

Treatment of Refinery Wastewater by a Waste Plastic based Activated Carbon

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Abstract

It is essential to focus on the removal of phenol from contaminated water due to its harmful effects on humans. Recently, the circular economy has drawn a lot of interest since it attempts to reduce waste and continually use resources. When creating new value goods in a circular economy, resource recovery employs recovered garbage as the primary raw material. This research focuses on a low-cost approach that employs hydrothermal calcination and acids activation to create an activated carbon (AC) adsorbent from used cation exchange resin. SEM, XRD, ICP, and BET were used to analyze the surface chemistry and structure of AC. It was discovered that the bases and acid treatment might enhance the number of pores and functional groups on the AC surface that contain oxygen. According to experimental findings, AC modified with HCl had the maximum efficiency of phenol removal, demonstrating the influence of acidification on AC's adsorption ability. To match the experimental data, Freundlich and Langmuir adsorption isotherms were used.

Keywords: Phenol; Wastewater; Plastic waste; Activated carbon.

1. Introduction

The carbon and water cycles are greatly affected by Petroleum refineries. The Sustainable Development Goals (SDGs) of the United Nations (UN) state that Zero Liquid Discharge (ZLD), zero carbon disposal, and minimization of solid wastes are crucial for reducing waste and enhancement of recycling [1]. Operational efficiency in waste management in petroleum refineries is essential [2]. Benefits of this include better resource utilization, lower cost, and decreased risk to both people and the environment. This paper presents a complete and useful reference for the refinery waste management [3]. It covers the waste types, waste characterization, and significant treatment methods and technologies in detail. It is primarily designed to provide nations with little to no regulatory oversight as well as refineries' present waste management procedures [4] with guidance and aid in controlling refinery trash. Thermosetting polymers (phenolic resins) are often known as phenol-formaldehyde resins, as well as being employed in a variety of applications. Due to their adaptability, variety of applications, and affordability, phenolic resins are expected to continue to rise at a compound yearly growth rate of 5.4%, with a market value of US\$12.63 billion in 2019 [4].

Furthermore, there is a problem with the accumulation of various kinds of waste generated from different resources is an issue. By introducing innovative techniques for processing waste plastic, a circular economy can help to protect the environment by minimizing the amount of plastic trash generated and the pollutants it emits when burned. Refiners are receiving sustainable feedstock from waste recycling technologies, which are advancing in the downstream sector and lowering their dependency on fossil fuels [5]. For refiners, navigating the existing environment is not an easy task. Low- and intermediate-level waste can be processed using a variety of methods.

Volume reduction is significantly a crucial part of waste treatment since waste volume is one of the factors that determine the cost of disposal to the waste generator. Injection molding, extrusion, rotational molding, and heat pressing are the most popular techniques for this kind of mechanical recycling processing. Therefore, polypropylene (PP), polyethylene (PE), polyethyleneterephthalate (PET) polystyrene (PS), and polyvinylchloride (PVC) are the polymers that can typically be mechanically recycled are thermoplastic polymers like Chemical recycling of monomer feedstock is increasing in interest as it is ideal for the preservation of finite non-renewable resources as well to decrease non-degradable waste thus protecting the environment. The different types of chemical recycling include methanolysis, hydrogenation, glycolysis, gasification, pyrolysis, hydrolysis, and ammonolysis. The process is selected based on the product that must be recycled. For example, the degradation of PET to dimethyl terephthalate and ethylene glycol by methanol is called methanolysis.

Plastic waste has been utilized to produce carbon-based compounds including graphene that used as a high-voltage supercapacitor, porous carbon to absorb CF_4 , N-doped microporous carbon to absorb CO_2 , carbon nanomaterials and activated carbon and its fibers use to remove contamination from air and water. Activated carbon (AC) generally refers to carbonaceous materials characterized by large surface area, surface reactivity, and porosity, capable of absorbing a range of gases and pollutants in a liquid phase. AC has been successfully used for the removal of contamination from water, CO_2 , dye removal, storage of Adsorbed Natural Gas (ANG), methane capture, electrode materials for supercapacitors, solvent recovery, contaminated soil remediation, as well as use as a green fuel.

The structural composition of plastic waste reveals microcrystallites made of carbon atoms arranged in hexagonal rings, stacked in planes, interconnected by functional groups, and held by van der Waals forces. Because of its structure, AC is a remarkable adsorbent due to its high porosity and surface affinity for various chemicals. Two different thermal processes form physical activation. The first one is pyrolysis or carbonization of the carbonaceous precursor at high temperatures, usually in the range of 700–900°C, under an inert atmosphere to avoid combustion of the carbonaceous matter. The second step of the physical activation process is gasification. This consists of the selective removal of the most reactive carbon atoms by controlled gasification reactions that generate the characteristic porosity of the activated carbons. A series of experiments have been conducted by to study the effects of different carbonization temperatures (400, 600, 800, and 1000°C) on characteristics of porosity in carbonized coconut shell char and AC derived from carbonized coconut shell char by steam with different activation times (30, 60, 90 and 120 min) at activation temperature of 900 °C. The results showed that with increasing carbonization temperatures, more volatiles were released and more micropores were formed, giving rise to a decrease in yield, and increasing surface area, total volume, and microporous volume of the char. When using different activation times at a temperature of 900oC, the results showed that the yields and average pore diameters decreased while the BET surface area, total volume, and microporous volume increased with increasing activation time. Moreover, the ACs derived from high carbonization temperature chars had a larger BET surface area, total volume, and microporous volume than the ACs derived from low carbonization temperature chars. The optimum BET surface area of 1926 $\text{m}^2 \text{g}^{-1}$ of AC prepared from char was obtained at 1000°C with an activation time of 120 min. The maximum BET surface area was found to be around 1000–1200 $\text{m}^2 \text{g}^{-1}$. According to Sun and Chun Jiang, the rubber-seed shell was used as a raw material to produce AC with a two-stage process of physical activation. The material was pyrolyzed at 650°C followed by steam activation at 880°C for 1 h resulting in carbon with a surface area of up to 950 $\text{m}^2 \text{g}^{-1}$. Although having three distinct phases of synthesis, the chemical activation process used to create activated carbons only requires one heat step. The precursor is first impregnated with the activation agent. The literature has historically explored a variety of activating substances, including zinc chloride, potassium hydroxide, NaOH, and KOH, H_3PO_4 , zinc chloride, and potassium hydroxide. The impregnation procedure can be accomplished by various techniques. For example, some researchers use an aqueous solution of the activating agent put in contact with the carbonaceous precursor. However, other studies perform a direct and simpler physical mixing

of the precursor and the activating agent. After impregnation, the second step of the chemical activation procedure is thermal treatment in an inert atmosphere at different temperatures depending on the chosen activating agent. During this step, reactions of de-polymerization, dehydration, and condensation take place, resulting in higher carbon yields than in physical activation due to the restriction in the formation of tars and volatiles. Finally, the last stage involves washing to remove the remaining activating agents and reaction byproducts that occlude the newly formed porosity and drying. Oummam *et al.* [6] Compared chemical and physical activation processes at Moroccan oil shale adsorbents to the treatment of water loaded with a metal (Cr^{6+} ion) and organic (methylene blue (MB)). They concluded that the chemical activation process of oil shale at low temperatures (250°C) affords the best material.

The material's yield is good in comparison with the physical activation at the same temperature and the process is energy saving differently from that at 450°C . Moreover, the chemical activation of oil shale with phosphoric acid at 250°C produces a material with a good yield (about 70 %), a high specific surface area (approximately $600\text{ m}^2/\text{g}$), and a highly porous structure, which gives it high retention of methylene blue and the Cr^{6+} ion. The thermochemical conversion of polymer solid wastes into activated carbon with strong adsorption propensity and energy is a beneficial conversion technique. Waste formed of polymers are an essential source of raw materials for the manufacture of products containing activated carbon. Polymeric waste in the form of polyolefin wax (POW), which has an average molecular mass of 1100 and a melting point of approximately 115°C , decomposes into low-molecular-weight compounds that slowly evaporate when heated in the air at 360°C . To create activated carbon, 200 g of POW are heated to 115°C (the melting point) to generate activated carbon. At which moment 98% H_2SO_4 is added dropwise while stirring continuously raising the temperature to 160°C . The final solid product is carbonized at 600°C , after washing and dried at 150°C . After carbonization, the POW product processes a 60-minute, 800°C water steam activation procedure. It was found that waste ion-exchange resin could be used to make activated carbon, which not only manages the challenging terminal processing of waste resin but also turns waste into wealth. Waste ion-exchange resin was utilized by Bratek *et al.* [8] to make activated carbon, which was then activated by CO_2 physical activation. The activated carbon (AC) effectively cleans the toluene-contaminated water. Shi *et al.* [7] employed KOH chemical activation to manufacture activated carbon with waste ion-exchange resin for naphthalene adsorption. Martin *et al.* [8] produced adsorbents that separate CO_2 in pre-combustion using a variety of phenolic resins as precursor materials. The highest rate of CO_2 adsorption at atmospheric pressures was 10.8 wt%, whereas the highest rate of CO_2 adsorption at high pressures at room temperature was 44.7 wt% at 25 bar. Activated carbon was created by Meng and Park [9] using an ion-exchange resin with a nanoporous basis. The resulting activated carbons have a high ability to absorb CO_2 . The creation of phenolic or ion-exchange resin raises the price of activating carbon before use. In the present study, a novel method for phenolic refinery wastewater treatment was developed using an activated carbon adsorption process based on the recycling of the ion exchange resin.

2. Experimental work

This section presents the formation, characterization as an adsorbent, and evaluation of the activated carbon for phenol removal from refinery wastewater. Table 1 shows the adsorption process variables. Total number of experiments= $3 \times 3 \times 4 \times 5 = 180$.

2.1. Materials

The chemicals and reagents used for the preparation of the activated carbon are shown in Table 2.

Table 1. Variables of the adsorption process of the phenolic compounds in the refinery wastewater.

Variables number	Parameter	Values
3	Temperature ($^\circ\text{C}$)	25, 35, 45
3	Phenol concentration (ppm)	250, 500, 1000
4	Residence time (min)	10, 20, 30, 40, 50, 60, 70
3	Dosage of AC, g	1, 3, 5

Table 2. Chemicals used in the preparation of the activated carbon.

Chemicals and materials	Purity %	Function	Manufacturer/Provider
Spent ion exchange resin	----	Precursors	-
Hydrochloric acid	95%	Chemical activator	Sigma Aldrich/ Germany
Ethanol	98%	Chemical activator	Sigma Aldrich/ Germany
Deionized water	-	Washing liquid	Lab. of Chemical Engineering
Distilled water	-	Washing liquid	Lab. of Chemical Engineering
KOH	95%	Activation	Panreac /Spain
N ₂ gas	99%	Heating atmosphere	Local provider

2.2. Preparation of activated carbon

The activated carbon was formed from the ion exchange resin that was disposed of after six years of being used in the water boiler pretreatment units at NRC (North Refineries Company).

- The WIER was first washed with demineralization boiler water and the waste was filtered and dried.
- The dried WIER was immersed in the ethanol solution overnight. This immersion was conducted to remove the organic impurities that were adsorbed on the surface of the resin at the time of being used in the utility unit in the refinery.
- After immersion, the WIER was washed with distilled water until the pH of the washing water was close to 7.
- The WIER was then impregnated with 5% hydrochloric acid (HCl) for 24 hours.
- The impregnated WIER was dried in a drying oven (Gallen Kamp Sanyo/Weiss, hot box oven, size 1, maximum temperature: 240°C, UK) at 250°C for 24 hours and kept overnight in the desiccator.
- The dried WIER was placed in an alumina crucible boat inside the calcination chamber of a tubular furnace (SafeTherm, China, heating length 300 mm, maximum temperature 1200°C) at a heating rate of 2°C/min to 800°C and maintained at this temperature for 1 hr. This step is called carbonization and was conducted under a nitrogen atmosphere.
- The furnace was brought to room temperature using the control system of the heating unit.
- The nitrogen flow rate was gradually lowered and switched off after 30 min.
- The WIER (before carbonization) and the char (after carbonization) were weighed, and the yield of the char was determined using equation (1):

$$Y_C = \frac{m_C}{m_W} \times 100 \quad (1)$$

where Y_C : the yield of char; m_C : mass of char; m_W : mass of waste ion-exchange resin.

- A solution of KOH was formed at a concentration of 35% by diluting the KOH pellets with distilled water and the char was added to the solution. The KOH to char mass ratio (impregnation ratio) was 1.0 [10].
- The sample was transferred to an ultrasonic homogenizer sonicator processor mixer (Top-tion, China, ultrasonic power 650W, volume 0.1-600 mL) and mixed at a power of 40% and 0.1 pulses for 80 min, the sample was left to rest for 12 h.
- The mixture was left at room temperature overnight and left to dry in the drying oven for 24 hrs.
- The dried mixture was dried before being placed into the tubular furnace to be heated for 60 min at a rate of 2°C/min from ambient temperature to 600°C. The furnace was evacuated by purging a flow rate of 100 m/min of nitrogen for 30 min.
- After cooling the furnace back to room temperature, the activated carbons were taken out of the furnace.
- The prepared activated carbons were then weighed and the activated carbons' yield and burn-off was measured by the equation (2).

$$Y_b = \frac{m_C - m_{AC}}{m_C} \times 100 \quad (2)$$

$$Y_{AC} = \frac{m_{AC}}{m_r} \times 100 \quad (3)$$

where, Y_b , Y_{AC} , m_{AC} the burn off, the yield of activated carbon and the mass of the AC.

2.3. Characterization of the catalyst

2.3.1. BET (N_2 adsorption/desorption)

The specific surface area SBET, total pore volume, micropore volume, mesopore volume, and average diameter of the activated carbon were calculated based on the multipoint surface area analysis method. The test was carried out in Quantachrome Instrument (Hitit University, Samson, Turkey). 0.2738 g of the activated carbon powder is weighed and placed in a sample cell assembly then heated to 90°C in 10 min and the temperature is held for 1 hour, after then the temperature is increased to 350°C and kept for 2 h. The physisorption gas was molecular nitrogen, and the cross-section area of the nitrogen molecule was 16.2 nm². Isotherms of adsorption and desorption used in the BET surface area analysis were obtained at the boiling temperature of liquid nitrogen (78K).

2.3.2. SEM- EDX

Energy dispersive spectroscopy (EDS) analysis was carried out with a scanning electron microscope (SEM) for the AC to obtain the elemental mapping and morphology of the materials. The working principle of energy dispersive X-ray (EDX) spectroscopy is the calculation of the elemental composition of the specimen by detecting the X-ray emitted by the sample. A scanning electron microscope (SEM) for the AC was carried out to determine the components of it and the surface distribution. The electron microscope has some advantages including great resolution, high magnification, large focus depth, and ease of sample preparation and observation compared to traditional optical microscopes. Images of the AC surface were obtained by microscopy using a Jeol Jsm-7001F Scanning Electron Microscope at 19 Mayıs University, Advanced Technology Research and Application Center, Turkey. Energy-dispersive X-ray spectroscopy (EDX), secondary electron (SE) detector, wavelength-dispersive X-ray spectroscopy (WDX), backscatter electron detector (BSD), and electron backscatter diffraction are all included in the Jeol JSM-7001F SEM (EBSD).

2.3.3. XRD diffraction

A versatile and effective non-destructive method for describing crystalline materials is X-ray diffraction (XRD). To study its structure, XRD was operated between 10 and 80 (2 θ) at a scan rate of 3 C/min. To using Rigaku Smart Lab XRD, the composition and crystal structure of the Pd/AC and Pd/AC coating were characterized. The experiment which was carried out at 40 kV and 40 mA, CuK radiation was used for the measurements, the. XRD test was conducted through in Turkey at the Advanced Technology Research and Application Center, Turkey at 19 Mayıs University.

2.3.4. TGA

Thermogravimetric analysis is a type of thermal analysis in which, as the temperature increases, the mass of a sample is determined over time. TGA is a widely used instrument for investigating the thermal characteristics of a material in heating environments based on this process. TGA (thermogravimetric analysis) was conducted at 19 Mayıs University, Advanced Technology Research and Application Center, Samson, Turkey. The analysis protocol was to heat the AC sample from room temperature to 1000°C with a heating ramp of 20°C/min under a nitrogen atmosphere.

2.4. Activated carbon evaluation

2.4.1. Experimental setup

The adsorption isotherm of the phenol compounds removal using the activated carbon prepared from waste ion exchange resin was obtained by conducting a series of adsorption experiments in a batch experimental setup where a 500 mL three-necked glass flask was fitted to a coiled condenser for water or oil condensation reflux, magnetic heating stirrer (JISICO, Korea) and an oil bath at atmospheric pressure. The feedstock used was the refinery

wastewater taken at different operation times where the concentration of phenol was fluctuating. Before the adsorption runs, the flask was pretreated with the heater, and different AC dosages were added to the mixture (wastewater) and agitated at 250 rpm for different times at different temperatures. The flask was connected to a glass condenser (0.5 m length), such that any vapors given off were cooled back to a liquid and fell back into the reaction flask. The heater was set to the desired temperature and left in contact with the AC for different residence times. When the desired time was approached, a sample of the mixture was withdrawn and labeled for analysis. At the end of each run, the heating magnetic stirrer was stopped and cleaned. The flask was cleaned by washing and drying to prepare for the next run. The same procedure was repeated at three different temperatures (25, 35, and 45°C), and adsorption times (10, 20, 30, 40, 50, 60, and 70 min), as shown in Table 1. Each experiment was repeated two times and error bars were applied to obtain the Standard Deviation of the experiments.

2.4.2. Running of experiments

The experimental evaluation of the prepared activated carbon in the present study was divided into two parts; the first part was adsorption isotherms experiments to determine the model of adsorption and to earn information on the most appropriate conditions for the second part of the study. The second part was conducted to evaluate the performance of the prepared AC in the process of phenolic compounds removal from the refinery wastewater. The target of the second part was to obtain the highest phenol uptake and examine the lifetime of the prepared AC against saturation.

2.4.2.1. Kinetic and adsorption isotherms experiments

Table 3 show the matrix of experiments of the kinetics runs conducted to obtain the model of the kinetics of phenolic compounds adsorption from refinery wastewater. It can be seen that 24 runs were conducted for the kinetics part. For all kinetics experiments, the AC dosage was 1 g/500 mL of the wastewater mixture.

Table 3. Design of experiments (full factorial method) for kinetics of adsorption.

Run	Temperature, (°C)	Phenol (ppm)	Time (min)	Run	Temperature, (°C)	Phenol (ppm)	Time (min)
1	25	250	30	13	25	500	30
2	25	250	60	14	25	500	60
3	25	250	90	15	25	500	90
4	25	250	180	16	25	500	180
5	35	250	30	17	35	500	30
6	35	250	60	18	35	500	60
7	35	250	90	19	35	500	90
8	35	250	180	20	35	500	180
9	45	250	30	21	45	1000	30
10	45	250	60	22	45	1000	60
11	45	250	90	23	45	1000	90
12	45	250	180	24	45	1000	180

For the experimental runs of adsorption isotherms, the runs were planned according to the full factorial design shown in Table 1 as 180 runs were conducted to obtain the adsorption isotherms. The numerous models of adsorption isotherms have been represented by a wide range of theoretical and empirical models. There is now no solitary model that adequately describes all mechanisms and forms. In applications involving wastewater treatment, the Langmuir and Freundlich models have been frequently employed to characterize adsorption isotherms. The Langmuir isotherm [11] presupposes that the sorbate will bind consistently and uniformly to the surface of the adsorbent, which is often defined by:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (4)$$

where, q_e : the equilibrium quantity of phenol adsorbed in mg/g_{AC}; C_e : the equilibrium concentration of phenol in wastewater in mg/l (ppm); q_m and b : adsorption isotherm constants measured in mg/g and l/mg respectively.

In the present study, another adsorption isotherm model will be examined, the Freundlich isotherm and it is unlike the Langmuir isotherm in that it is not equilibrium dependent isotherm and is more adapted to adsorption of hazardous materials from waste water [12-13]:

$$q_e = a_F C_e^{1/n} \quad (5)$$

where a_F and n are constants.

For the adsorption kinetic model, the following model will be examined in the present study. Lagergren [14-15] developed a pseudo-first-order model to represent the kinetics of adsorption:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (6)$$

where q_t : quantity of phenol adsorbed at time= t , (mg_{phenol}/g_{AC}) ; q_e : quantity of phenol adsorbed at equilibrium, (mg_{phenol}/g_{AC}); k_1 : pseudo-first-order absorption rate constant, min⁻¹.

Ho [16] suggested a pseudo-second-order adsorption model defined as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (7)$$

where k_2 is the pseudo-second-order rate constant (g_{AC}/mg_{phenol}.min).

The sample of the wastewater was mixed inside the magnetic heater stirrer for the time designated with the dosages of the AC. A sample of the treated solution was withdrawn periodically (every 10 min), labeled, and analyzed for the remaining phenol concentration. Phenol absorption efficiency was calculated as shown in Equation (8):

$$X_{Ph} = \frac{[Ph]_{in} - [Ph]_{out}}{[Ph]_{in}} \quad (8)$$

2.4.3. Analysis of products

A UV spectrophotometer (JASCO ultraviolet/visible (UV-VIS/530)) was used to measure the phenol concentration in the activated carbon treatment cycle.

Prior to each adsorption experiment phenol calibration curve of the UV, spectrophotometer was developed to fix deviations in peak height, which could occur due to the unstable operation of the spectrophotometer. The calibration curve was developed by collecting samples of phenol solution in the range of 0.00 to 1500 mg/L (ppm) and the absorbency was measured in the apparatus against each concentration, then they both were plotted (absorbency vs. concentration).

3. Results and discussion

3.1. Catalyst characterization

This section depicts and discusses the results that were obtained from different advanced material characterization methods. Via these methods, the textural properties, morphology, crystallinity, phase structure, and metal composition of the prepared activated carbon were examined.

3.1.1. Specific surface area, pore volume, and pore size distribution

The BET surface area is calculated from the isotherms by using the Brunauer-Emmett-Teller (BET) equation [17]. The Dubinin- Radushkevich (DR) method is used to calculate the micropore volume [18]. The micropore size distribution is ascertained by Non-local Density Functional Theory (NLDFT) [19] by minimizing the grand potential as a function of the fluid density profile. The total volume is estimated by converting the amount of N₂ gas absorbed at a relative pressure of 0.95 to the equivalent liquid volume of the adsorbate (N₂). Langmuir Surface area and average diameter for all the prepared activated carbon were carried out by using nitrogen gas analysis at 77 K with degassing lasted for 12 h, pore volume and pore size of synthesized support and catalysts are summarized in Table 4.

Table 4. Surface area and pore volume information for the activated carbon.

BET surface area (m ² /g)	Total pore volume (cc/g)	Micropore volume (cc/g)	Mesopore volume (cc/g)	D _{Average} (nm)
520.3	0.125	0.115	0.036	1.02

From the surface area, pore-volume, and pore-volume distribution it can be seen basically that the utilization of the waste ion exchange resin in the present study and using the preparation method described in section 2.2 was efficient in the production of high surface area activated carbon (AC) compared to a previous relevant works [10,20-21]. The BET surface area was as high as 520.3 m²/g. This indicated that the preparation agents (KOH, ethanol, and HCl), carbonization steps, and drying used in the present study effectively contributed to the production of a high surface area AC along with the effective heat treatment in the tubular furnace [22]. The total pore volume of the AC was 0.125 cm³/g with an average pore diameter of 1.02 nm indicating that micropore size is dominant in the prepared AC ($d \leq 2$ nm) [23-25].

3.1.2. SEM-EDX

The morphology of the AC material prepared in the present study was examined by SEM. After the HCl activation and the hydrothermal process during AC preparation, the texture and the structure of this AC material became irregular and more porous than in the rough state (native state of plastic), and the number of pores is much higher [26]. The porosity and increased cavities of these materials cause an increase in the adsorption capacity, which allows these materials to adsorb high concentrations of adsorbates [27]. They can therefore be used as adsorbent materials with high efficiency and can be used in many industrial and environmental applications. Morphological pictures of these samples of AC are presented in Figure 1.

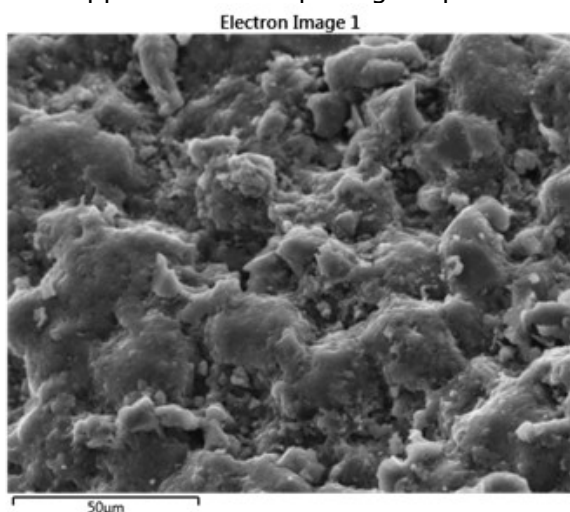


Figure 1. SEM Images of the AC.

The SEM micrographs of waste-activated carbons made from ion-exchange resin are shown in Figure 1. By SEM, the morphology of the AC was investigated. The particles or crystals have a spherical form. The size distribution of the particles is satisfactory. Some of the activated carbons that are formed during carbonization and activation maintain their nice spherical shape, while the others are crushed. Instead of being smooth, the surface of activated carbons becomes rough [28]. Because they can allow CO₂ to penetrate the interior of the activated carbons [29], the generated cracks and pores are advantageous for the following CO₂ adsorption during calcination in the tubular furnace.

Energy dispersive X-ray (EDX) was used to determine the surface composition of the prepared ACs. The spectrum obtained from EDX shown in Figure 2 obtained by using a tubular furnace for AC calcination shows a presence of surface elements of 44.4% oxygen (O), 23.4% silicon (Si), 23.0% carbon (C), 3.3 iron (Fe), aluminum (Al), 1.8 and other trace elements. The surface elemental analyses indicated that the carbonization step during the AC preparation was successful in reduction of polymeric compounds to provide a unique structure of the AC [30-31]. The high percentage of oxygen was present in the AC due to the high content of oxygen within the polymeric compounds which are the main components of the waste ion exchange resin. It also shows that there a lot of iron was strongly bound to oxygen, carbon, and silica. Table 5 shows the same results.

Table 5. The elemental mapping of the prepared AC by EDX.

Element	Line Type	Apparent concentration	k Ratio	wt%	wt% Sigma	Standard label	Factory standard
C	K series	15.87	0.15869	70.86	0.27	C Vit	Yes
O	K series	4.24	0.01426	17.98	0.19	SiO ₂	Yes
Mg	K series	0.28	0.00189	0.64	0.02	MgO	Yes
Al	K series	0.61	0.00440	1.34	0.02	Al ₂ O ₃	Yes
P	K series	2.77	0.01550	4.11	0.06	GaP	Yes
S	K series	0.06	0.00052	0.14	0.02	FeS ₂	Yes
Fe	K series	0.33	0.00325	0.92	0.05	Fe	Yes
Total:				100.00			

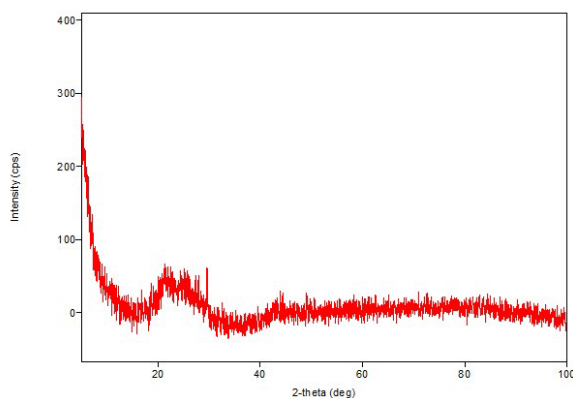


Figure 2. XRD patterns of the AC prepared from waste ion exchange resin.

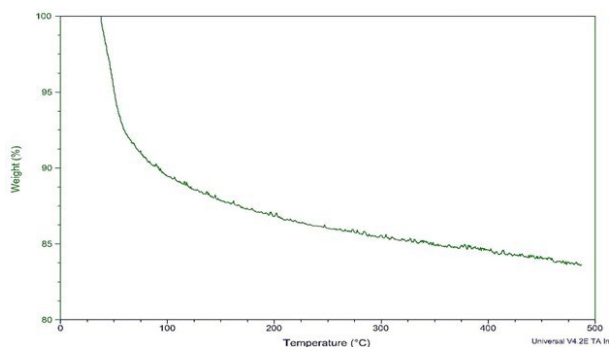


Figure 3. TGA for the prepared AC.

3.1.3. XRD patterns

The AC formed from waste ion exchange resin using chemical activation can be crystallographically characterized utilizing X-ray Diffraction. Figure 2 displays the XRD patterns of the AC sample. It is clear that following HCl treatment, the inherent lattice structure of AC was developed and no other solid phase was produced [32–33]. The American Society for Testing and Materials (ASTM) [34] data can be used to examine the peaks in the XRD patterns of the AC sample prepared in the present study. The XRD patterns of AC have peaks at $2\theta=24$, and 43 [35–36], which closely resemble the distinctive peaks of AC [37]. This suggests that AC crystals are present in the material prepared.

All X-ray measurements were repeated on at least two sets of specimens to verify the trend, and further research is underway to clarify the apparent relationship between microstructure and transformation to rutile at 650°C [38–39]. Rutile formation was enhanced by calcination in the tubular furnace in the presence of HCl solution and resulted in large particles and less dense microstructures, they were relatively insensitive to heat-treatment temperature.

3.1.4. Thermal gravitational analysis (TGA)

The thermogravimetric analysis (TGA) curve for the AC catalyst originated from waste ion exchange resin as shown in Figure 3. The TGA curves of the AC exhibited that the decomposition of AC occurred in three phases and that these decomposition phases. The AC heating at 25 to 175°C removes moisture that was lost 5% weight. Loss of 10% weight in the second decomposition reaction was observed in the range of 175 – 400°C . The loss at this range of thermal treatment temperatures could be attributed to the decomposition of polymeric chains [40–41]. The last part of the weight loss was 2% weight loss occurred at 400 – 550°C , which indicates the decomposition of a structure with high stability [42]. Above 400°C , the mass loss is small and becomes almost constant. Thus, it is concluded that the preparation method used and the

step of preparation including carbonization and drying resulted in a satisfactory resistance of the AC to heat exposure and contributed to the increase in thermal stability of the prepared AC [43].

3.2. Proximate analysis

The proximate analysis for the precursor (waste ion exchange resin), the char, and the activated carbon is shown in Table 6. The elementary composition of the waste ion exchange resin was found using the ICP apparatus described in section 2.2. It was found that it consists of the following elements: C: 30.3%; H: 6.35%, S: 13.2%, and N: 0.78. The elemental analysis of the ash shows that contains the following elements measured in element/kg of ash; Ca: 42.2 Na: 29.5, Mg: 25.8, K: 5.3, Fe: 1.85, Mn: 0.34, Cu:0.2, and SiO₂: 0.102. The activated carbon elemental analysis shows the following elements measured in g_{element}/kg of ash; Ca: 3.1; Na: 12.5, Mg: 3.1 K: 0.2, Fe: 0.12, Mn: 0.032, and Cu:0.102.

Table 6. Proximate analysis of the precursor, and products of activation.

Parameter	Waste ion exchange resin	Char	Activated carbon
Moisture	20.1	0.89	3.2
Ash	7.4	32.5	23.4
Volatile matters	42.2	8.56	12.4
Carbon	30.3	58.05	61

3.3. Adsorption isotherms

By calculating the phenol loading q (mg of phenol per gram of AC prepared), the adsorption capacity of the AC was examined as a function of different operating variables shown in Table (1) as a function of the initial phenol concentration, AC dosage, temperature of the process, and time in the cycle. According to equation (9) of Langmuir:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (9)$$

Also, equation (10) of Freundlich:

$$q_e = a_F C_e^{1/n} \quad (10)$$

Based on the experimental data obtained via the experimental work described in section 2.2.

3.4. Kinetics of the adsorption process

The kinetic data obtained via conducting the experimental runs mapped in Table 3 were fitted to both pseudo-first-order and pseudo-second-order models shown in equations (9) and (10) after integration to yield equation (11) and (12) respectively [44]:

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (11)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (12)$$

Figure 4 show the kinetic plot of the adsorption of phenol from wastewater on the prepared AC at 1 g dosage of AC starting from 250 ppm of phenol at different temperatures.

Figure 5 represent the kinetic plot of the adsorption of phenol from wastewater on the prepared AC at 1 g dosage of AC starting from 500 ppm of phenol at different temperatures and Figure 6 show the same trend at 1000 ppm initial concentration of phenol in the wastewater. Figure 7 show profiles of the phenol uptake on the prepared AC based on fitting the data in Figure 4 on the equation (9).

The kinetic data are fitted using the pseudo-first order as shown in Figure (8). This profile explains the phenol adsorption behavior on the prepared AC, and the kinetics parameters are reported in Table 7. The computed phenol adsorption capacity (q_e (cal.)) and the correlation coefficients (R^2) might be utilized to assess if the adsorption kinetics model is applicable [29,45-46]. The pseudo-first-order model's R^2 values are, in sequence, 0.9810, 0.968 and 0.954 for 25°C, 35°C and 45°C.

Figures 8-12 shows the profiles of phenol kinetic adsorption of the prepared AC fitted on the pseudo-second-order model shown in equation (10). It can be seen that the R^2 values are

between 0.98-0.99 (also obvious in Table 7), indicating that it is a better fit to represent the experimental data than the pseudo-first-order model.

On the other hand, the observed adsorption capacity is greater than the q_e (cal.) values for the pseudo-first-order model. The pseudo-second-order model's q_e (cal.) values are in good agreement with the q_e (exp.) values for phenol (q_e (exp.)). The pseudo-second-order model is often suitable to express the kinetics of adsorption.

Adsorption is a multi-step process that includes external diffusion, intraparticle diffusion, and real surface adsorption [29]. The phenol adsorption process' rate-controlling stage is shown by fitting the experimental data to the intra-particle diffusion model. The fact that the adsorption procedure is broken down into two parts in the figures of adsorption kinetics that shows the intricate adsorption procedure is governed by many mechanisms [47-48].

The desorption process is regulated by many mechanisms. The two phases correspond to macro/mesoporous diffusion and micro-porous diffusion, respectively, since the prepared AC has micro-, meso-, and macro-pores. This suggests that the pore structure of the AC plays a major role in controlling phenol diffusion. Additionally, the values of the intercept C are not zero, demonstrating that both pore diffusion and exterior layer diffusion are involved in regulating the adsorption rate. Table 7 show the values for the rate parameters, the k_{is} , a , and R^2 .

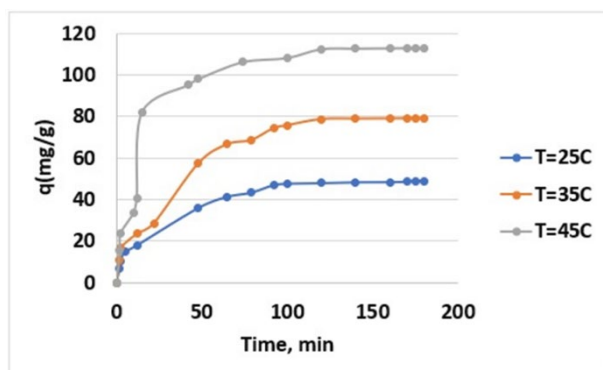


Figure 4. Kinetic plot of the adsorption of phenol (initial=250 ppm) from wastewater on the prepared AC at 1 g dosage of AC and different temperatures.

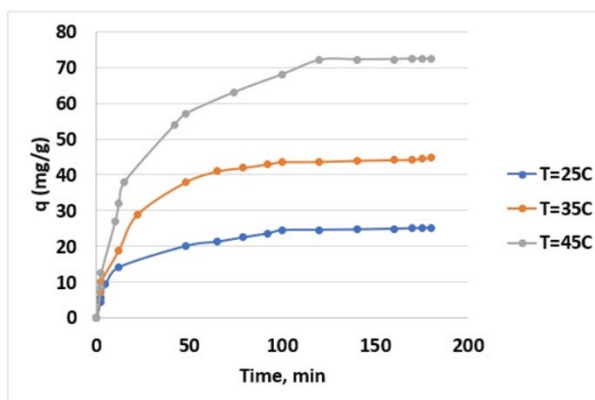


Figure 5. Kinetic plot of the adsorption of phenol (initial=500 ppm) from wastewater on the prepared AC at 1 g dosage of AC and different temperatures.

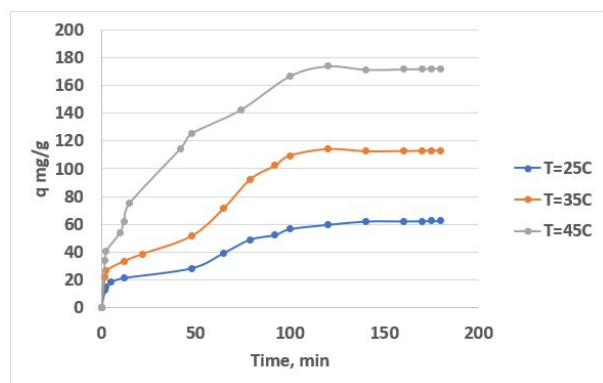


Figure 6. Kinetic plot of the adsorption of phenol (initial=1000 ppm) from wastewater on the prepared AC at 1 g dosage of AC and different temperatures.

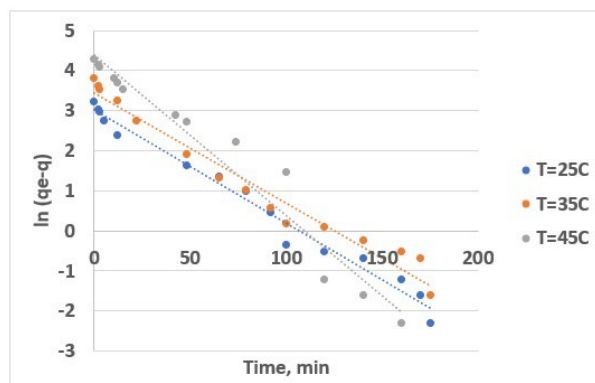


Figure 7. Fitted kinetic plot of the adsorption of phenol (initial=250 ppm) based on pseudo first order model (data in Figure (4))

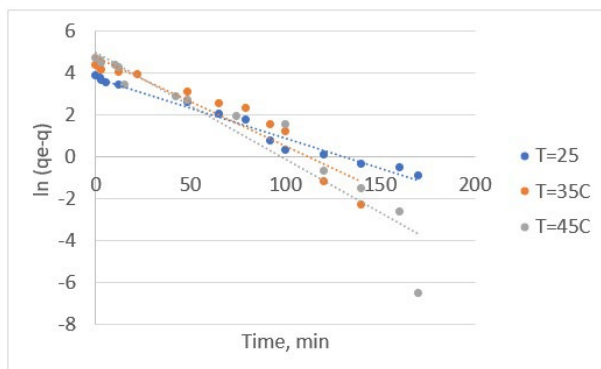


Figure 8. Fitted kinetic plot of the adsorption of phenol (initial=500 ppm) based on pseudo-first-order model (data in Figure (5)).

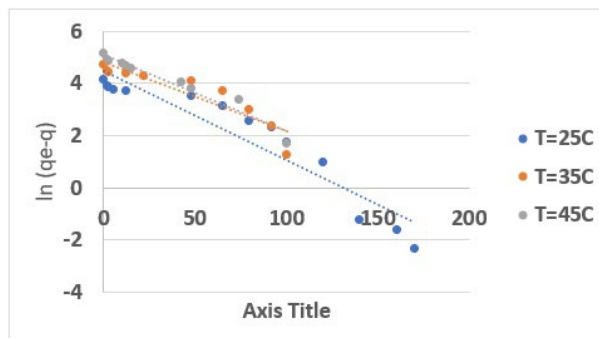


Figure 9. Fitted kinetic plot of the adsorption of phenol (initial=1000 ppm) based on pseudo first order model (data in Figure (6)).

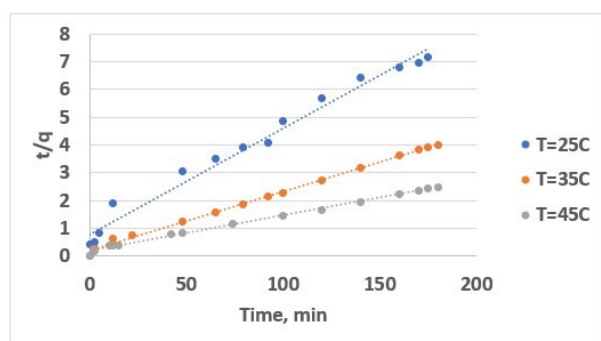


Figure 10. Fitted kinetic plot of the adsorption of phenol (initial=250 ppm) based on pseudo-second-order model (equation (10)).

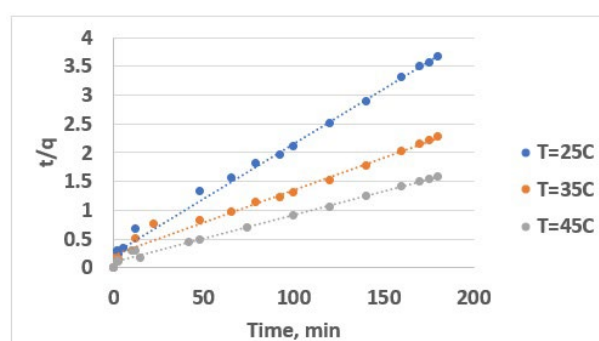


Figure 11. Fitted kinetic plot of the adsorption of phenol (initial=500 ppm) based on pseudo-second-order model (equation (10)).

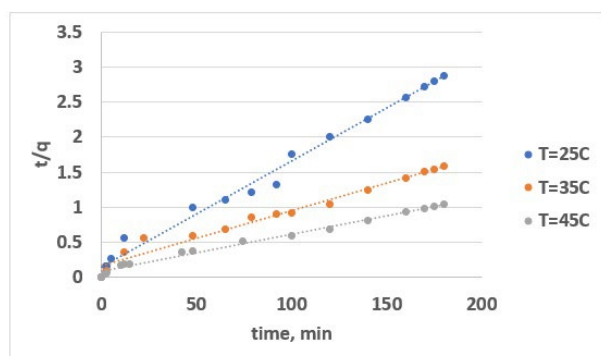


Figure 12. Fitted kinetic plot of the adsorption of phenol (initial=1000 ppm) based on pseudo-second-order model (equation (10)).

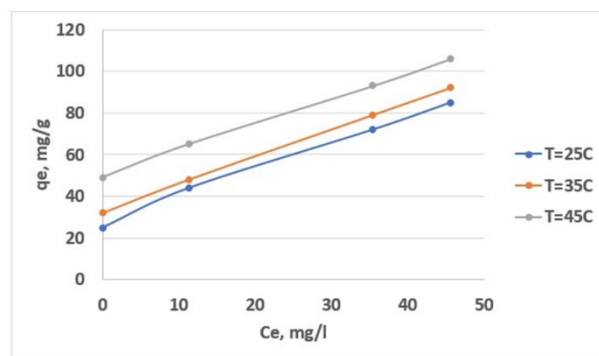


Figure 13. Adsorption isotherm profile of the phenol adsorbed from the wastewater on the prepared AC (initial=250 ppm).

Table 7. Kinetic parameters fitting for phenol adsorption from refinery wastewater on the prepared AC.

Temperature (°C)	AC dosage (g)	Phenol concentration (ppm)	R ²	Model	k ₁ min ⁻¹	k ₂ g/mg.min
25	1	250	0.981	First order	0.0521	-
35	1	250	0.968	First order	0.0684	-
45	1	250	0.954	First order	0.0874	-
25	1	500	0.9807	First order	0.0954	-
35	1	500	0.9073	First order	0.121	-
45	1	500	0.910	First order	0.154	-

Temperature (°C)	AC dosage (g)	Phenol concentration (ppm)	R ²	Model	k ₁ min ⁻¹	k ₂ g/mg.min
25	1	1000	0.893	First order	0.0985	-
35	1	1000	0.840	First order	0.165	-
45	1	1000	0.945	First order	0.185	-
25	1	250	0.9815	Second order	-	0.321
35	1	250	0.997	Second order	-	0.485
45	1	250	0.995	Second order	-	0.357
25	1	500	0.994	Second order	-	0.412
35	1	500	0.978	Second order	-	0.532
45	1	500	0.992	Second order	-	0.587
25	1	1000	0.989	Second order	-	0.624
35	1	1000	0.972	Second order	-	0.651
45	1	1000	0.988	Second order	-	0.512

3.5. Adsorption isotherm

Figure 13 illustrates how temperature affects phenol adsorption. It is clear that when the adsorption temperature rises, the phenol adsorption capacity on the prepared AC increases, demonstrating the endothermic nature of the phenol adsorption process. The electron donor-acceptor complex, dispersion interactions, and solvent effects are all involved in the adsorption of phenol on activated carbon.

The donor-acceptor complex accounts for the main bonding mechanism because the basic surface functional groups on the prepared AC may function as electron donors and the aromatic rings of phenol can operate as electron acceptors [49].

On the other hand, the prepared AC has a great attraction for water molecules because of the oxygen-containing groups on the polar surfaces of the activated carbon. Thus, while processing phenol adsorption, the effects of the solvent should be taken into account. As adsorption temperature increases, water's capacity for adsorption declines but phenolic compounds' capacity for adsorption increases due to a reduction in their degree of hydration.

4. Conclusions

It was demonstrated that the Langmuir model, which implies homogenous adsorption, is better compatible with phenol adsorption on AC. The results of the adsorption kinetic analysis showed that the adsorption followed the pseudo-second-order model, demonstrating that chemical adsorption predominates in the adsorption of phenol on acidified AC. According to the study, waste ion exchange resin is an appropriate starting material for carbon adsorbent for phenolic compounds. This is an affordable approach.

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