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Enhanced Removal of Everzol Orange and Supra Yellow Dyes from Wastewater using Optimized Multi-Layred Fixed-Bed Columns with Hibred Adsorbents of Blended Rice Husk and Carbonized Palm Shell

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تحسين إزالة صبغات ايفرزول البرتقالي وسوبرا الأصفر من مياه الصرف باستخدام أعمدة ذات طبقات متعددة محسنة ومواد هجينة ماصة مخلوطة من قشور النخيل وقش الأرز المكربنة

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Abstract:
The global shortage of safe drinking water due to contamination by pollutants, particularly synthetic dyes, poses significant environmental and health challenges. This study investigates the adsorption of Everzol Orange 3R (EO-D) and Supra Yellow RL (SY-D) dyes from simulated wastewater using combined modified adsorbents derived from blended rice husk and carbonized palm shell (BRH-CPS) in a multi-layered fixed-bed columns system. Six types of adsorbents were prepared, including pure BRH, pure CPS, and four hybrid adsorbents with varying BRH:CPS ratios (20%, 40%, 60%, 80%). Each adsorbent was characterized through element analysis, BET surface area measurements, and field emission scanning electron microscopy (FESEM). Performance was evaluated using removal efficiency and area under the graph analysis. The results demonstrated that the hybrid adsorbent of 20% BRH and 80% CPS exhibited superior performance compared to pure adsorbents, with removal efficiencies of 97.93% for EO-d and 99.75% for SY-D, demonstrating the effectiveness of multi-layered bed columns over single-layer systems. The present study reveals the novelty of combining multi-layered bed columns with hybrid adsorbents, offering enhanced dye removal efficiency, overcoming limitation such as vacant spaces, and channeling effects observed in single-layer systems. This approach provides a cost-effective and sustainable solution for treating dye-contaminated wastewater.

Keywords: Adsorption, Hybrid Adsorbents, Wastewater, Water Pollutants.

الملخص
يشكل النقص العالمي في مياه الشرب الآمنة بسبب التلوث بالملوثات، وخاصة الأصباغ الاصطناعية، تحديات بيئية وصحية كبيرة. تبحث هذه الدراسة في امتزاز صبغتي إيفرزول البرتقالي 3*R (EO-D)* وسوبرا الاصفر *RL (SY-D)* من مياه

الصرف الصناعية المحضرة باستخدام مواد ماصة معدلة مشتقة من خليط قش الأرز وقشور النخيل المكربنة (*BRH-CPS*) في نظام أعمدة ذات طبقات متعددة. تم تحضير ستة أنواع من المواد الماصة، تشمل قش الأرز النقي (*BRH*)، وقشور النخيل المكربنة النقية (*CPS*)، وأربعة مواد ماصة هجينة بنسب مختلفة من *BRH:CPS* (20%، 40%، 60%، 80%). تم توصيف كل مادة ماصة من خلال تحليل العناصر، قياس مساحة السطح باستخدام طريقة *BET*، ومجهر المسح الإلكتروني الميداني الانبعاثي (*FESEM*). تم تقييم الأداء باستخدام كفاءة الإزالة وتحليل المساحة تحت المنحنى. أظهرت النتائج أن المادة الماصة الهجينة المكونة من 20% *BRH* و80% *CPS* تفوقت في الأداء مقارنة بالمواد الماصة النقية، حيث بلغت كفاءة الإزالة 97.93% لصبغة *EO-D* و99.75% لصبغة *SY-D*، مما يثبت فعالية أعمدة الطبقات المتعددة مقارنة بأنظمة الطبقة الواحدة. تكشف هذه الدراسة عن إبداع الجمع بين أعمدة الطبقات المتعددة والمواد الماصة الهجينة، مما يوفر كفاءة محسنة في إزالة الأصباغ ويتغلب على قيود مثل الفراغات الفارغة وتأثيرات القنوات التي لوحظت في أنظمة الطبقة الواحدة. يوفر هذا النهج حلاً فعالاً من حيث التكلفة ومستدامًا لمعالجة مياه الصرف الملوثة بالأصباغ.

الكلمات المفتاحية: الامتصاص، المواد المازة، مياه الصرف، الملوثات المائية.

Introduction

The dyeing industry is one of the largest consumers of water globally, producing over 7×10^5 tons of commercial dyes annually [1-3]. Approximately 10–15% of these dyes are discharged into the environment through industrial effluents [4, 5], posing significant risks to human health and ecosystems. Synthetic dyes, which are complex aromatic compounds, are often toxic, non-biodegradable, and resistant to conventional wastewater treatment methods [6]. Major consumers of dyes include the textile, pulp, tannery, and paint industries, whose untreated wastewater often contains high concentrations of dyes. These compounds can cause skin irritation, respiratory issues, and other adverse health effects upon exposure [7,8]. Moreover, the release of dye-contaminated water into aquatic ecosystems can lead to reduced sunlight penetration, disrupting photosynthesis and harming aquatic life [9].

To mitigate these environmental and health risks, various wastewater treatment technologies have been developed, including chemical precipitation, solvent extraction, oxidation, reduction, dialysis/electrodialysis, electrolytic extraction, reverse osmosis, ion exchange, evaporation, adsorption, filtration, and biological processes [10,11]. Among these, adsorption has emerged as a highly effective and versatile method due to its high reliability, energy efficiency, design flexibility, technological maturity, and ability to regenerate exhausted adsorbents [12,13]. Activated carbon remains the most widely used adsorbent for dye removal due to its large surface area and porous structure [14]. However, its high manufacturing and regeneration costs limit its widespread application, particularly in developing countries [15].

In recent years, there has been growing interest in low-cost adsorbents derived from agricultural waste materials, such as rice husk, palm kernel shells, and coconut coir, as sustainable alternatives to activated carbon [16]. These materials are abundant, inexpensive, and environmentally friendly, making them ideal for large-scale wastewater treatment applications. However, untreated agricultural residues often exhibit limited adsorption capacity due to their low surface area and lack of functional groups [17]. To address this limitation, physical and chemical modifications, such as pyrolysis, acid treatment, and surface functionalization, have been employed to enhance their adsorption performance [18].

Previous studies have demonstrated the potential of agricultural waste-based adsorbents for removing individual dyes, such as methylene blue [19], malachite green [20], rhodamine B [21], and acid orange 52 (AO 52) [22]. However, industrial wastewater typically contains a mixture of dyes with varying chemical structures and properties, making their simultaneous removal a more complex challenge [23]. Furthermore, few studies have investigated the impact of multi-bed column configurations on adsorption efficiency, which can address limitations such as vacant spaces, non-uniform flow distribution, and channeling effects [24].

This study aims to develop a hybrid adsorbent by blending coconut pith slurry (CPS) with banana rachis husk (BRH) and evaluate its performance in a multi-layered fixed-bed column for the simultaneous removal of two structurally different synthetic dyes, Eosin Y (EO-D) and Sunset Yellow (SY-D), from simulated wastewater. The results are compared with those obtained using a single-layer fixed-bed column [24] to demonstrate the advantages of the proposed approach. Specifically, this work addresses the following points:

- Multi-Layered Column Design: Unlike previous studies focusing on single-layer systems, this research employs a multi-layered column configuration to overcome limitations such as vacant spaces, non-uniform flow distribution, and channeling effects. This design enhances contact time between the adsorbent and dye molecules, improving overall removal efficiency [25].

- Optimized Hybrid Adsorbent Composition: The study investigates the effect of hybrid adsorbent composition on removal efficiencies and compares the results to single adsorbents. By blending CPS and BRH, the hybrid adsorbent leverages the complementary properties of both materials, such as high surface area and functional group diversity, to achieve superior dye removal performance [26].
- Simultaneous Removal of Multiple Dyes: The study explores the simultaneous removal of two structurally different synthetic dyes, highlighting the versatility of the proposed adsorbent system. This approach is particularly relevant for industrial applications, where wastewater often contains a mixture of dyes with varying chemical properties [27].

By addressing these key points, this study contributes to the development of cost-effective and sustainable wastewater treatment technologies, offering a viable solution for the dyeing industry's environmental challenges. The findings have the potential to inform the design of large-scale adsorption systems for the treatment of dye-contaminated wastewater, promoting environmental sustainability and public health. Multi-Layered column Design; unlike previous studies focusing on single layer systems, this research employs a multi layered column configuration to overcome limitations such as vacant spaces, non-uniform flow distribution, and channeling effects.

Material and methods

Materials

In this study, hybrid adsorbent of blending CPS and BRH were used to treat a wastewater that contaminated with various types of dyes.

Methods

Preparation of Modified Combined Adsorbents

Raw rice husk and palm kernel shells were washed with distilled water, dried at 105–110°C, and processed to achieve particle sizes of 150–250 µm. Rice husk was blended and sieved using a Retsch mechanical sieve shaker, while palm kernel shells were carbonized at 600°C for 5 hours in a furnace. The carbonized material was ground and sieved to the same size range, referred to as CPS. Six adsorbents were prepared: two pure adsorbents (100% BRH and 100% CPS) and four hybrid adsorbents mixed at varying BRH:CPS ratios (20%, 40%, 60%, and 80%).

Characterization of Adsorbents

Elemental Analysis

Elemental compositions of carbon (C), hydrogen (H), nitrogen (N), oxygen (O), and sulfur (S) in BRH and CPS were determined using a Flash EA Elemental Analyzer (CHNS-O). Samples weighing 2.5–3.0 mg were placed in tin cups, sealed, and analyzed.

Surface Morphology Analysis

Field emission scanning electron microscopy (FESEM, ZEISS SUPRA 40VP) was employed to examine the surface morphology of BRH and CPS at an acceleration voltage of 1 kV and magnification of 1000×. Samples were coated with a thin layer of gold to improve electrical conductivity.

BET Surface Area

Specific surface areas of BRH and CPS were measured using a Micromeritics ChemiSorb Surface Area Analyzer and the Brunauer–Emmett–Teller (BET) method. Samples were pre-treated by evacuation in an inert gas to remove moisture before analysis.

Preparation of Simulated Wastewater

Simulated wastewater containing EO-D and SY-D was prepared by dissolving 0.2 g of each dye powder in 250 mL of distilled water, followed by dilution to 10 L to achieve an initial concentration of 20 ppm for each dye.

Adsorption Study

Adsorption experiments were conducted using burettes with a diameter of 1.6 cm as multi-layered fixed-bed columns (Figure 1). Each column contained 6 g of hybrid adsorbent divided into three layers of 2 g each, separated by cotton beds to prevent settling. Simulated wastewater was passed through the columns in a downward flow mode, and treated samples were collected at regular intervals for analysis.

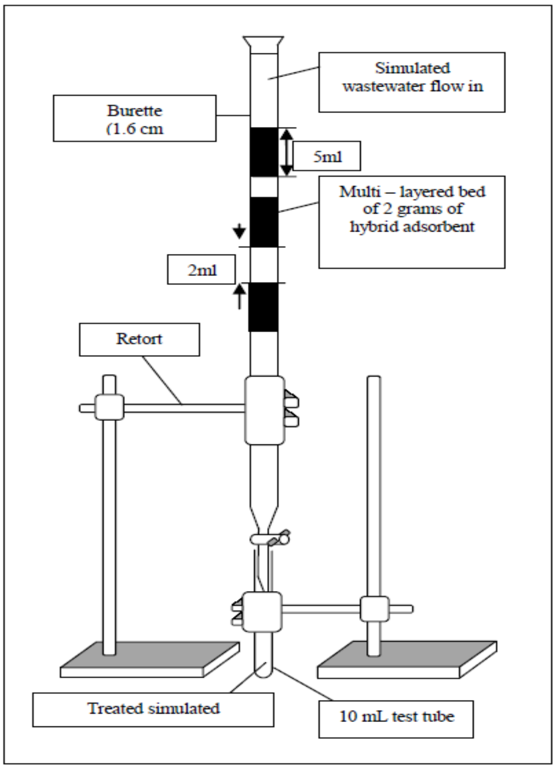


Figure 1: Schematic diagram of experimental set up for multi – layered fixed bed column used in adsorption study.

Data Analysis

Area under the Graph Analysis

Adsorption performance was quantified using the trapezoidal rule of integration (Equation 1) to calculate the area under the graph for each experiment over 180 minutes.

$$\int_a^b f(x)\,dx \approx \frac{1}{2}\sum_{k=1}^{N}(x_{k+1} - x_k)\left(f(x_{k+1}) + f(x_k)\right) \quad (1)$$

Where:
a: value at first point of time
b: value at last point of time
N: number of intervals
K: point of value

Removal Efficiency Analysis

Removal efficiency was calculated using the following equation:

$$\%\ \text{Removal} = \left[\frac{C_0 - C}{C_0}\right] \times 100 \quad (2)$$

Where:
Co: Initial concentration of dye.
C: Concentration of dye after adsorption at any time.

Results and discussion

The analysis of the data commenced with the creation of a standard curve (Figure 2) for each dye. For both dyes, solutions with varying known concentrations were prepared, and the average absorbance was plotted against the dye concentration at their respective maximum wavelengths (λ_{max}), which were 493 nm for (EO-D) and 393 nm for (SY-D). The absorbance exhibited a linear relationship with the concentration of both dyes, as indicated by R^2 values of 0.998 and 0.999 for (EO-D) and (SY-D), respectively. The calibration curves aligned with Beer's law, which establishes a linear correlation between absorbance and concentration.

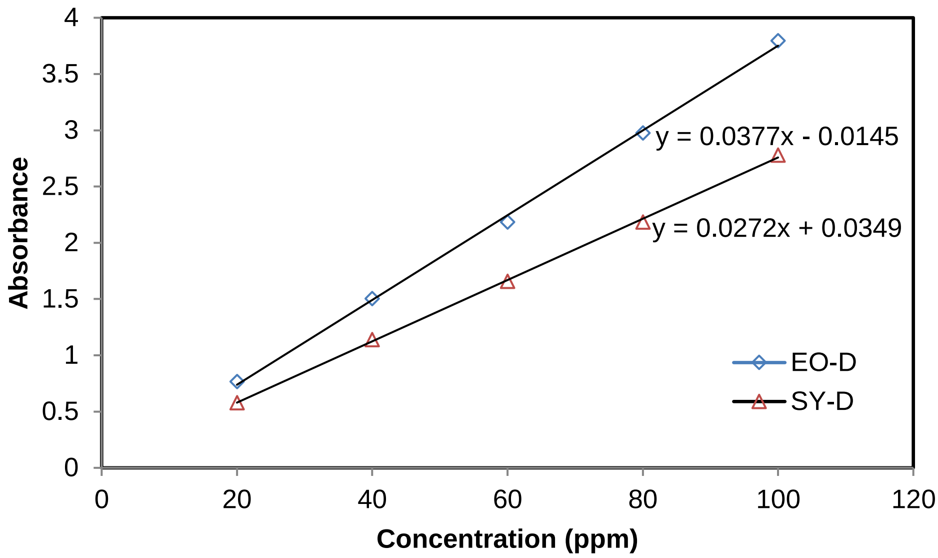


Figure 2: Calibration curve for EO and SY Dyes.

Characterization of Adsorbents

Elemental Analysis

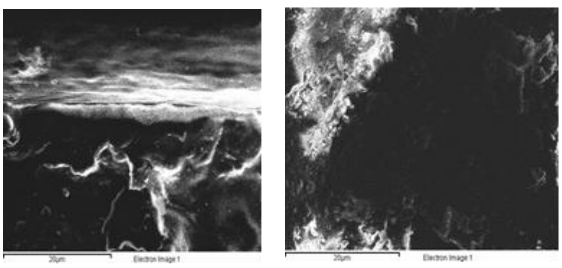
Table 1 summarizes the elemental compositions of BRH, raw palm shell (RPS), and CPS. Carbon content increased significantly after carbonization, indicating the formation of a carbon-rich residue conducive to adsorption.

Table 1: Elemental percentage of different types of adsorbents.

	C	H	N	O	S
BRH (%)	36.96	4.58	1.14	55.14	0
RPS (%)	47.3	5.45	47.13	1.52	0
CPS (%)	55.1	1.12	39.6	2.82	0

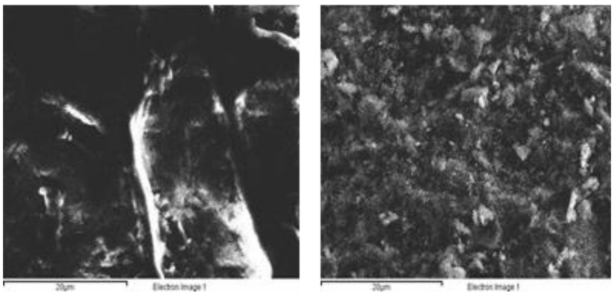
Surface Morphology

FESEM images (Figures 3 and 4) revealed that mechanical treatment of rice husk produced a rougher, more heterogeneous surface, enhancing its adsorptive properties. Similarly, carbonization of palm shells eliminated volatile compounds and moisture, creating porous structures ideal for adsorption.



(a) (b)

Figure 3: Surface morphology of (a) RRH, and (b) BRH adsorbent.



(a) (b)

Figure 4: Surface morphology of (a) RPS, and (b) CPS adsorbent.

BET Surface Area

BRH exhibited a specific surface area of 5.12 m²/g, while CPS demonstrated a significantly higher value of 279.24 m²/g due to its porous nature.

Evaluation of Adsorption Capacity

Adsorption of EO-D

Figure 5 illustrates the adsorption behavior of EO-D by the six adsorbents. The hybrid adsorbent with a 20% BRH and 80% CPS ratio achieved the highest removal efficiency (97.93%) within 180 minutes, attributed to strong interactions between the dye ions and the adsorbent surface.

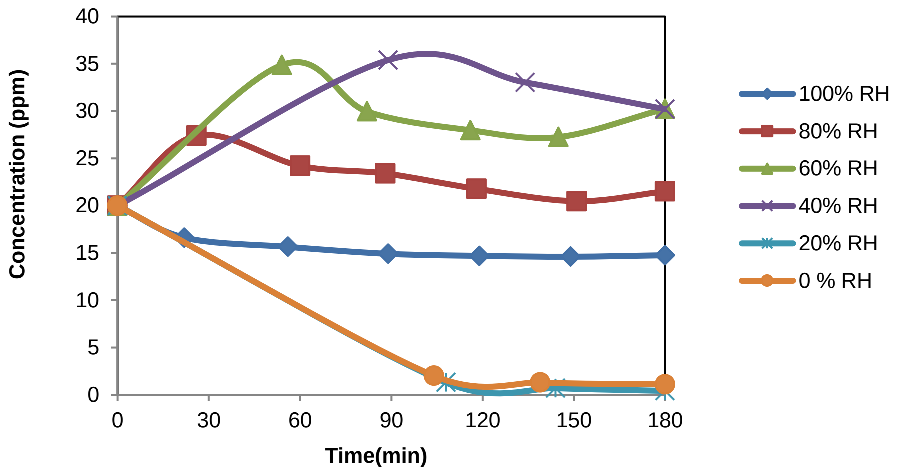


Figure 5: Adsorption of **EO-D** by prepared adsorbents in multi layered column.

Adsorption of SY-D

Similarly, Figure 6 shows that the 20% BRH and 80% CPS hybrid adsorbent performed best for SY-D removal, achieving 99.75% efficiency. Limitations in removal efficiency for other combinations were likely due to weak interactions or dye desorption.

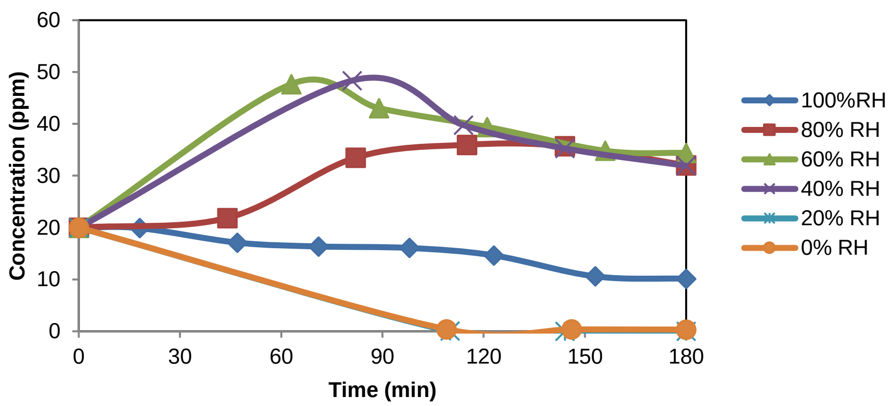


Figure 6: Adsorption of SY-D by adsorbents in Multi Layered column.

Comparison with Single-Layer Columns

Table 2 shows the area under the graph of removed dyes in Multi-Layered column by different types of adsorbents. The results were compared with a single-layer columns obtained elsewhere [24]. Multi-layered columns exhibited superior performance, reducing the total area under the graph from 4597.78 to 2309.12 for the 20% BRH and 80% CPS combination. This improvement is attributed to better distribution of wastewater droplets across layers, reduced channeling effects, and increased contact time between solutes and adsorbents.

Table 2: Area under the graph of removed dyes in Multi Layered column by different types of adsorbents.

Dye	Results of area under the graph for proposed adsorbents					
	0% RH	20%RH	40%RH	60%RH	80%RH	100%RH
EO-D	1251.52	1205.76	5459.30	5180.92	4144.22	2793.69
SY-D	1137.58	1103.36	6760.180	6557.13	5377.084	2776.96
Total	2389.1	2309.12	12219.48	11738.05	9521.304	5570.65

This study introduces several aspects that distinguish it from previous research on dye removal using agricultural waste-based adsorbents. Unlike prior studies employing single-layer columns [24], this research demonstrates that a multi-layered column design enhances the performance of hybrid adsorbents by redistributing wastewater droplets, minimizing channeling effects, and increasing residence time. In addition, the hybrid adsorbent with a 20% BRH and 80% CPS ratio achieved the highest removal efficiencies for both EO-D (97.93%) and SY-D (99.75%), surpassing the performance of single adsorbents and other hybrid combinations. Moreover, most previous studies focused on the removal of individual dyes. In contrast, this study investigates the simultaneous removal of two structurally different synthetic dyes, demonstrating the practical applicability of the proposed system in real-world scenarios.

Conclusion

This study demonstrates the effectiveness of hybrid adsorbents composed of blended rice husk and carbonized palm shell for removing Everzol orange 3R and Supra yellow RL dyes from simulated wastewater. The 20% BRH and 80% CPS combination achieved the highest removal efficiencies (97.93% for EO-D and 99.75% for SY-D) in a multi-layered fixed-bed column system. Compared to single-layer columns, the multi-layer design significantly improved adsorption performance by overcoming limitations associated with vacant spaces and non-uniform flow distribution. Future research should explore multi-step chemical treatments to further enhance the adsorption capacity of these materials.

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