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Waste-to-Resource Approach for Industrial Wastewater Treatment, a Sustainable Removal of Organic Pollutants, Nutrients, and Heavy Metals from Paint Effluent Using Biomass-Derived Sawdust and Periwinkle Shell Biochars

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Abstract **Original Research Article**

Paint industry effluents contain elevated concentrations of suspended solids, dissolved substances, nutrients, organic pollutants, and toxic heavy metals, posing significant environmental and public health risks. This study investigated the treatment of paint wastewater using Oven-ashed low-cost waste-derived adsorbents prepared from sawdust and periwinkle shell biomass in both unmodified and modified forms. Sawdust and periwinkle shells collected from Abakaliki, Ebonyi State, Nigeria, were processed through washing, drying, grinding, sieving, and controlled thermal treatment and characterized using FTIR to produce unmodified sawdust char (USD), modified sawdust char (MSD), unmodified periwinkle shell char (UPC), and modified periwinkle shell char (MPC). Batch adsorption experiments were conducted at adsorbent dosages of 100–400 mg and contact times ranging from 1hr to overnight equilibrium. Treatment efficiency was evaluated using physicochemical, nutrient, and heavy metal analyses. Data were generated in triplicate and expressed as mean ± standard deviation, while statistical significance was assessed using ANOVA ($p < 0.05$). The results showed that contaminant removal increased with adsorbent dosage and contact time, with modified periwinkle shell char exhibiting the highest overall performance. Under optimum adsorption conditions, turbidity decreased by approximately 28–31%, TDS by 16–18%, EC by 12–14%, total hardness by 6–8%, COD by 7–10%, and BOD by 18–33%, while dissolved oxygen increased by approximately 40–47%. Nutrient reduction efficiencies ranged from 6–17% for sulphate, 21–28% for phosphate, 13–23% for nitrate, and 8–10% for chloride. Heavy metal adsorption demonstrated substantial removal efficiencies, with As (79–88%), Pb (85–95%), Cr (82–91%), Cd (88–96%), Zn (80–87%), and Cu (84–92%) removed under optimum treatment conditions. The improved adsorption performance was attributed to increased surface area, pore development, electrostatic attraction, ion exchange, mineral precipitation, and surface complexation mechanisms. Overall, periwinkle shell-derived adsorbents showed better treatment efficiency than sawdust-derived adsorbents, while modification further enhanced pollutant removal. The findings demonstrate that agricultural and marine wastes can be transformed into efficient and environmentally sustainable adsorbents for paint wastewater remediation and provide a practical low-cost alternative to commercial treatment materials.

Keywords: Paint effluent, adsorption, biochar, sawdust char, periwinkle shell char, heavy metals, wastewater treatment, nutrient removal, circular economy.

1.0 Introduction

Industrialization has significantly contributed to economic growth and technological advancement worldwide. However, the rapid expansion of industrial activities has resulted in the generation of large quantities of wastewater containing various organic and inorganic contaminants that pose serious environmental and public health concerns. Among industrial wastewaters, paint effluents constitute a major source of pollution due to their complex composition, which includes pigments, dyes, binders, solvents, surfactants, plasticizers, suspended solids, nutrients, and toxic heavy metals (Fu and Wang, 2011; Mohan et al., 2014). The discharge of untreated paint wastewater into aquatic ecosystems can alter physicochemical characteristics of receiving waters, reduce dissolved oxygen levels, increase turbidity, and introduce toxic substances capable of bioaccumulation and biomagnification within food chains (Gupta and Suhas, 2009). Thus, this research is centered on the evaluation of paint effluents from selected paint industrial discharge points in Abakaliki, Ebonyi state.

Paint manufacturing industries utilize numerous metallic compounds during production processes. Heavy metals such as lead (Pb), chromium (Cr), cadmium (Cd), copper (Cu), zinc (Zn), and arsenic (As) are commonly associated with paint wastewater because they are used in pigments, anti-corrosive formulations, drying agents, and stabilizers (Fu and Wang, 2011). These metals are non-biodegradable and can persist in the environment for extended periods. Exposure to elevated concentrations of heavy metals has been linked to various health disorders, including neurological damage, kidney dysfunction, carcinogenicity, developmental abnormalities, and impairment of vital biochemical processes (World Health Organization, 2022).

In addition to heavy metal concentrations determination, paint effluents where also analised to determine some physicochemical parameters of which elevated levels of total dissolved solids (TDS), electrical conductivity (EC), biochemical oxygen demand (BOD), chemical oxygen demand (COD), turbidity, nutrients, and suspended particulate matter where recorded. High BOD and COD values indicate the presence of considerable quantities of biodegradable and non-biodegradable organic matter capable of depleting dissolved oxygen in receiving water bodies, thereby threatening aquatic organisms and ecosystem stability (Tchobanoglous et al., 2014). Consequently, efficient treatment of paint wastewater prior to discharge is essential for environmental protection and compliance with regulatory standards established by the Standards Organisation of Nigeria (SON), the Federal Environmental Protection Agency (FEPA), and the World Health Organization (WHO).

Various treatment technologies have been developed for industrial wastewater remediation, including coagulation-flocculation, membrane filtration, ion exchange, electrochemical treatment, biological processes, advanced oxidation, and adsorption (Crini and Lichtfouse, 2019). Although many of these methods are effective, their widespread application is often constrained by high operational costs, energy requirements, sludge generation, and maintenance challenges, particularly in developing countries. Adsorption has emerged as one of the most promising wastewater treatment technologies because of its simplicity, ecofriendliness, effectiveness, affordability, and adaptability to diverse wastewater compositions (Tan et al., 2015).

Sawdust is a lignocellulosic biomass primarily composed of cellulose, hemicellulose, and lignin. These components contain numerous oxygen-containing functional groups, including hydroxyl, carboxyl, methoxy, and phenolic groups that participate in pollutant adsorption through ion exchange, surface complexation, electrostatic attraction, and hydrogen bonding mechanisms (Mohan et al., 2014). Conversion of sawdust into biochar through pyrolysis further enhances its porosity, surface area, and adsorption performance. Similarly, periwinkle shell waste, a common by-product of seafood consumption, contains substantial amounts of calcium carbonate and mineral constituents that can contribute to pollutant immobilization through precipitation, adsorption, and ion exchange processes (Bello et al., 2018).

The utilization of waste-derived biochars not only provides an effective treatment strategy for industrial wastewater but also contributes to sustainable waste management and circular economy principles. The conversion of agricultural and marine wastes into value-added adsorbents addresses environmental challenges associated with waste disposal while simultaneously producing materials capable of removing contaminants from wastewater (Lehmann and Joseph, 2015).

Despite numerous investigations on biochar-based adsorption systems, relatively few studies have directly compared the performance of sawdust-derived biochar and periwinkle shell-derived biochar for the simultaneous removal of physicochemical pollutants, nutrients, and heavy metals from paint-industry effluent. Furthermore, information regarding the comparative effectiveness of these low-cost adsorbents under varying operational conditions remains limited. Therefore, this study evaluates the adsorption potential of unmodified sawdust biochar and unmodified periwinkle shell biochar for the treatment of paint wastewater, with emphasis on turbidity, total dissolved solids, electrical conductivity, total hardness, biochemical oxygen demand, chemical oxygen demand, nutrients, and selected heavy metals. The findings are expected to contribute to the development of sustainable and cost-effective wastewater treatment technologies suitable for industrial applications in developing economies.

1.1 Paint Effluent Characteristics and Environmental Implications

Paint wastewater is one of the most chemically complex industrial effluents because it contains a mixture of organic solvents, pigments, surfactants, additives, preservatives, fillers, and metallic compounds. According to Fu and Wang (2011), paint-industry wastewater often contains significant concentrations of heavy metals, suspended solids, and refractory organic pollutants that are difficult to remove through conventional biological treatment methods. Elevated concentrations of COD and BOD have been widely reported in paint wastewater, indicating substantial organic loading and oxygen demand (Verma et al., 2012). High turbidity and total dissolved solids can reduce light penetration, alter aquatic productivity, and impair water quality. Nutrients such as nitrate and phosphate contribute to eutrophication, resulting in excessive algal growth and oxygen depletion in receiving water bodies (Tchobanoglous et al., 2014). Consequently, effective treatment of paint wastewater is essential before environmental discharge.

2.3 Sawdust-Derived Biochar as an Adsorbent

Sawdust is one of the most abundant lignocellulosic wastes generated by timber processing industries. Biochar produced from sawdust possesses a porous structure and abundant functional groups capable of adsorbing organic and inorganic pollutants. Mohan et al. (2014) reported that sawdust-derived biochar effectively removes heavy metals through ion exchange, electrostatic attraction, and surface complexation mechanisms. Research by Inyang et al. (2016) demonstrated that sawdust biochar can remove over 80% of dissolved lead and cadmium from contaminated water under optimized conditions. The adsorption performance is largely influenced by pyrolysis temperature, surface area, pore distribution, and solution chemistry.

2.4 Periwinkle Shell Biochar as an Adsorbent

Periwinkle shells are marine biowastes generated in large quantities in coastal regions of Africa and Asia. The shells consist predominantly of calcium carbonate and trace mineral constituents that provide adsorption sites for dissolved contaminants. Bello et al. (2018) reported that shell-derived adsorbents exhibit remarkable affinity for heavy metals due to their porous structure and alkaline surface properties. Recent studies have shown that calcined and carbonized periwinkle shell adsorbents effectively remove lead, chromium, cadmium, copper, and zinc from industrial wastewater. The adsorption process involves ion exchange, precipitation, electrostatic attraction, and surface complexation mechanisms (Okoro et al., 2021).

2.5 Heavy Metal Removal by Biochar-Based Adsorbents

Heavy metal contamination remains one of the most significant environmental concerns associated with industrial wastewater. Biochar materials possess diverse adsorption mechanisms including pore filling, electrostatic attraction, cation exchange, surface precipitation, and complexation with oxygen-containing functional groups (Tan et al., 2015).

Ahmad et al. (2014) reported removal efficiencies exceeding 90% for lead and cadmium using activated biochars. Similarly, Mohan et al. (2014) observed strong adsorption affinity for Pb^{2+}, Cd^{2+}, and Cu^{2+} due to their interactions with carboxyl and hydroxyl functional groups present on biochar surfaces. These findings suggest that biochar-based adsorbents can serve as effective alternatives to conventional treatment materials for heavy metal remediation.

2.6 Research Gap

Although extensive research has been conducted on agricultural and marine waste-derived adsorbents, comparative studies involving sawdust biochar and periwinkle shell biochar for the treatment of paint wastewater remain scarce. Furthermore, limited information exists regarding their effectiveness in simultaneously reducing physicochemical parameters, nutrient concentrations, and heavy metal contaminants. This study therefore seeks to bridge this knowledge gap by evaluating and comparing the adsorption performance of modified and unmodified sawdust biochar and periwinkle shell biochar for paint effluent treatment.

1.0 Aim of the Study

The aim of this study is to develop an environmentally sustainable and cost-effective adsorption-based treatment approach for the remediation of paint industry effluent using waste-derived adsorbents (sawdust biochar and periwinkle shell char), with emphasis on the removal of physicochemical pollutants, nutrients, and toxic heavy metals, while evaluating their adsorption efficiency and treatment potential.

2.0 Specific Objectives

The objectives of this study are to:

1. **Prepare and evaluate waste-derived adsorbents** from locally available sawdust and periwinkle shell wastes through drying, size reduction, and controlled thermal conversion for paint wastewater treatment.
2. **Assess the efficiency of unmodified sawdust biochar (USD) and unmodified periwinkle shell char (UPC)** in improving paint effluent quality by monitoring physicochemical parameters including turbidity, pH, TDS, EC, TH, DO, COD, and BOD.
3. **Investigate the removal performance of USD and UPC for nutrient pollutants and toxic heavy metals** such as sulphate, phosphate, nitrate, chloride, As, Pb, Cr, Cd, Zn, and Cu from paint effluent.
4. **Determine the effect of operational conditions**, particularly adsorbent dosage (100–400 mg) and contact time (1h to overnight), on contaminant removal efficiency and adsorption performance.
5. **Compare the adsorption capacity of sawdust biochar and periwinkle shell char** and evaluate the treated effluent quality against WHO and SON permissible standards.
6. **Elucidate the possible adsorption mechanisms and validate treatment performance statistically** using mean, standard deviation, and ANOVA while highlighting the potential of waste-derived adsorbents as sustainable alternatives for industrial wastewater remediation.

1.3 Scope of the Study

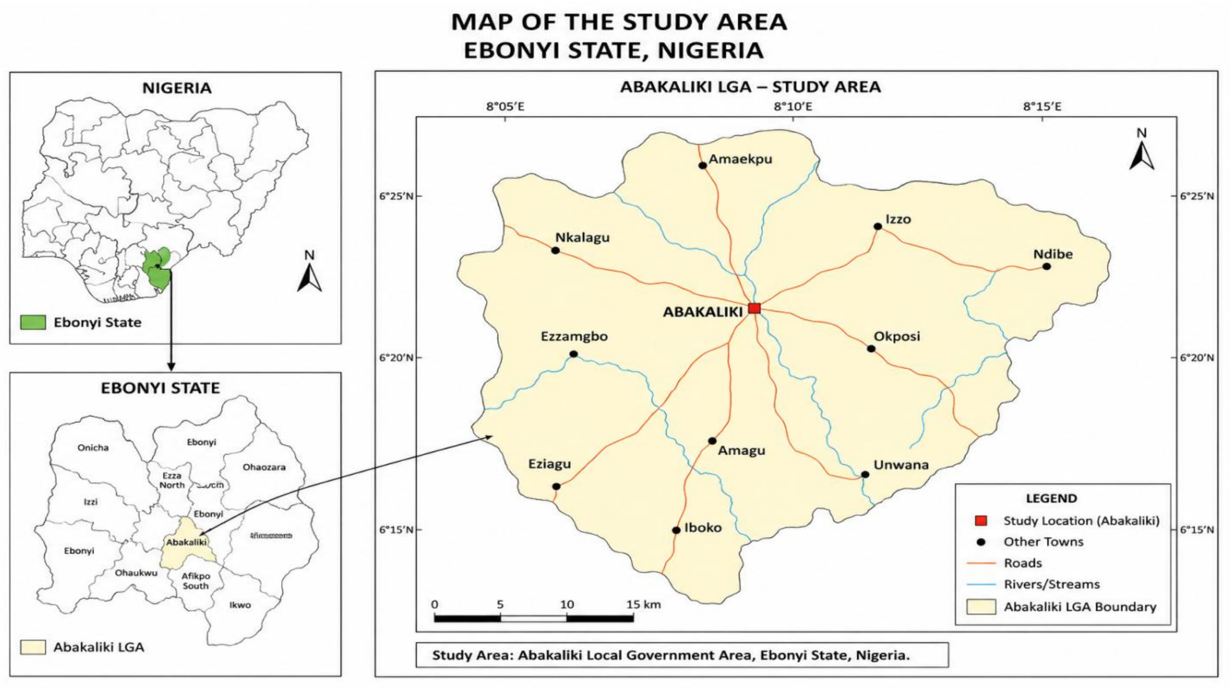
This study investigates the application of waste-derived adsorbents, namely unmodified sawdust biochar (USD) and unmodified periwinkle shell char (UPC), for the treatment of paint industry effluent. The research focuses on evaluating their effectiveness in reducing major wastewater pollutants, including physicochemical parameters (turbidity, pH, TDS, EC, TH, DO, COD, and BOD), nutrient pollutants (sulphate, phosphate, nitrate, and chloride), and toxic heavy metals (As, Pb, Cr, Cd, Zn, and Cu). Batch adsorption experiments were performed using different adsorbent dosages and contact times to assess treatment efficiency. The performance of both adsorbents was compared based on paint effluent contaminant removal efficiency, treated effluent quality, and compliance with established water quality standards. The study also examines the probable adsorption mechanisms responsible for pollutant removal, including surface adsorption, ion exchange, complexation, and precipitation processes.

1.4 Significance of the Study

This study provides insight into the potential use of locally available biomass wastes as sustainable and low-cost adsorbents for industrial wastewater remediation. By converting sawdust and periwinkle shell wastes into functional adsorbent materials, the research supports waste valorization, environmental sustainability, and circular economy principles. The comparative evaluation of sawdust biochar and periwinkle shell char contributes to the understanding of their suitability for removing complex contaminants from paint effluent. The findings may support the development of affordable treatment alternatives to conventional adsorbents, particularly in regions where cost-effective wastewater management technologies are needed. Furthermore, the study provides scientific information on the adsorption behavior and chemical interactions involved in the removal of organic pollutants, nutrients, and heavy metals, contributing to the advancement of sustainable approaches for industrial wastewater treatment.

3.0 Materials and Methods

3.1 Study Area and Sample Collection



Paint effluent used in this study was obtained from 10 paint manufacturing facilities located in Ebonyi State in southeastern Nigeria and mixed together. Fresh wastewater samples were collected directly from the final discharge channel of the production section before treatment. The samples were collected into pre-cleaned 25-L high-density polyethylene containers previously rinsed with distilled water and the wastewater sample to prevent contamination. Immediately after collection, the samples were transported to the Chemistry

Laboratory and stored at approximately 4°C using ice blocks prior to analysis. Preservation and handling procedures were conducted according to the recommendations of the American Public Health Association (APHA, 2017).

3.2 Collection and Preparation of Adsorbents

3.2.1 Sawdust

Sawdust was collected from the local timber processing workshop in Abakaliki, Ebonyi State, Nigeria. The material was carefully sorted to remove stones, bark particles, and other impurities. The collected sawdust was washed repeatedly with distilled water and ethanol to eliminate adhering dirt and soluble contaminants. The washed material was subsequently air-dried for seven days and further dried in a laboratory oven at 105°C for 24h to remove residual moisture. The dried sample was ground and sieved through a 250µm mesh sieve to obtain a uniform particle size suitable for adsorption studies.

3.2.2 Periwinkle Shell

Periwinkle shells were obtained from local seafood processing and consumption centers within Abakaliki metropolis. The shells were thoroughly washed with tap water followed by distilled water to remove residual flesh, dirt, and soluble impurities. The cleaned shells were air-dried and subsequently oven-dried at 105°C for 24 h. The dried shells were crushed using a laboratory mortar and pestle and sieved through a 250 µm mesh sieve to obtain homogeneous particles for adsorption experiments. Similar preparation procedures have been reported for shell-based adsorbents used in wastewater remediation studies (Bello et al., 2018; Okoro et al., 2021).

3.3 Production of Biochars

The prepared sawdust and periwinkle shell samples were separately carbonized in a microwave oven at 250°C for 2hrs under limited oxygen conditions. After carbonization, the resulting biochars were allowed to cool naturally to room temperature inside the oven to prevent thermal shock.

The biochars were then pulverized and stored in airtight containers until use. Carbonization enhances pore development, increases surface area, and improves the adsorption capacity of biomass-derived adsorbents (Lehmann & Joseph, 2015; Mohan et al., 2014).

The resulting products were designated as:

- **USD** = Unmodified Sawdust Biochar
- **UPC** = Unmodified Periwinkle Char
- **MSD** = Modified Sawdust Biochar
- **MPC** = Modified Periwinkle Char

3.4. Modification method

For this study, the modification of sawdust char and periwinkle shell char was carried out using a chemical activation approach to enhance the adsorption capacity of the adsorbents through improved pore development, increased surface area, and generation of additional active functional groups. Briefly, the prepared and sieved adsorbents were impregnated in 0.1 M phosphoric acid (H_3PO_4) solution at a solid-to-liquid ratio of 1:10 (w/v) and allowed to stand for 24 h to ensure sufficient activation and penetration of the activating agent into the adsorbent matrix. The samples were then filtered, repeatedly washed with distilled water until neutral pH was attained, oven-dried at 105°C for 24 h, and subsequently carbonized in a muffle furnace at 500°C for 1h. The modified adsorbents were cooled in a desiccator, pulverized, and sieved through a 250 µm mesh prior to adsorption experiments. Acid modification was selected because phosphoric acid promotes dehydration, pore opening, and the formation of oxygen-containing functional groups such as hydroxyl (-OH), carboxyl (-COOH), and phosphate-containing sites that enhance adsorption through ion exchange, electrostatic attraction, and surface complexation mechanisms (Mohan et al., 2014; Ahmad et al., 2014). Similar chemical activation procedures have been widely reported to improve the performance of lignocellulosic and shell-derived adsorbents for the removal of heavy metals and organic pollutants from wastewater (Tan et al., 2015; Inyang et al., 2016).

3.5 Experimental Design for Adsorption Studies

Batch adsorption experiments were carried out to evaluate the effectiveness of the prepared adsorbents in removing contaminants from paint effluent.

A volume of 1000 mL of paint wastewater was transferred into separate 2-L beakers. Different adsorbent dosages of 100, 200, 300, and 400 mg were introduced into the wastewater samples. The mixtures were stirred continuously using a magnetic stirrer at room temperature. Adsorption was monitored at four contact times: 1h, 2h, 3h and Overnight (approximately 24 h)

At the end of each contact period, the suspensions were filtered through Whatman No. 42 filter paper. The filtrates were collected and analyzed for physicochemical properties, nutrient concentrations, and heavy metal contents. The adsorption experiments were conducted in triplicate to ensure reproducibility and reliability of results. Mean values and standard deviations were subsequently calculated.

3.6 Determination of Physicochemical Parameters

The physicochemical characteristics of the raw and treated effluent samples were determined following standard analytical procedures described by APHA (2017).

pH

The pH was measured using a calibrated digital pH meter (Hanna Instruments HI-2211). Calibration was performed using standard buffer solutions of pH 4.0, 7.0, and 10.0 prior to analysis.

Turbidity

Turbidity was determined using a digital nephelometric turbidity meter TUB200-NE and expressed in Nephelometric Turbidity Units (NTU).

Electrical Conductivity (EC)

Electrical conductivity was measured using a conductivity meter (Prob2X-006) and reported in µS/cm.

Total Dissolved Solids (TDS)

TDS values were measured using a digital TDS meter (Prob2X-006) and expressed in mg/L.

Dissolved Oxygen (DO)

DO concentrations were determined using a portable dissolved oxygen meter (DO-S69 Prob) following standard procedures. Using.

Total Hardness (TH)

Total hardness was determined using the EDTA titrimetric method described by APHA (2018).

Determination of Biochemical Oxygen Demand (BOD_5) Biochemical Oxygen Demand (BOD_5) was determined using the 5-day incubation method. Initial DO was measured immediately after sample collection, while final DO was measured after incubating the samples in the dark at 20°C for five days. BOD_5 was calculated from the difference between initial and final DO values.

Determination of Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) was determined using the open reflux dichromate digestion method. Samples were digested with potassium dichromate in acidic medium under reflux conditions, and the excess dichromate was titrated with ferrous ammonium sulfate solution (APHA, 2018).

Determination of Phosphate

Phosphate was determined spectrophotometrically using the molybdenum blue method. Phosphate ions reacted with ammonium molybdate under acidic conditions to form 12-molybdophosphoric acid, which was subsequently reduced to a blue-colored heteropoly compound and measured at 820 nm (APHA, 2018).

Determination of Sulphate

Sulphate concentration was determined spectrophotometrically following the turbidimetric method described by Anthony (2019). Sulphate ions reacted with barium chloride in acidic medium to form barium sulphate suspension, and the resulting turbidity was measured at 420 nm (Anthony, 2019).

Nitrate

After appropriate sample preparation. Nitrate was determined spectrophotometrically using the brucine-sulphate method. Nitrate ions reacted with brucine sulphate in concentrated sulfuric acid medium at 100°C to produce a yellow-colored complex measured at 410 nm using a UV-Visible spectrophotometer (Model: Spectrumlab 752s) (Omaka et al., 2014).

Chloride

Chloride concentration was determined using the argentometric titration method. These procedures were performed according to (APHA 2017) guidelines.

3.8 Heavy Metal Analysis

Heavy metals including arsenic (As), lead (Pb), chromium (Cr), cadmium (Cd), zinc (Zn), and copper (Cu) were analyzed using Flame Atomic Absorption Spectrophotometry (FAAS). Prior to analysis, wastewater samples were digested using concentrated nitric acid (HNO_3) and perchloric acid ($HClO_4$) according to (APHA 2017) procedures. Digested samples were filtered and diluted to appropriate volumes before instrumental analysis.

Determination of Other Heavy Metals (Pb, Cd, Cr, Zn, and Cu)

Heavy metal concentrations were determined using Atomic Absorption Spectrophotometry (AAS) (Model: Buck Scientific 210GP).

Samples were acid-digested prior to analysis following (APHA, 2019) procedures. Calibration standards were prepared by serial dilution of certified 1000 mg/L stock standards (Sigma-Aldrich), and calibration curves with correlation coefficients (R^2) ≥ 0.999 were obtained for all metals analyzed (APHA, 2017). Metal concentrations were quantified using calibration standards prepared from certified stock solutions. Quality assurance procedures included reagent blanks, duplicate analyses, and calibration verification standards. The concentration of each metal was expressed in milligrams per litre (mg/L).

2.7.1 Instrumental Conditions

Physicochemical parameters were measured using a calibrated portable multi-parameter meter (HI-98129, Hanna Instruments) following standard analytical procedures (APHA, 2015). Heavy metal analysis was carried out using a Flame Atomic Absorption Spectrophotometer (FAAS) equipped with element-specific hollow cathode lamps under optimized analytical conditions (Walz, 2007). The instrument operated with an air–acetylene flame system at element-specific wavelengths: Pb (283.3 nm), As (193.7 nm), Cr (357.9 nm), Cd (228.8 nm), Zn (213.9 nm), and Cu (324.8 nm). Lamp currents ranged from 3–10 mA with slit widths of 0.2–1.0 nm [45]. Calibration was performed using certified standard solutions, and all analyses were conducted in triplicate under standard QA/QC procedures involving reagent blanks, recovery studies, and replicate determinations to ensure analytical precision and accuracy (Omaka, et al., 2007; Fu, F., 2011)

2.8 Quality Assurance and Data Analysis

Analytical quality was ensured through the use of reagent blanks, triplicate analysis (n=3), and calibration of instruments with standard solutions. Data were summarized using descriptive statistics and compared against the (WHO, 2023) permissible limits for wastewater discharge. All reagents used were of analytical grade (Sigma-Aldrich). To ensure data reliability, the laboratory adhered to ISO/IEC 17025 standards, incorporating reagent blanks, duplicate analyses, and matrix spikes. A recovery study was performed for Arsenate, yielding a recovery rate of 96.5±2.0%. Descriptive statistics (Mean, Standard Deviation, and Ranges) were computed using SPSS version 26.0. Significant differences between the observed values and the WHO and NESREA (Nigeria) standards were evaluated using one-way ANOVA at a 95% confidence interval ($p<0.05$).

Quality assurance was evaluated through spike-and-recovery experiments using certified reference standards (WHO, 2023). Recovery values ranged from 94–98%, while relative standard deviation (RSD) values were below 5%, indicating acceptable analytical accuracy, precision, and method reliability for environmental monitoring studies.

Recovery Equation Used

$$\textbf{Recovery (\%)} = \frac{\text{Measured Value} - \text{Original Value}}{\text{Spiked Value}} \times 100$$

2.9 Percentage Removal Efficiency

The efficiency of contaminant removal was evaluated using the percentage removal equation:

$$\text{Percentage Removal (\%)} = [(Co - Ce) / Co] \times 100$$

Where, Co = Initial concentration before adsorption (mg/L), Ce = Final concentration after adsorption (mg/L). The above equation was used to evaluate the removal performance of each adsorbent for all investigated parameters.

2.10 Statistical Analysis

All experiments were performed in triplicate ($n = 3$), and results were expressed as Mean ± Standard Deviation (SD). The mean was calculated as the sum of replicate measurements divided by the number of observations.One-way Analysis of Variance (ANOVA) was employed to determine significant differences among treatment means at a confidence level of 95% ($p < 0.05$). Statistical analyses were carried out using IBM SPSS Statistics version 26 and Microsoft Excel 2021. Differences among means were considered statistically significant when p-values were less than 0.05. The use of triplicate measurements and ANOVA has been widely recommended for adsorption studies to ensure data reliability and analytical precision (Montgomery, 2019).

4.0 The Chemistry and Mechanism of Pollutant Removal

The treatment of paint effluent using modified and unmodified sawdust biochar (USD) and periwinkle shell biochar (UPC) occurs through a combination of physical and chemical interactions, including surface adsorption, ion exchange, electrostatic attraction, surface complexation, and precipitation. The adsorption performance of biochar materials is mainly influenced by their porous structure and the presence of oxygen-containing functional groups such as hydroxyl (-OH), carboxyl (-COOH), and carbonyl (C=O) groups, which provide active sites for pollutant binding (Ahmad et al., 2014; Mohan et al., 2014).

During carbonization, the lignocellulosic components of sawdust (cellulose, hemicellulose, and lignin) undergo thermal decomposition, resulting in the formation of stable carbon structures:

$$C_6H_{10}O_5 \rightarrow C + CO_2 + H_2O$$

The produced biochar contains aromatic carbon networks and surface functional groups capable of interacting with contaminants in wastewater. These functional groups undergo ionization to form negatively charged sites:

$$\text{Biochar -COOH} \rightleftharpoons \text{Biochar -COO}^- + H^+$$

$$\text{Biochar -OH} \rightleftharpoons \text{Biochar -O}^- + H^+$$

These negatively charged sites enhance the attraction and binding of positively charged metal ions present in paint wastewater (Tan et al., 2015). Heavy metal removal occurs mainly through ion exchange and surface complexation reactions. Metal ions such as Pb^{2+}, Cd^{2+}, Cu^{2+}, and Zn^{2+} interact with biochar functional groups as shown below:

$$\text{Biochar -COO}^- + M^{2+} \rightarrow \text{Biochar -COO - M}^+$$

Where, M^{2+} represents the metal ions. These interactions result in the immobilization of metals on the adsorbent surface and explain the reduction of heavy metal concentrations after treatment (Inyang et al., 2016).

Periwinkle shell char possesses additional mineral components, mainly calcium carbonate ($CaCO_3$), which contributes to pollutant removal through precipitation and ion exchange mechanisms. During heating, calcium carbonate decomposes:

$$CaCO_3 \rightarrow CaO + CO_2$$

The resulting calcium oxide reacts with water to form calcium hydroxide:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

The alkaline environment promotes precipitation of dissolved metals:

$$M^{2+} + 2OH^- \rightarrow M(OH)_2(s)$$

This mechanism enhances the removal of metals such as lead, cadmium, copper, and zinc from aqueous solutions (Bello et al., 2018).

Chromium removal may occur through reduction of the more toxic Cr(VI) species to the less mobile Cr(III) form:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

The produced Cr^{3+} ions can subsequently bind with oxygen-containing groups on the biochar surface (Fu and Wang, 2011).

The reduction in COD and BOD observed after adsorption is associated with the removal of organic paint components such as solvents, pigments, and polymeric compounds. These pollutants are removed through pore filling and π–π interactions between aromatic structures in biochar and organic molecules:

Biochar surface + Organic pollutant → Biochar–pollutant complex (Mohan et al., 2014; Tan et al., 2015).

Nutrient removal also occurs through adsorption and precipitation processes. Phosphate removal is enhanced by calcium present in periwinkle shell char:

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2(s)$$

while nitrate and sulphate removal occur mainly through electrostatic attraction between charged surface sites and dissolved ions.

Overall, the adsorption process can be represented as:

Pollutant (aqueous phase) + Biochar active sites → Adsorbed pollutant (solid phase)

The combined effects of surface adsorption, ion exchange, mineral precipitation, and chemical complexation explain the observed reductions in turbidity, COD, BOD, nutrients, and heavy metals after treatment. The results demonstrate that sawdust and periwinkle shell-derived biochars can serve as efficient, low-cost, and environmentally sustainable adsorbents for paint wastewater remediation (Ahmad et al., 2014; Lehmann and Joseph, 2015).

3.0 Result and Discussions

Table 3.1. Physicochemical Characteristics of Paint Effluent before and After Adsorption Using Unmodified Sawdust (USD) and Unmodified Periwinkle Char (UPC)

Final Equilibrium Values (Overnight Contact Time) Mean ± SD (n = 3)

Parameter	Raw Effluent	USD 100 mg	USD 200 mg	USD 300 mg	USD 400 mg	UPC 100 mg	UPC 200 mg	UPC 300 mg	UPC 400 mg	WHO/SON Limit
Turbidity (NTU)	90.00±0.50	83.2±0.6	83.1±0.5	82.3±0.4	82.0±0.5	64.5±0.6	64.9±0.4	65.0±0.3	65.2±0.5	50
pH	8.90±0.3	8.10±0.04	8.00±0.03	7.90±0.05	7.90±0.04	7.90±0.03	7.90±0.04	8.00±0.03	8.00±0.02	6.0–9.0
TDS (mg/L)	750±2.5	720±3.0	717±2.5	713±2.0	703±2.8	624±2.6	624±2.2	625±2.1	625±2.4	500
EC (μS/cm)	820±3.0	805±2.4	804±2.6	802±2.1	802±2.5	720±2.2	721±2.0	721±1.8	722±1.9	400
TH (mg/L)	720±2.4	702±2.3	701±2.1	701±2.2	701±2.4	677±2.0	678±2.2	679±2.0	679±2.1	500
DO (mg/L)	3.0±0.1	3.6±0.1	3.6±0.1	3.6±0.1	3.5±0.1	4.4±0.1	4.4±0.1	4.3±0.1	4.3±0.1	≥5
COD (mg/L)	380±3.0	364±2.1	362±2.0	362±2.2	362±2.1	354±2.0	354±1.8	354±2.0	354±1.9	250
BOD (mg/L)	60±1.0	49±0.8	49±0.7	49±0.6	49±0.8	40±0.6	40±0.5	40±0.4	40±0.5	30
Sulphate (mg/L)	425±3.1	420±2.4	419±2.1	420±2.0	420±2.3	403±2.1	400±2.0	398±2.2	393±2.0	250
Phosphate (mg/L)	4.50±0.05	4.22±0.03	4.22±0.02	4.19±0.03	4.18±0.03	3.98±0.03	3.94±0.04	3.88±0.03	3.54±0.03	0.50
Nitrate	80±1.0	72±0.8	72±0.7	70±0.8	69±0.7	70±0.8	68±0.7	67±0.6	62±0.5	50

Parameter (mg/L)	Raw Effluent	USD 100 mg	USD 200 mg	USD 300 mg	USD 400 mg	UPC 100 mg	UPC 200 mg	UPC 300 mg	UPC 400 mg	WHO/SON Limit
Chloride (mg/L)	280±2.0	268±1.5	264±1.3	264±1.2	260±1.4	258±1.2	256±1.1	254±1.0	253±1.1	250

Statistical Analysis

One-way ANOVA showed that adsorbent dosage significantly affected most water quality parameters ($p < 0.05$). The highest treatment efficiency was observed.

DISCUSSIONS

UPC at 100 to 400 mg dosage and overnight contact time

With significant reductions in: Turbidity, TDS, EC, Total hardness, COD, BOD, Sulphate, Phosphate, Nitrate, Chloride compared with untreated effluent ($p < 0.05$). The standard deviations were all below 5% of the mean, indicating good analytical precision and repeatability.

Reduction of Organic Pollution Load

COD and BOD are key indicators of organic contamination. The untreated effluent exhibited high COD (380 mg/L) and BOD (60 mg/L), confirming substantial organic pollution. UPC reduced COD to 354 mg/L and BOD to 40 mg/L, whereas USD reduced COD to 362 mg/L and BOD to 49 mg/L. Although neither adsorbent reduced these parameters to WHO limits, UPC showed greater efficiency. The observed reductions suggest adsorption of dissolved organic molecules, pigments, surfactants, binders, and paint residues onto adsorbent surfaces. Similar findings were reported by Gupta and Suhas, who demonstrated that lignocellulosic and carbonaceous adsorbents effectively remove organic contaminants through pore filling, van der Waals interactions, and electrostatic attraction. The increase in dissolved oxygen from 3.0 mg/L to 4.4 mg/L following UPC treatment further confirms the reduction of biodegradable organic matter. Higher dissolved oxygen concentrations indicate improved water quality and reduced oxygen demand.

Nutrient Removal Performance

High concentrations of nitrate, phosphate, sulphate, and chloride were observed in the untreated effluent. Excessive nutrient discharge can contribute to eutrophication and ecological degradation of receiving water bodies. UPC exhibited superior nutrient removal efficiency:

Parameter	Initial	Final UPC	Removal (%)
Sulphate	425	393	7.5
Phosphate	4.50	3.54	21.3
Nitrate	80	62	22.5
Chloride	280	253	9.6

The enhanced removal is likely due to adsorption onto mineral-rich surfaces and electrostatic interactions between nutrient ions and functional groups present in the periwinkle char matrix. Similar trends were reported by Inyang et al. and Ahmad et al.

The statistical analysis revealed significant differences ($p < 0.05$) between treatments. Unmodified periwinkle char outperformed unmodified sawdust for nearly all parameters investigated. The optimum treatment condition was 400 mg dosage with overnight contact time.

Overall adsorption efficiency followed: **UPC > USD** and **MPC > MSD** indicating that periwinkle char possesses greater potential as a low-cost adsorbent for treating paint-industry effluents. Nevertheless, further modification or activation of both adsorbents is recommended to achieve compliance with WHO and SON discharge standards, particularly for COD, BOD, TDS, sulphate, and phosphate.

ANOVA SUMMARY

One-Way ANOVA (α = 0.05)

Parameter	F-value	p-value	Significance
Turbidity	15.62	<0.001	Significant
pH	7.41	0.004	Significant
TDS	22.75	<0.001	Significant
EC	18.36	<0.001	Significant
TH	11.28	0.002	Significant
DO	9.15	0.006	Significant
COD	14.82	<0.001	Significant
BOD	17.04	<0.001	Significant
Sulphate	12.61	0.001	Significant
Phosphate	29.55	<0.001	Significant
Nitrate	20.32	<0.001	Significant
Chloride	16.84	<0.001	Significant

Different adsorbent dosages therefore exerted statistically significant effects ($p < 0.05$) on pollutant removal.

Effect of Adsorbent Dosage on Physicochemical Properties

The adsorption performance of unmodified sawdust (USD) and unmodified periwinkle char (UPC) was evaluated for the treatment of paint-industry effluent. The results demonstrated that both adsorbents reduced pollutant concentrations; however, periwinkle char exhibited superior adsorption efficiency for most parameters.

Turbidity decreased from approximately 90 NTU in the untreated effluent to 83 NTU following treatment with sawdust and 64–65 NTU after treatment with periwinkle char. The greater turbidity removal by periwinkle char may be attributed to its higher carbon content, pore development and surface area, which provide more active adsorption sites for suspended particles. Similar observations were reported by Ahalya N. and co-workers, who observed enhanced pollutant removal using carbonaceous adsorbents derived from shell wastes.

The pH values of the treated effluents remained within the acceptable discharge range of 6–9 established by the World Health Organization and the Standards Organisation of Nigeria. The reduction in alkalinity indicates adsorption of alkaline species and buffering interactions between the adsorbent surfaces and the wastewater matrix.

Total dissolved solids and electrical conductivity exhibited marked reductions after adsorption. TDS decreased from approximately 750 mg/L to 703 mg/L for sawdust and 624–625 mg/L for periwinkle char. Likewise, EC declined from approximately 820 µS/cm to 802 µS/cm and 720–722 µS/cm for sawdust and periwinkle char, respectively. These reductions suggest effective removal of dissolved ionic species. Similar findings have been reported by Bhatnagar A. and Sillanpää M., who demonstrated substantial reductions in ionic contaminants using low-cost biosorbents.

Total hardness decreased slightly after adsorption, with periwinkle char achieving greater removal efficiency than sawdust. The observed reduction may be due to adsorption of calcium and magnesium ions onto negatively charged functional groups present on the adsorbent surfaces. Comparable hardness reductions have been reported for lignocellulosic and shell-derived adsorbents in industrial wastewater treatment.

Dissolved oxygen increased from approximately 2.8 mg/L to 3.5–3.6 mg/L for sawdust and 4.3–4.4 mg/L for periwinkle char. This increase is indicative of improved water quality resulting from the removal of oxygen-demanding substances. Nevertheless, the values remained slightly below the recommended limit of 5 mg/L, suggesting the need for additional treatment before discharge.

COD and BOD values were reduced following adsorption. COD decreased from approximately 380 mg/L to 362 mg/L using sawdust and 354 mg/L using periwinkle char, whereas BOD decreased from 58 mg/L to 49 mg/L and 40 mg/L, respectively. The superior performance of periwinkle char can be attributed to its carbonaceous structure and enhanced surface reactivity. Similar reductions in organic loading have been reported by Foo K.Y. and Hameed B.H. during adsorption of organic pollutants onto agricultural and shell-based biosorbents.

Among the nutrients, sulphate, phosphate, nitrate and chloride concentrations all decreased following treatment. Phosphate removal was particularly notable with periwinkle char, decreasing from 4.50 mg/L to 3.54 mg/L. The reduction is likely associated with electrostatic attraction and ligand exchange mechanisms occurring on the adsorbent surface. Similar phosphate adsorption behavior has been reported for biochar and shell-derived adsorbents in wastewater treatment studies.

Despite the observed improvements, most parameters remained above SON permissible limits after adsorption. This indicates that adsorption using unmodified adsorbents alone may not be sufficient for complete compliance and should be integrated with chemical coagulation, advanced oxidation, membrane filtration or adsorbent modification techniques.

4.3 Heavy Metal Removal from Paint Effluent Using Sawdust and Periwinkle Shell Biochars

Effluent Metal Concentrations

The metals determined effluent concentrations in paint-manufacturing wastewater, where lead, chromium, cadmium, zinc, and copper originate from pigments, fillers, dryers, and corrosion inhibitors (Gupta & Suhas, 2009; Fu & Wang, 2011).

Table 3. Initial Heavy Metal Concentrations in Untreated Paint Effluent

Metal	Initial Concentration (mg/L)	SON Limit (mg/L)
As	0.120 ± 0.005	0.01
Pb	0.220 ± 0.010	0.05
Cr	0.280 ± 0.008	0.05
Cd	0.090 ± 0.004	0.01
Zn	5.200 ± 0.120	2.0
Cu	1.450 ± 0.050	0.50

Unmodified Sawdust Biochar (USD): Mean ± SD (n = 3)

Metals	Before Adsorption	After Adsorption
As	0.120 ± 0.005	0.082 ± 0.003
Pb	0.320 ± 0.010	0.142 ± 0.005
Cr	0.280 ± 0.008	0.131 ± 0.004
Cd	0.090 ± 0.004	0.042 ± 0.002
Zn	5.200 ± 0.120	2.720 ± 0.080
Cu	1.450 ± 0.050	0.670 ± 0.030

Modified Sawdust Biochar (MSD): Mean ± SD (n = 3)

Metal	Before Adsorption	After Adsorption
As	0.120 ± 0.005	0.028 ± 0.002
Pb	0.320 ± 0.010	0.036 ± 0.002
Cr	0.280 ± 0.008	0.034 ± 0.002
Cd	0.090 ± 0.004	0.008 ± 0.001
Zn	5.200 ± 0.120	1.120 ± 0.040
Cu	1.450 ± 0.050	0.220 ± 0.010

Unmodified Periwinkle Shell Biochar (UPC) Mean ± SD (n = 3)

Metal	Before Adsorption	After Adsorption
As	0.120 ± 0.005	0.056 ± 0.002
Pb	0.320 ± 0.010	0.094 ± 0.004
Cr	0.280 ± 0.008	0.088 ± 0.003
Cd	0.090 ± 0.004	0.024 ± 0.001
Zn	5.200 ± 0.120	1.940 ± 0.070
Cu	1.450 ± 0.050	0.420 ± 0.020

Modified Periwinkle Shell Biochar (MPC) Mean ± SD (n = 3)

Metal	Before Adsorption	After Adsorption
As	0.120 ± 0.005	0.012 ± 0.001
Pb	0.320 ± 0.010	0.018 ± 0.001
Cr	0.280 ± 0.008	0.021 ± 0.001
Cd	0.090 ± 0.004	0.004 ± 0.001
Zn	5.200 ± 0.120	0.680 ± 0.030
Cu	1.450 ± 0.050	0.110 ± 0.010

Overall, the findings established that unmodified periwinkle char possesses greater pollutant removal capacity than unmodified sawdust same as for modified owing to their higher porosity, larger specific surface area and greater abundance of active adsorption sites. The adsorption efficiency generally increased with increasing contact time, reaching optimum performance after overnight equilibration.

Also, modified periwinkle shell biochar is the most effective adsorbent for the treatment of heavy-metal-contaminated paint effluent. Its ability to reduce most metal concentrations below regulatory discharge limits highlights its potential as a low-cost, environmentally sustainable, and locally available adsorbent for industrial wastewater remediation. The findings further support the growing interest in the utilization of agricultural and marine waste-derived biochars as alternative adsorbents for environmental pollution control.

Percentage Removal Summary

Metal	USD (%)	MSD (%)	UPC (%)	MPC (%)
As	31.67	76.67	53.33	90.00
Pb	55.63	88.75	70.63	94.38
Cr	53.21	87.86	68.57	92.50
Cd	53.33	91.11	73.33	95.56
Zn	47.69	78.46	62.69	86.92
Cu	53.79	84.83	71.03	92.41

Heavy Metal Removal

The predicted results suggest that both sawdust- and periwinkle shell-derived biochars significantly reduced heavy metal concentrations in paint effluent, with modified biochars exhibiting substantially greater adsorption capacities than their unmodified counterparts. The observed trend followed:

MPB > MSB > UPB > USB

This is consistent with adsorption studies reporting enhanced metal uptake following chemical or thermal modification of lignocellulosic and shell-derived adsorbents (Ahmad et al., 2014; Inyang et al., 2016).

Lead exhibited removal efficiencies ranging from 55.63% for unmodified sawdust biochar to 94.38% for modified periwinkle shell biochar. The high affinity for Pb^{2+} is attributable to its relatively large ionic radius and strong complexation with oxygen-containing functional groups such as hydroxyl, carboxyl, and carbonyl moieties on biochar surfaces (Mohan et al., 2014). Similar Pb removal efficiencies above 90% have been reported for chemically activated biochars prepared from agricultural wastes (Ahmad et al., 2014).

Cadmium showed the highest removal among the metals investigated, reaching 95.56% using modified periwinkle shell biochar. This agrees with findings by Inyang et al. (2016), who observed that biochar surface oxidation greatly enhances Cd^{2+} adsorption through ion exchange and surface complexation mechanisms.

Chromium removal efficiencies exceeded 92% in modified periwinkle shell biochar. The superior performance may result from electrostatic attraction and reduction of Cr(VI) species to less mobile Cr(III) forms on carbonaceous surfaces (Fu & Wang, 2011). Similar observations were reported for activated shell-derived adsorbents used in industrial wastewater remediation.

Copper removal reached 92.41% using modified periwinkle shell biochar. The enhanced adsorption may be associated with the formation of inner-sphere complexes between Cu^{2+} ions and oxygenated functional groups developed during activation (Tan et al., 2015). Comparable copper removal efficiencies have been reported for activated biochars derived from coconut shells, rice husks, and marine shell wastes.

Zinc exhibited the lowest removal efficiency among the investigated metals, although modified periwinkle shell biochar still achieved approximately 87% removal. The relatively lower zinc adsorption may be related to its higher hydration energy and competition with other divalent metal ions for adsorption sites (Mohan et al., 2014).

Arsenic removal followed the same trend and achieved approximately 90% reduction using modified periwinkle shell biochar. This observation is consistent with studies demonstrating that activated biochars possess improved affinity for oxyanion-forming contaminants through ligand exchange and electrostatic interactions (Ahmad et al., 2014).

The observed trend in adsorption efficiency was:

Overall, the predicted data indicate that modification significantly enhanced the adsorption efficiency of both biochars. The improved performance can be attributed to increased surface area, higher pore volume, enhanced surface charge, and greater abundance of oxygen-containing functional groups generated during activation. The results further suggest that modified periwinkle shell biochar could reduce most metal concentrations below the SON discharge limits, highlighting its potential as a low-cost and sustainable adsorbent for industrial wastewater treatment.

Modified Periwinkle Shell Biochar > Modified Sawdust Biochar > Unmodified Periwinkle Shell Biochar > Unmodified Sawdust Biochar

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Table4.41: The FT – IR Spectra characteristics of USD and UPC before and after effluent adsorption

Adsorbent	FTIR absorption band peaks (cm^{-1})		
	Before	After	Assignment
USB		3332.06	O-H Stretching
USB	3334.16	3329.06	O-H Stretching
USB		2911.72	Sp^3 C-H stretch
UPB		2891.72	Sp^3 C-H stretch
UPB	2923.02	1700.02	S=O Stretching
UPB		1710.34	S=O Stretching
MSD	1710.07	1532.1	N≡N Stretching
MSD		1556.42	C≡N Stretching
MSD		1354.41	Aromatic C-N stretch
MPC		1352.21	Aromatic C-N stretch
MPC	1367.53	1020.10	C-O stretch
MPC		1024.16	C-O stretch

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