in a ZHICHENG brand shaker at a constant mixing speed of 150 rpm and a constant temperature of 25 °C. 0.1 M NaOH/HCl solutions were used to adjust the pH. pH, time, and CP doses are tested at different values, and MB, RB-5 removal efficiencies at equilibrium “R (%)” and adsorption capacity of CP “qe (mg/g)” are calculated according to the formulas below.

$$q_e = \frac{(C_0 - C_e) \text{ x } V}{1000 \text{ x } m}$$

$$R\ (\%) = \frac{(C_0 - C_e)}{C_0} \text{x}100$$

Where; R: MB, RB-5 yield (%), C_0 and C_e: Initial and final concentrations (mg/L), m: CP dose (mg), V: solution volume (mL).

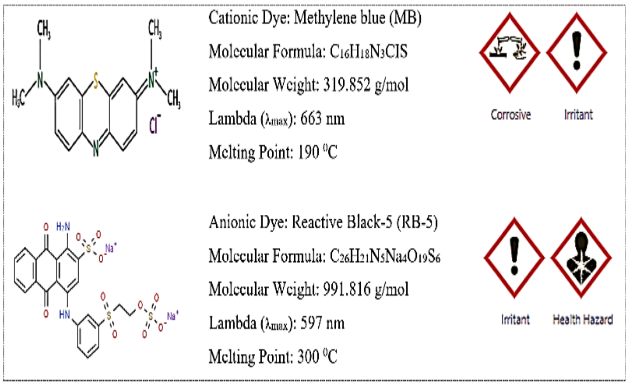


Figure 1. Description of MB and RB-5

3. Results and Discussion

The SEM and EDX distribution of CP are shown in Figure 2. Before batch adsorption experiments, the raw CP surface resembles a confetti-like structure at 250x magnification. The 1000x SEM images show that the surface has a heterogeneous/amorphous microporous structure. The surface element distribution of CP was evaluated by EDX analysis (Figure 2). EDX data showed that CP was composed of high percentages of C (53.09%) and O (44.66%). Trace element N on the surface is 2.25% by weight. The FTIR analysis to detect the functional groups of the CP is shown in Figure 3 as typical spectrum peaks. As seen in Figure 3, large peaks at 3288.76 cm^{-1} and 2920.08 cm^{-1} indicate the presence of O-H (hydroxyl) stretching. C-O-H band forms were observed at the peaks of 1732.72 and 1608.10 cm^{-1}. (Aragaw & Alene, 2022; Badawi et al., 2021). The peaks observed at 1367.12, 1234.86 and 1015.03 cm^{-1} can be attributed to the C=O, C-H and C-C stretching vibrations of the carboxylic groups attached to the carboxylic acids (Al Ashik et al., 2023; Du et al., 2023). Peaks of 814.99, 602.80, and 556.28 cm^{-1} in the fingerprint region show special vibrations such as O-H, C=C and C-H bending and C-O, C-N, C-I and S=O stretching in this region. According to the FTIR analysis, these functional groups in the amorphous CP contribute to the MB and RB-5 removal process.

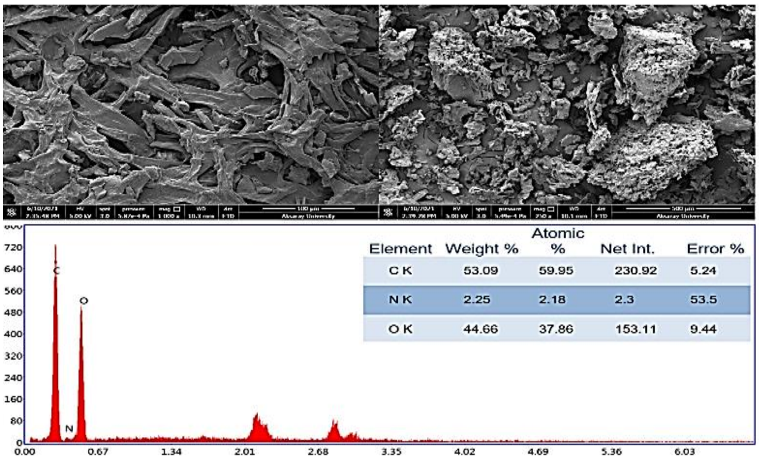


Figure 2. SEM images and EDX distribution of CP

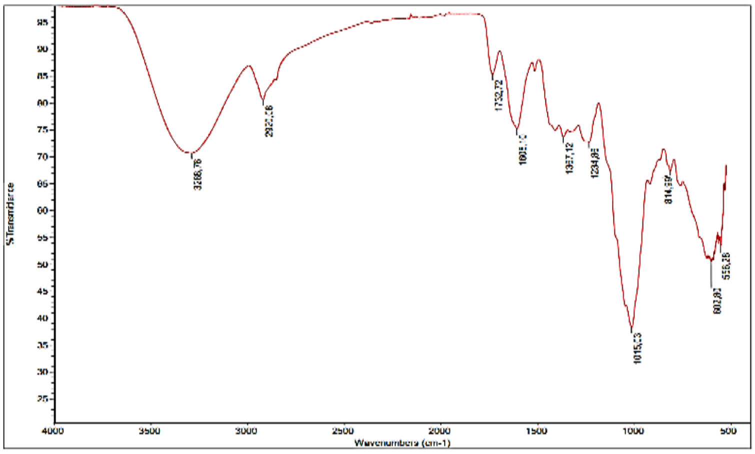


Figure 3. FT-IR spectrum distribution of CP adsorbent

4. Conclusions

The removal of MB and RB-5 from the synthetic solution was evaluated in terms of morphological and functional distribution with batch parameter-based experiments using organic CP. SEM images of CP showed that the surface was heterogeneous/amorphous, microporous. According to EDX results, carbon (C) and oxygen (O) were found intensely. Four main functional groups were identified for CP: O–H, C–H, and C=C and C–O. It can be said that CP is a suitable adsorbent for MB and RB-5 removal in water and can be widely applied in the future.

References

Al-Tohamy, R., Ali, S.S., Li, F., Okasha, K.M., Mahmoud, Y.A.-G., Elsamahy, T., Jiao, H., Fu, Y. and Sun, J. (2022). A critical review on the treatment of dye-containing wastewater: Ecotoxicological and health concerns of textile dyes and possible remediation approaches for environmental safety. *Ecotoxicology and Environmental Safety*, **231**, 113160.

Al Ashik, A., Rahman, M.A., Halder, D. and Hossain, M.M. (2023). Removal of methylene blue from aqueous solution by coconut coir dust as a low-cost adsorbent. *Applied Water Science*, **13**, 81.

Aragaw, T.A. and Alene, A.N. (2022). A comparative study of acidic, basic, and reactive dyes adsorption from aqueous solution onto kaolin adsorbent: Effect of operating parameters, isotherms, kinetics, and thermodynamics. *Emerging Contaminants*, **8**, 59–74.

Badawi, A.K., Abd Elkodous, M. and Ali, G.A.M. (2021). Recent advances in dye and metal ion removal using efficient adsorbents and novel nano-based materials: an overview. *RSC Advances*, **11**, 36528–36553.

Ben Mbarek, W., Daza, J., Escoda, L., Fiol, N., Pineda, E., Khitouni, M. and Suñol, J.-J. (2023). Removal of Reactive Black 5 Azo Dye from Aqueous Solutions by a Combination of Reduction and Natural Adsorbents Processes. *Metals*, **13**, 474.

Benkhaya, S., M' rabet, S. and El Harfi, A. (2020). A review on classifications, recent synthesis and applications of textile dyes. *Inorganic Chemistry Communications*, **115**, 107891.

Berradi, M., Hsissou, R., Khudhair, M., Assouag, M., Cherkaoui, O., El Bachiri, A. and El Harfi, A. (2019). Textile finishing dyes and their impact on aquatic environs. *Heliyon*, **5**, e02711.

Çelebi, H., Şimşek, İ., Bahadir, T. and Tulun, Ş. (2023). Use of banana peel for the removal of boron from aqueous solutions in the batch adsorption system. *International Journal of Environmental Science and Technology*, **20**, 161–176.

Chikri, R., Elhadiri, N., Benchanaa, M. and El maguana, Y. (2020). Efficiency of Sawdust as Low-Cost Adsorbent for Dyes Removal. *Journal of Chemistry*, **2020**, 8813420.

Choi, W. S. and Lee, H.-J. (2022). Nanostructured Materials for Water Purification: Adsorption of Heavy Metal Ions and Organic Dyes. *Polymers*, **14**, 2183.

Danso-Boateng, E., Fitzsimmons, M., Ross, A.B. and Mariner, T. (2023). Response Surface Modelling of Methylene Blue Adsorption onto Seaweed, Coconut Shell and Oak Wood Hydrochars. *Water*, **15**, 977.

Donkadokula, N.Y., Kola, A.K., Naz, I. and Saroj, D. (2020). A review on advanced physico-chemical and biological textile dye wastewater treatment techniques. *Reviews in Environmental Science and Bio/Technology*, **19**, 543–560.

Du, P., Zhang, J., Cai, Z. and Ge, F. (2023). High adsorption of cationic dyes from aqueous solution using worm-like porous nanosilica: Isotherm, kinetics and thermodynamics. *Materials Today Communications*, **35**, 105697.

Dutta, S., Gupta, B., Srivastava, S.K. and Gupta, A.K. (2021). Recent advances on the removal of dyes from wastewater using various adsorbents: a critical review. *Materials Advances*, **2**, 4497–4531.

Ishak, S.A., Murshed, M.F., Md Akil, H., Ismail, N., Md Rasib, S.Z. and Al-Gheethi, A.A.S. (2020). The Application of Modified Natural Polymers in Toxicant Dye Compounds Wastewater: A Review. *Water*, **12**, 2032.

Kishor, R., Purchase, D., Saratale, G.D., Saratale, R.G., Ferreira, L.F.R., Bilal, M., Chandra, R. and Bharagava, R.N. (2021). Ecotoxicological and health concerns of persistent coloring pollutants of textile industry wastewater and treatment approaches for environmental safety. *Journal of Environmental Chemical Engineering*, **9**, 105012.

Kumar, R., Qureshi, M., Vishwakarma, D.K., Al-Ansari, N., Kuriqi, A., Elbeltagi, A. and Saraswat, A. (2022). A review on emerging water contaminants and the application of sustainable removal technologies. *Case Studies in Chemical and Environmental Engineering*, **6**, 100219.

Rápó, E. and Tonk, S. (2021). Factors Affecting Synthetic Dye Adsorption; Desorption Studies: A Review of Results from the Last Five Years (2017–2021). *Molecules*, **26**, 5419.

Rathi, B.S. and Kumar, P.S. (2021). Application of adsorption process for effective removal of emerging contaminants from water and wastewater. *Environmental Pollution*, **280**, 116995.

Selvaraj, V., Swarna Karthika, T., Mansiya, C. and Alagar, M. (2021). An over review on recently developed techniques, mechanisms and intermediate involved in the advanced azo dye degradation for industrial applications. *Journal of Molecular Structure*, **1224**, 129195.

Slama, H. Ben, Chenari Bouket, A., Pourhassan, Z., Alenezi, F. N., Silini, A., Cherif-Silini, H., Oszako, T., Luptakova, L., Golińska, P. and Belbahri, L. (2021). Diversity of Synthetic Dyes from Textile Industries, Discharge Impacts and Treatment Methods. *Applied Sciences*, **11**, 6255.

Umar, A., Khan, M.S., Alam, S., Zekker, I., Burlakovs, J., Dc Rubin, S.S., Bhowmick, G.D., Kallistova, A., Pimenov, N. and Zahoor, M. (2021). Article synthesis and characterization of Pd-Ni bimetallic nanoparticles as efficient adsorbent for the removal of acid orange 8 present in wastewater. *Water*, **13**, 1095.

Yeow, P.K., Wong, S.W. and Hadibarata, T. (2020). Removal of Azo and Anthraquinone Dye by Plant Biomass as Adsorbent – A Review. *Biointerface Research in Applied Chemistry*, **11**, 8218–8232.