Article preview

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Zinc oxide decorated plantain peel activated carbon for adsorption of cationic malachite green dye:

Mechanistic, kinetics and thermodynamics modeling

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Highlights

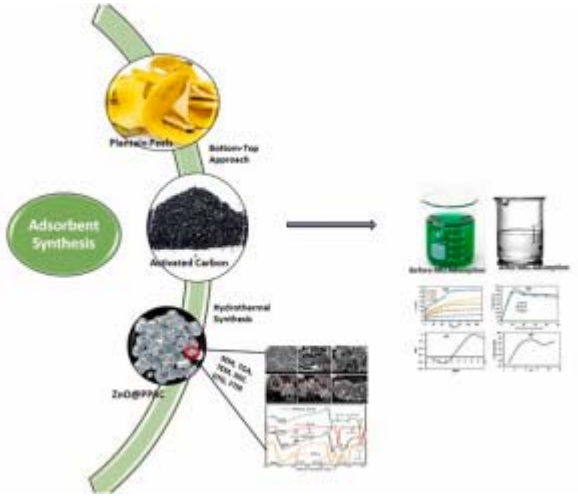
- •
Zinc oxide decorated plantain peels activated carbon (ZnO@PPAC) was developed via a hydrothermal technique.
- •
Physicochemical characterization of the ZnO@PPAC nanocomposite enhanced excellent adsorption performance.
- •
Characterization by SEM, DSC, DTG, TGA, FTIR, TEM, and HR-TEM confirmed the development of decorated ZnO@PPAC.
- •
Effective adsorption of Malachite green onto ZnO@PPAC demonstrated a dependence on operational parameters.
- •
Freundlich isotherm, Pseudo second-order and pore diffusion mechanism governed the thermodynamically feasible adsorption system.

Abstract

Reports have shown that malachite green (MG) dye causes various hormonal disruptions and health hazards, hence, its removal from water has become a top priority. In this work, zinc oxide decorated plantain peels activated carbon (ZnO@PPAC) was developed via a hydrothermal approach. Physicochemical characterization of the ZnO@PPAC nanocomposite with a 205.2 m^2/g surface area, porosity of 614.68 and dominance of acidic sites from Boehm study established the potency of ZnO@PPAC. Spectroscopic characterization of ZnO@PPAC vis-a-viz

thermal gravimetric analyses (TGA), Fourier Transform Infrared Spectroscopy (FTIR), Powdered X-ray Diffraction (PXRD), Scanning Electron Microscopy and High Resolution – Transmission Electron Microscopy (HR-TEM) depict the thermal stability via phase transition, functional group, crystallinity with interspatial spacing, morphology and spherical and nano-rod-like shape of the ZnO@PPAC heterostructure with electron mapping respectively. Adsorption of malachite green dye onto ZnO@PPAC nanocomposite was influenced by different operational parameters. Equilibrium data across the three temperatures (303, 313, and 323 K) were most favorably described by Freundlich indicating the ZnO@PPAC heterogeneous nature. 77.517 mg/g monolayer capacity of ZnO@PPAC was superior to other adsorbents compared. Pore-diffusion predominated in the mechanism and kinetic data best fit the pseudo-second-order. Thermodynamics studies showed the feasible, endothermic, and spontaneous nature of the sequestration. The ZnO@PPAC was therefore shown to be a sustainable and efficient material for MG dye uptake and hereby endorsed for the treatment of industrial effluent.

Graphical abstract



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Introduction

Dyes are highly hazardous to human health on account of their carcinogenic and mutagenic properties. Their complex structures and synthetic origin make them inert, not easily biodegraded and highly toxic (Bayode et al., 2020a; Thi et al., 2023). Most industries use dyes for most of their products, the yearly consumption is about 10,000 tons and disposal has become a challenge (Mosebolatan et al., 2023). Over 10–15 %

are indiscriminately introduced into water bodies which have undesirable effects on aquatic life and humans (Abewaa et al., 2023). Malachite green (MG) dyes are part of the major dyes in the triphenylmethane family(Somsiripan and Sangwichien, 2023). MG dyes are organic, water-soluble, and cationic. MG finds application in several industries such as the jute and silk industry, aquaculture and fisheries as ectoparasites and fungicides, and textile industries for colouring wool, cotton, paper, acrylic fibres and leather (Liu et al., 2020), (Cui et al., 2023). The extensive use of MG dye has led to its entrance into the food chain which causes harm to humans and animals through direct contact, inhalation, or ingestion due to its mutagenic, carcinogenic, and teratogenic properties (Elwardany et al., 2023), (Hock et al., 2023). MG dye has been highlighted as one of the causes of palpitations (Bai et al., 2022), headaches (Obayomi et al., 2023a), eye irritations (Obayomi et al., 2023b), several skin diseases and hormonal disruptions (Giri et al., 2022). Similarly, the breakdown products of MG can also be toxic and carcinogenic and the decontamination of MG from water is a great challenge owing to its complex chemical structure(Merrad et al., 2023), (Taha, 2023). Therefore, MG must be eliminated from industrial effluents before their disposal in aquatic environments.

Several conventional approaches and technical routes have been reported for the sequestration of dyes (Abewaa et al., 2023). Most of these methods suffer some weaknesses which eventually place adsorption as a preferred and cost-effective technique. Various studies have established the efficacy of the adsorption technique for the uptake of different pollutants (Hock et al., 2023; Taha, 2023; Dada et al., 2023). The sorption technique is generally known for its simple operation (Li et al., 2023), minimal initial cost (Guo et al., 2023) and excellent removal performance. Amongst the several applicable sorbents like clay (Taha, 2023), chitosan (Wang et al., 2024a), (Muinde et al., 2020), and activated alumina (Kuang et al., 2018), (Y et al., 2022), there have been reports on the use of activated carbon as an adsorbent as being highly efficient and is preferred by dint of their large surface area (Feng et al., 2024), multiple sites for adsorption, ease of modification, high porosity and functional groups (Obayomi et al., 2023a, 2023b). Because the cost of the precursor for commercially sold activated carbon is high, therefore is a need to identify more cost-effective alternatives form indigenous and readily available material.

Wastes from agricultural sources have been identified and reported as cheap and efficient alternatives that could be applied as sustainable adsorbents effective for decontamination of wastewater (Giri et al., 2022; Merrad et al., 2023) ranging from removal of heavy metals (Taha, 2023; Dada et al., 2023), dyes (Thi et al., 2023; Li et al., 2023) and phenols (Hemmati et al., 2016), (Anna et al., 2018). Various techniques to boost the porosity, pore volume and surface area of agricultural wastes have been previously reported (Alipanahpour Dil et al., 2019), (Firdaus et al., 2023). This is carried out via surface modification either through carbonization (physical activation) or through treatment with acids, bases and salts (chemical activation) (Adegoke and Bello, 2015). The conversion and application of plantain peel for wastewater treatment are identified as a technique for waste-to-wealth conversion. The adsorptive removal of lead (II) heavy metal was investigated by (Sudhakar et al., 2015) using unripe plantain peels. The uptake was discovered as being endothermic, favourable, and feasible. In a similar study, the uptake of Chromium present in battery recycling effluent using plantain

wastes was studied by Adeolu et al. (2016) and the report established that the activated carbon obtained in the treatment of plantain peel had the highest sorption capacity. Similar outcomes were obtained by Adekola et al. (2019) who explored the potency of plantain peel-activated biochar to remediate Rhodamine B (RhB) dye-contaminated media. RhB dye removal efficiency of 54.78% was observed with an 84.41 mg/g maximum adsorption for 120 min.

Furthermore, adsorbents with higher adsorption capacity can be derived by the preparation of nanocomposites (Zheng et al., 2020), (Shayesteh et al., 2016). The loading of nanoparticles onto the activated carbon to form nanocomposites incorporates and creates unique features in the adsorbent such as greater pore size and volume, as well as a higher surface area (Xu et al., 2023). The nanocomposites have been reported to have high reusability and regeneration capacity and can be utilized severally without a decrease in their adsorption effectiveness (Masoudian et al., 2019). Due to the unavoidable use of MG dye, it is a great necessity to develop cheap methods for removing this eco-threatening contaminant. As best as we could determine, there is not report found on the adsorption of MG onto ZnO@PPAC nanocomposite majorly the purpose of embarking on this study. PPAC was adorned with ZnO to develop enhanced characteristics that would give relevance to newly developed as-synthesized ZnO@PPAC.

The objectives of this research are to explore the hydrothermal synthesis of as-synthesized ZnO-adorned-doped-PPAC, study the physicochemical and spectroscopic characterization and in application investigate the mechanistic, kinetics, isotherm and thermodynamics modelling of adsorption of endocrine disruptive malachite green. The equilibrium data obtained at three temperatures (303, 313 and 323 K) were tailored differently to four (4) isotherm models (Dubinin-Kaganer-Raduskevich, Freundlich, Temkin and Langmuir). The adsorptive capacity of ZnO@PPAC for effective adsorption of MG was quantified using various isotherm models investigated at 303, 313 and 323 K. Most studies commonly reported have always been on one temperature which may not be the best replicate of the adsorption performance of adsorbent, hence the need for adsorption of investigation at three temperatures. Mechanistic and kinetic data obtained from kinetic studies helped in determining the controlling pathway of reaction (whether it be physisorption or chemisorption) and the mechanism of MG adsorption reaction if it is diffusion-dominated. Equilibrium studies were investigated at three (3) temperatures (303, 313 and 323 K) contrary to only one temperature which is commonly and always presented by researchers. At different adsorption temperatures, the actual and absolute performances of ZnO@PPAC nanocomposites were determined. Furthermore, insight into controlling pathways and mechanisms of malachite adsorption in terms of kinetics was studied. The rate at which this endocrine disruptive dye was removed using enhanced and adorned-doped ZnO@PPAC was demonstrated by kinetic models which were determined via Intraparticle Diffusion, Pseudo-first-order, Elovich and Pseudo-second-order. Detailed assessment of the thermodynamics parameters in terms of entropy, sorption energy enthalpy, Gibb's free energy and activation energy were all assessed. The outcome of this study earned credibility and relevance to sustainable, low-cost, and environmentally friendly ZnO@PPAC. Utilization of ZnO@PPAC in excellent and effective adsorption of problematic and endocrine

disruptor MG dye has successfully enlisted this as-synthesized among promising adsorbents recommended for industrial accessibility and large-scale utilization to solve waste-water pollution problems at a field scale.

Section snippets

Materials

All chemicals and reagents purchased and utilized were of analytical grade. Orthophosphoric acid (H_3PO_4) (supplied by BDH chemicals CAS: 7654-37-2), Zinc Nitrate (Zn $(NO_3)_2$, (LOBA Chemie CAS: 10176-18-17), distilled water, Malachite green, Sodium hydroxide (Carlo Erba CAS: 1311-74-3), Magnetic stirrer (Bante MS300), crucibles, centrifuge (SIGMA 4–5L), desiccator, oven, sieve, (GENLAB N30C), evaporating dish, furnace (Searchtech SX-5-12), pH meter (Hanna HI 2310), thermostat shaker model SI-300R

Physicochemical properties

ZnO@PPAC was discovered to have a pH value of 7.21, which is within the permitted range. According to reports, pH levels between 6 and 8 are suitable for wastewater decontamination purposes. The moisture, ash content and volatile matter contents of 7.54%, 12.18% and 31.48% were observed respectively for ZnO@PPAC. The low moisture content could be ascribed to the calcination step in the zinc oxide nanocomposite synthesis. The produced activated carbon and its nanoparticles are suitable materials

Conclusion

In this study, ZnO@PPAC was successfully synthesized by hydrothermal technique. ZnO@PPAC was demonstrated to be an effective sorbent for MG dye decontamination from water with a maximum monolayer capacity of 77.517 mg/g. The various physicochemical and spectroscopic characterization processes enhanced the surface characteristics and pore structure thereby positioning ZnO@PPAC as an effective nanocomposite adsorbent. The SEM results revealed the existence of pores on the ZnO@PPAC surface, which

CRediT authorship contribution statement

Adewumi Oluwasogo Dada: Methodology, Conceptualization, Supervision, Validation, Writing – original draft, Writing – review & editing, Data curation, Formal analysis, Investigation, Project administration, Resources, Software. **Abosede Adejumoke Inyinbor:** Investigation, Writing – review & editing. **Blessing Enyojo Tokula:** Investigation, Methodology, Supervision, Writing – original draft. **Abiodun**

Ajibola Bayode: Data curation, Investigation, Writing – review & editing. **Kehinde Shola Obayomi:**

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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