



Adsorption of Phenolic Compounds onto the Activated Carbon Synthesized from Pulp and Paper Mill Sludge: Equilibrium Isotherm, Kinetics, Thermodynamics and Mechanism Studies

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ABSTRACT

New activated carbon was produced from pulp and paper mill sludge as a low cost precursor via chemical activation by zinc chloride. The activated carbon was successfully used for the adsorption of phenol and two of its derivatives, i.e. 2-chlorophenol and 4-nitrophenol from aqueous solutions. The characterization of the prepared activated carbon demonstrated high textural properties for the synthesized activated carbon. The results revealed superior adsorption performance of the prepared activated carbon in this study compared to the commercial one. The effect of main affecting parameters such as pH, contact time, concentration and temperature on adsorption of phenolic compounds was experimentally investigated in discontinuous system. The adsorption capacities followed the order of 4-nitrophenol > 2-chlorophenol > phenol which was attributed to the property of substituent groups in their chemical structure. Amongst the isotherm models used to describe experimental equilibrium data, the best match was obtained by Sips isotherm which revealed the heterogeneous behavior of the adsorption sites on the adsorbent surface. Kinetic study demonstrated that the adsorption kinetics followed pseudo-second-order kinetic model. Based on thermodynamical analysis, the negative values obtained for Gibbs free energy, enthalpy and entropy indicated spontaneous, exothermic and random behavior of the adsorption process.

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1. INTRODUCTION

Nowadays, water pollution is considered as a major environmental issue in the world due to the discharge of various organic compounds available in industrial effluents to the environment. Shortage of water sources in most of areas in the world necessitates the treatment of contaminated water and its reuse. Phenolic compounds such as phenol, 2-chlorophenol (2-Cph) and 4-nitrophenol (4-Nph) are broadly used in many industries such as steel industry, pesticides, coal tar, herbicides, synthetic rubbers, pulp and paper mills, petroleum refineries and petrochemical plants, plastics, pharmaceuticals, textiles, insecticides[1, 2]. These

compounds are classified as one of the most important category of water pollutants by United States Environmental Protection Agency (USEPA) because of their toxicity, carcinogenicity and mutagenicity at high concentrations. The maximum concentration of phenol in industrial wastewater was determined as 1 mg/L by USEPA[3] and World Health Organization (WHO) counseled the valid phenolic compound content of 0.001 mg/L in potable water[4]. Therefore, it is urgent to eliminate these compounds from the urban and industrial wastewater to protect the environment.

Various treatment technologies such as different oxidation processes including catalytic, electrochemical and UV oxidation [5, 6], biodegradation [7], photo catalytic conversion[8], membrane separation[9], and adsorption by different adsorbents[10] are used for the removal of phenolic compounds from the effluent of many industries. Among the above mentioned

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technologies, adsorption offers some advantages in terms of easy design and operation and its wide applications for removing many types of impurities from water and wastewaters using various types of adsorbents. Activated carbon (AC) is the mostly used adsorbent in adsorption process for the removal of phenolic compounds because of its high adsorption capacity, large surface area, micro-porous structure [11]. However, widespread use of carbonaceous adsorbents are restricted due to high cost associated with their preparation. Therefore, preparation of ACs from low cost waste materials as precursors could improve the economy of adsorption process. Most of agriculture residues have the potential for being used as low cost precursors for producing AC as they possess sufficient carbonaceous backbones. A review of their application for preparing activated carbons has been well addressed by Ioannidou et al [12].

Sewage sludge is known as a waste solid material that is produced in high amount during biological treatment of municipal and industrial wastewaters. Therefore, management of their disposal is essential to avoid environmental hazards. Methods such as composting, incineration and land filling are severely restricted due to soil contamination, air pollution and space limitation, respectively [13]. Although, a number of efforts has been attempted to test direct application of the dried sewage sludge without any further activation, its low textural properties and adsorption capacity limits its applicability in a wide range of adsorption processes [14]. Improvement in textural properties of dried sewage sludge can be realized through physical or chemical activation. In physical activation, the precursor is first carbonized in an inert atmosphere (usually nitrogen or helium) and then activated by being subjected to steam or carbon dioxide stream in a temperature higher than pyrolysis temperature for pore development. In chemical activation, the precursor is first impregnated by a chemical agent such as $ZnCl_2$, H_3PO_4 , H_2SO_4 , KOH , etc. followed by pyrolysis of the impregnated mixture in an inert atmosphere. In comparison to the physical activation, chemical activation offers some advantages such simplicity of preparation, no need of the previous carbonization of raw material, lower temperatures for activation and better development of the porous structure [15]. The adsorption of phenolic compounds on different types of ACs has been well addressed in the literature [16]. Based on the results of previous studies, the main affecting parameters on the adsorption efficiency are AC characteristics, molecular properties of the adsorbents and operating condition of adsorption process. A number of efforts has been made to investigate the adsorption of phenol [17], chlorophenols [16], nitrophenols [18] by AC produced from sewage sludge. The pulp and paper mill sludge (PPMS) collected from pulp and paper industries has a good carbon backbone

because of the wood usage in the paper production process and therefore it can be considered as a suitable precursor for synthesis of ACs. Although the utilization of PPMS for preparing AC and its characterization has been reported in a number of research works, its application for adsorption of phenolic pollutants was rarely investigated. Khalili et al. [17] have reported synthesis and characterization of AC from paper mill sludge. However, the synthesized meso-porous AC showed very low adsorption capacity which restricts the application of the produced AC to very dilute solutions (<10 mg/l). Besides, the application of the produced AC in this study is limited to phenol and the other phenolic compounds were not considered. The main objective of present study was preparation and characterization of the high quality AC using PPMS as a low cost precursor and evaluating its efficiency for removal of phenolic compounds from wastewater. Textural properties and surface morphology of the prepared AC from PPMS were characterized using different analyses. The adsorption of phenol (ph) and two of its derivatives, i.e. 2-chlorophenols (2-Cph) and 4-nitrophenols (4-Nph) onto the PPMS-based AC was investigated. The adsorption capacity of AC was evaluated by adsorption isotherm at different pH, temperature and initial concentration of phenolic compounds. The experimental equilibrium data were fitted by various well-established isotherm models with frequent applications in literature, such as Langmuir, Sips, Temkin and Freundlich. The adsorption kinetics were investigated using different adsorption kinetic models to determine the rate-limiting step in adsorption of phenolic compounds onto the developed AC. Thermodynamic studies were carried out to give an insight about the thermal nature of the adsorption process.

2. EXPERIMENTAL

2. 1. Materials and Methods

All chemicals used in the present study were analytical grades used without any further processing. Potassium-hexacyanoferrate (III), 4-amino-2,3-dimethyl-1-phenyl-3-pyrazolin-5-one, potassium dihydrogen phosphate, phenol, 4-nitrophenol, hydrochloric acid fuming 37 %, $NaCl$, $NaOH$, HCl solution and commercial activated carbon were supplied by Merck (Darmstadt, Germany). The 26 % ammonia solution and 2-chlorophenol were purchased from Riedel-de Haën, Germany and BDH limited Poole England, respectively. To prepare a solution with desired concentration for adsorption experiment, a stock solution of each adsorbate with concentration of 1000 mg/L was prepared by dissolving proper amount of each adsorbate in distilled water.

TABLE 1. Some physical properties of phenolic compounds used in the present study

Phenolic compounds	Molecular weight (g/mol)	Molecular size	Solubility (g/l)	pK _a	Log K _{ow}
ph	94	5.76×4.17	93	9.89	1.46
2-Cph	128.5	5.76×4.82	28	8.52	2.16
4-Nph	139	6.84×4.17	1.7	7.15	2.93

TABLE 2. Elemental analysis of PPMS (wt%)

C	N	P	Ca	Si	Mg	Ash	Humidity (in factory)
44.8	0.4	0.054	1.25	30.7	0.17	36.4	70

Then, lower concentrations of each adsorbate were made by dilution of stock solution with distilled water. The properties of the phenolic compounds used in the present work are summarized in Table 1. The PPMS used in this study was collected from the wastewater treatment plant of paper producing factory (CHOKA) located in Gilan Province, Iran. Also, the elemental analysis of the PPMS used as the precursor is shown in Table 2.

2. 2. Synthesis and Characterization of AC To synthesize the AC from PPMS, the sludge was first dried at 108 °C for 12 hours, then crushed and sieved to have a uniform particle size of 25 mesh. For physical activation, the dried powder of PPMS was pyrolyzed in a vertical furnace for 25 minutes. The pyrolysis process was carried out at 540 °C with heating rate of 20°C/min under inert nitrogen flow of 300 mL/min. The carbonized PPMS was then physically activated at 560 °C for 20 minute under CO₂ stream with the flow rate of 200 mL/min.

For chemical activation, the dried PPMS was first impregnated with ZnCl₂ by weight ratio 0.9:1 (with respect to the mass of agent to the dried PPMS) at 80 °C for 6 h. Then, the impregnated solid mixture was dried at 108 °C for 12h, crushed and sieved to a uniform particle size of 25 mesh. Finally, it was carbonized in the vertical furnace at 560 °C under the same nitrogen flow rate and time conditions used for physical activation.

After chemical activation, the produced AC was washed with a 5 M HCl solution to eliminate the remaining ZnCl₂ and some of the soluble ashes. Next, it was rinsed with distilled water. Finally, the prepared AC was dried at 106 °C for 12h.

According to the our previous work [19], N₂ adsorption/desorption isotherms were performed in a surface area analyzer (BELsorp-mini II, Japan) at 77 K to give an estimation on the textural characteristics of

the prepared AC. The specific surface area was determined by the Brunauer–Emmet–Teller (BET) equation and micro-pore volume was estimated from the t-plot method. The pore size distribution was evaluated by the Barrett-Joyner-Halenda (BJH) method. Scanning electron microscopy (SEM, VEGA II TESCAN, CZECH) images were used for determination of the AC surface morphology. The chemical characteristics of the prepared AC were determined by energy dispersive X-ray spectroscopy (EDX), (VEGA II TESCAN, CZECH). The pH at which the charge on the adsorbent surface becomes zero is known as pH_{ZPC}. The pH drift method [20] was used to determine the pH_{ZPC} of the prepared AC surface using 50 mL of 0.1M NaCl solution in a sequence of Erlenmeyer flasks.

The pH of solution was set using either prepared 0.1M NaOH or 0.1M HCl in the range between 1 and 12. A 0.15g of AC was added to each of the flasks and the final pH of the solutions was measured after 32 hours. Then, the final pH values were plotted versus initial pH. The pH_{ZPC} was chosen as the pH at which the initial pH reaches to final pH.

2. 4. Adsorption Experiments

Adsorption experiments were performed in batch mode. For each experiment, a 0.1 g of the PPMS-based AC was added to 100 mL of the adsorbent solution in a 250 mL-Erlenmeyer flask. The flasks were closed with stoppers to avoid evaporation and were incubated in an incubator shaker (model KS 4000i control, IKA) with agitation rate of 250 rpm. In each experiment, sufficient time was dedicated to the adsorbate-adsorbent system to reach equilibrium. The solution absorbance was periodically measured by means of a UV visible spectrophotometer (model 2100 SERIES, UNICO) at 460, 470, 500 nm (based on the scanned wavelength) to determine the concentrations of ph, 2-Cph and 4-Nph, respectively.

The experiments were carried out at different temperatures (20, 35, 50 °C), initial concentration (50-400 mg/L), pH (1-12). The pH of solution was adjusted with either prepared 0.1 N HCl or 0.1 N NaOH solutions. After shaking, samples were filtered through a Whatman No.42 filter paper. The amount of adsorbed phenolic compounds, q_t (mg/g) and removal efficiency (R %) achieved by the PPMS-based AC were calculated using the following equations:

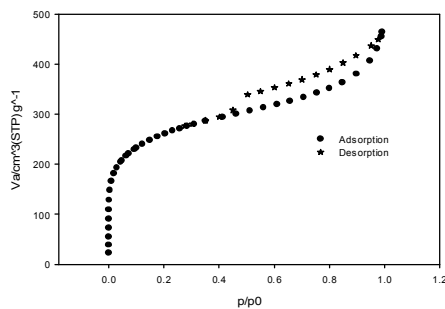
$$q_t = \frac{V(C_0 - C_t)}{m} \quad (1)$$

$$\%R = 100 \times \frac{C_0 - C_e}{C_0} \quad (2)$$

where q_t is the amount of adsorbed phenols per unit weight of PPMS-based AC at time t (mg/g), C_0 and C_e are the initial and equilibrium concentrations (mg/L), C_t the phenol concentration at time t (mg/L) in the solution, V the volume of the solution (mL) and m the dry weight of the PPMS-based AC (g).

TABLE 3. Main textural and some physio-chemical properties of the prepared PMS-based ACs (through chemical and physical activation) and commercial AC

Parameters	PMS-based AC		Commercial AC
	Physical activation	Chemical activation	
Average pore size(nm)	5.15	3.13	3.49
Total pore volume(cm ³ /g)	0.14	0.71	0.48
Microspore volume(cm ³ /g)	0.10	0.42	0.09
BET surface area(m ² /g)	107.77	907.20	545.00
Bulk density(g/ cm ³)	0.43	0.20	0.41
PH _{PZC}	5.7	4.6	5.5

**Figure 1.** The N₂ adsorption-desorption isotherm for the developed PMS-based AC at 77 K.

3. RESULTS AND DISCUSSION

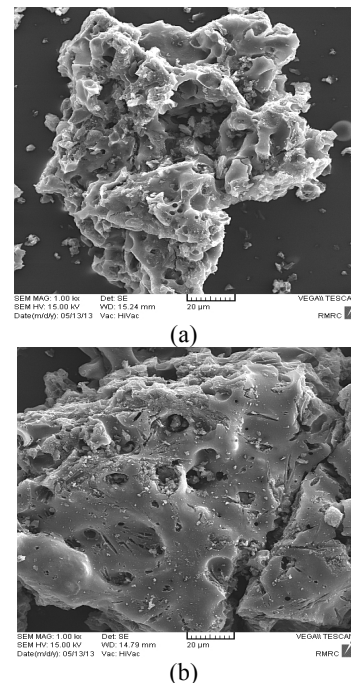
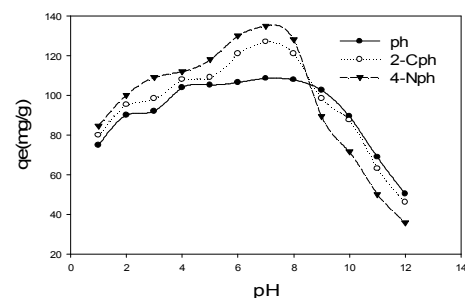
3.1. Characterization Results

3.1.1. BET Surface Area The N₂ adsorption-desorption isotherm of the PPMS-based AC (developed through chemical activation by ZnCl₂) at 77 K is shown in Figure 1. It has exhibited the type IV isotherm according to IUPAC classification.

The BET surface area of the prepared AC was obtained using N₂ adsorption isotherms at 77 K. The main textural properties of the synthesized AC as well as commercial AC are given for comparison in Table 3 along with some physio-chemical properties. As it can be observed from Table 3, the chemical activation of PPMS with ZnCl₂ led to development of the AC with better pore characteristics compared to the physical activation with CO₂. Also the developed PPMS-based AC has shown superior characteristics in comparison with the commercial AC in terms of average pore size, total pore volume and BET surface area. Besides, the different impregnation ratio employed in the present study compared to our previous study [21] led to the considerable improvement in the textural properties of the produced AC.

3.1.2. SEM Analysis Scanning electron microscopy (VEGA II TESCAN, CZECH) analysis was carried out

in order to investigate physical surface morphology of PPMS-based AC. The SEM photographs of PPMS-based ACs before and after adsorption of 4-Nph (as an example of adsorbed species) are shown in Figure 2. It is believed that the porosity of an AC is a function of the precursor used for the synthesis, the method and the extent of activation. Figure 2(a) revealed high porous structure of the PPMS-based AC before adsorption. From the micrograph, it can be seen that pores in open and external surfaces are irregular and heterogeneous. Figure 2 (b), represents the micrograph of the adsorbent after adsorption of 4-Nph from its solution with the initial concentration of 200 mg/L. From the image, it is obvious that most of the pores have been filled with the adsorbate.

**Figure 2.** The SEM photographs of PMS-based AC (a) pristine and (b) after adsorption of 4-Nph.**Figure 4.** Effect of pH on the adsorption of phenolic compounds (C₀: 150 mg/l; T: 20°C; contact time: 4 h).

3. 2. Adsorption Results

3. 2. 1. Effect of pH The pH of the solution is one of the most important factors that affect the reaction kinetics on solid/liquid interfaces. Indeed, the surface charge of both adsorbent and adsorbate depends on the pH of the solution. The effect of the solution pH on the capacity of the PPMS-based AC for adsorption of three mentioned phenolic compounds was investigated in the pH range of 1-12. The adsorption capacities of the synthesized PPMS-based AC versus the pH of solution have been plotted in Figure 4. The adsorption capacities of phenols increased steadily till near the neutral pH and decreased sharply afterward. This can be explained by knowing that phenol is a weak acid which can be present in both ionic and molecular forms in aqueous solutions. The AC surface is positively charged at $pH < pH_{pZC}$ and negatively charged at $pH > pH_{pZC}$ due to positive and negative charge in solution, respectively. Also, the phenols are present in aqueous solution mainly in protonated state at $pH < pK_a$ and in deprotonated form at $pH > pK_a$ [22]. Phenolic compounds used in the present study, all had the pK_a values higher than the pH_{pZC} values with respect to the PPMS-based AC (4.6). At $pH > pK_a$, the phenols are almost in ionic form (negative charge) and the AC surface is also negatively charged. Thus, this caused to establish an electrostatic repulsion force between the phenols and the AC surface leading to reduced adsorption. Also, at low pH values, additional protons were introduced in the solution which competed for basic functional groups available onto the AC surface. This also led to suppress the adsorption. At $pH_{pZC} < pH < pK_a$, the phenols are both in molecular and ionic shapes and the AC surface is negatively charged, thus moderate electrostatic repulsion force exists between the phenols and activated surface and adsorption was almost constant (pH:6-8) (see Figure 4). Hence, according to experimental observations the neutral pH (pH=7) was selected as the optimum pH for further experiments.

3. 2. 2 Effect of Temperature In order to survey the effect of the temperature on phenols adsorption, the adsorption isotherms of phenols on the PPMS-based AC were determined at three different temperatures, i.e. 20, 35 and 50 °C, the results are shown in Figure 5. The adsorption capacity (q_e) was found to decrease by increasing the temperature, which indicated the exothermic nature of the adsorption process. So, removal of phenolic compounds by the PPMS-based AC was more favorable at lower temperature (20°C). This might be due to the increase in tendency of adsorbed molecules to escape from the adsorbed phase to the bulk phase by increasing the temperature. This tendency can be attributed to weakening of attraction forces between adsorbed phenols and the PPMS-based AC surfaces. Similar results have been reported in the literature by some researchers working on liquid adsorption [23].

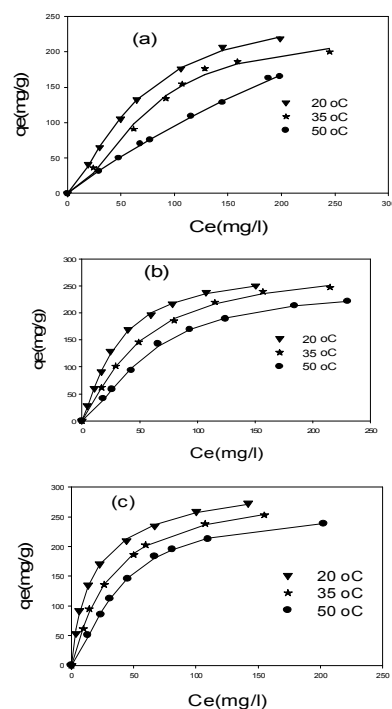


Figure 5. The effect of temperature on the adsorption of phenolic compounds onto PMS-based AC (pH: 7, adsorbent dosage of 1 g/l), solid lines are fitted Sips equation (a: ph, b: 2-Cph, c: 4-Nph).

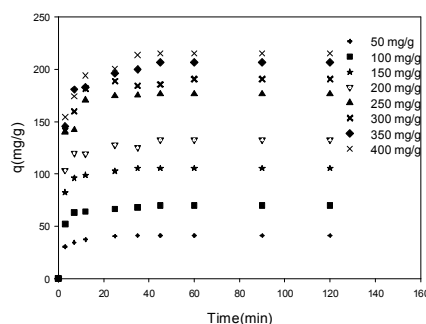


Figure 6. Effect of contact time and initial concentration on phenol adsorption onto the PMS-based AC, ($T: 20^\circ\text{C}$; pH: 7, adsorbent dosage of 1 g/l).

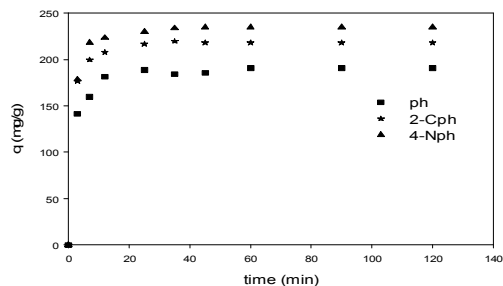


Figure 7. Effect of contact time and comparison between phenols adsorption onto PMS-based AC (C_0 : 300 mg/l; T : 20°C ; pH: 7).

3. 2. 3. Effect of Contact Time and Initial Phenol Concentration

To assess the effect of contact time and concentration, adsorption experiments were conducted with the fixed adsorbent dosage of 1 g/L, solution pH of 7 and temperature of 20°C at different concentrations (50-400 mg/L). Variation of the amount of phenol uptake by the PPMS-based AC versus time is shown in Figure 6. Obviously, the adsorption capacity of the AC was increased by increasing the initial concentration of phenols due to the fact that by increasing the concentration, more amounts of adsorbate from the solution is subjected to the AC surfaces. Besides the rate of adsorption is fast at initial stage of adsorption experiment due to the large number of vacant active sites on the AC surfaces, which are gradually saturated leading to low adsorption rate. The data clearly showed that the time required to achieve equilibrium gradually increased while increasing the initial concentrations in all cases.

To compare the adsorption capacity of different phenolic compounds on synthesized AC, similar trends were observed for the two other phenolic compounds; the transient adsorption data at initial concentration of 300 mg/L of each species are shown in Figure 7. It indicates that the equilibrium contact time has followed the order of $ph > 2-Cph > 4-Nph$, while the adsorption capacity shows an opposite order, $4-Nph > 2-Cph > ph$. The differences in required contact times for various adsorbates to reach equilibrium can be attributed to their molecular sizes. Indeed, the micro-pore volume filling for phenol occurs more rapidly than its derivatives due to small molecular size. However, the comparative adsorption capacities cannot be simply explained based on difference in molecular size. In fact, the adsorption capacity of an AC for uptake of phenolic compounds is mostly affected by the chemical nature of its surface, rather than its pore characteristics[15]. Substituent groups in the chemical structure of 4-Nph and 2-Cph, Nitro and then chloro groups, act as a strong electron-withdrawing group which reduces the overall electron density in the π bond of the aromatic ring. This implies that the attraction between the adsorbate and carbon surface is enhanced compared to interaction of phenol with the surface.

3. 3. Determination of the Adsorption Isotherm

The adsorption isotherm illustrates the relationship between concentration of the adsorbate in bulk and adsorbed phases. Having such correlation is important for optimizing adsorption conditions. Theoretical and empirical models have been frequently used to describe experimental isotherm data [24, 25]. In the present study, four well-known sorption isotherm models; i.e. Langmuir, Freundlich, Sips and Temkin have been applied to describe the adsorption isotherm of phenolic compounds on PPMS-based AC. Model equations with their physical parameters are presented in Table 4. The experimental data were fitted to the above mentioned model isotherms using Sigmaplot non-linear regression (Version 12.0) to recover the models parameters. The models parameters extracted through non-linear fit of experimental data to the model equations are summarized in Table 5. As it can be observed from Table 5, the best fit is obtained using Sips isotherm with respect to the values of regression correlation coefficients (R^2). This equation is a combination of Langmuir and Freundlich isotherms which approaches Langmuir model at high concentration with a maximum limiting capacity, while it reduces to Freundlich equation at low concentration. This feature may be an indication of the heterogeneous nature of the adsorbent surface. The fitting results obtained with Sips model isotherm are also shown in Figure 5 along with experimental data for comparison.

3. 4. Adsorption Kinetics The kinetic study is carried out to investigate the mechanism of adsorption and the rate limiting step in overall transport process. It also provides some information about how fast the species are adsorbed on the adsorbent surfaces. This is important in designing and modeling of the adsorption process. In order to investigate the mechanism of adsorption, two different kinetic models; i.e. pseudo-first-order, and pseudo-second-order are widely used in kinetic studies [26-29]. The kinetic models were examined to identify the adsorption kinetics of phenolic compounds on the PPMS-based AC.

TABLE 4. Isotherm equations and their parameters

Model	Equation	Parameters
Langmuir	$q_e = \frac{q_m b C_e}{1 + b C_e}$	q_m (mg/g): the Langmuir maximum adsorption capacity at equilibrium b (l/mg): the Langmuir constant
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	K_F (mg/g (l/mg) ^{1/n}): Freundlich heterogeneous adsorbent proportionated with the adsorption capacity $1/n$ (-): Freundlich constants associated with adsorption intensity and the adsorbent site energy distribution
Sips	$q_e = \frac{q_{ms} K_s C_e^{ms}}{1 + K_s C_e^{ms}}$	q_{ms} (mg/g) : the Sips maximum adsorption capacity K_s ((l/mg) ^{ms}): the Sips equilibrium constant, ms: the Sips model exponent
Temkin	$q_e = \left(\frac{RT}{b_T}\right) \ln K_T C_e$	b_T (KJ /mol) :the Temkin isotherm K_T (l /mg): the Temkin equilibrium constant

TABLE 5. Isotherm constants for the adsorption of phenolic compounds onto the PMS-based AC

Temperature Adsorbate		20 °C			35 °C			50 °C		
		Ph	4-Nph	2-Cph	Ph	4-Nph	2-Cph	Ph	4-Nph	2-Cph
Lang	q_m	370.4	296.1	325.1	333.4	311.9	332.7	672.7	314.9	328.1
	B	0.008038	0.06316	0.02492	0.007294	0.02954	0.01551	0.001658	0.01829	0.01017
	R^2	0.988	0.9939	0.9948	0.9564	0.9975	0.9934	0.9988	0.9847	0.9833
Feundlish	K_f	9.897	53.75	26.58	10.3	34.61	23.65	1.932	11.77	13.46
	N	1.668	2.935	2.144	1.79	2.45	2.21	1.185	1.928	1.886
	R^2	0.9572	0.9603	0.9447	0.8975	0.9472	0.9453	0.9981	0.8982	0.9363
Sips	q_{ms}	265.4	326.1	284.4	228.9	294.5	288.6	695.8	261.5	249
	K_s	0.002347	0.08041	0.01467	0.0005052	0.02354	0.007562	0.001641	0.005919	0.002291
	M_s	1.449	0.8335	1.241	1.772	1.105	1.263	0.9936	1.411	1.504
	R^2	0.9986	0.9972	0.9989	0.9886	0.9986	0.9984	0.9988	0.9986	0.9983
Temkin	b_T	68.96	93.84	80.35	76.34	84.05	76.29	84.16	84.02	81.18
	K_{tem}	0.07908	0.7391	0.263	0.06376	0.2695	0.1334	0.04219	0.1541	0.08935
	R^2	0.9916	0.9985	0.9869	0.9673	0.9942	0.9913	0.9624	0.9804	0.9896

The pseudo-first-order equation is usually associated with the physical adsorption in which the adsorption process is controlled by weak interactions between the adsorbate and the adsorbent surface [30]. The kinetic model was given by Langergren and Svenska[31] is stated as follows:

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (3)$$

where q_e and q_t are the quantities of the species adsorbed (mg/g) at the equilibrium state and at time t (min), respectively. k_1 (1/min) is the kinetic constant of pseudo first-order. The pseudo-second-order kinetic model is based on the assumption that the adsorption is controlled by chemisorption [32] as described as follows[33, 34]:

$$q_t = \frac{k_2 q_e^2}{1 + k_2 q_e t} t \quad (4)$$

where k_2 (g/mg.min) is the second-order rate constant.

Transient adsorption data at different concentrations and temperatures were used to determine the rate constant. The average values of regression coefficient (R^2) and kinetic rate constant of the pseudo-first-order kinetic model (k_1) and the pseudo-second-order kinetic model for the adsorption of phenolic compounds onto the adsorbent at various initial concentrations (50-400 mg/l) and temperatures are reported in Table 6. It can be observed from Table 6 that the values of adsorption capacities predicted by the pseudo-second-order kinetic were mostly closer to the experimental values compared to those predicted by the pseudo-first-order kinetic model. Also the fitted data are illustrated in Figure 8 for better examined kinetic models.

3. 5. Adsorption Thermodynamics Thermodynamic study provides useful information about the heat management of the adsorption process to achieve the maximum removal efficiency. Equilibrium concentration of adsorbed species in bulk phase (C_e) and adsorbed phase (q_e) in different temperatures can be

appropriately correlated to estimate thermodynamic parameters.

$$K_{eq} = \frac{C_0 - C_e}{C_e} \quad (5)$$

Combining Equation (1) and (5), the equilibrium constant can be correctly correlated in terms of equilibrium uptake:

$$K_{eq} = \frac{mq_e}{VC_e} \quad (6)$$

In principal, the equilibrium constant should be dimensionless, the fact that is frequently ignored in the literature. Equation (5) is the correct form of equilibrium constant in dimensionless form. Changes in free enthalpy (ΔH^0), free entropy (ΔS^0) and Gibb's free energy (ΔG^0) per unit mole of adsorbed species are correlated as follows:

$$\ln K_{eq} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R T} \quad (7)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (8)$$

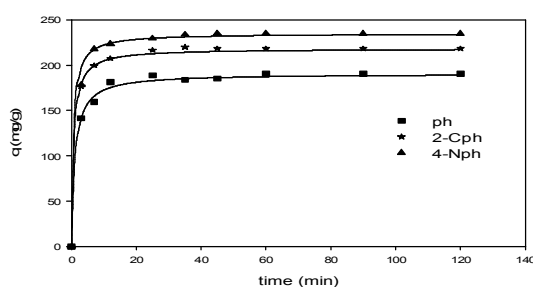
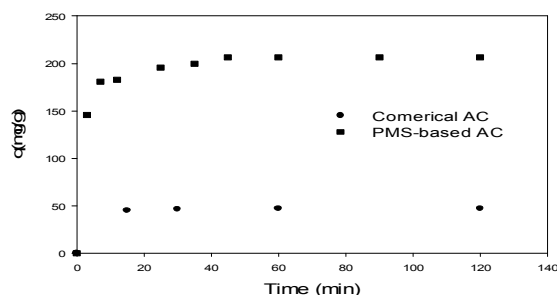
where q_e is the amount of adsorbed phenols (mg/g) at equilibrium. ΔH^0 and ΔS^0 are obtained from the slope and intercept of a linear plot of $\ln K_e$ versus $1/T$, respectively. A set of equilibrium data obtained at different temperatures was used to evaluate the thermodynamic parameters through a linear fit to Equation (7). According to data presented in Table 7, values of calculated Gibb's free energy changes are negative and by decreasing the temperature it becomes more negative. This indicated that the adsorption of phenolic compounds on PPMS-based AC is spontaneous and becomes more spontaneous by decreasing the temperature as the adsorption capacity increases. The negative values of calculated ΔH^0 demonstrated the exothermic nature of phenolic compounds adsorption onto the PPMS-based AC. This result confirms the isotherm study which has shown the adsorption of phenolic compounds on the prepared AC is more favorable at lower temperatures (see Figure 5).

TABLE 6. Pseudo-first-order and pseudo-second-order constants for the adsorption of phenols onto the PMS-based AC.

	20 °C				35 °C				50 °C			
	k_1	R^2	$k_2 \times 1E+3$	R^2	k_1	R^2	$k_2 \times 1E+3$	R^2	k_1	R^2	$k_2 \times 1E+3$	R^2
phenol	0.410	0.9793	9.52	0.9958	0.266	0.9783	5.76	0.9878	0.183	0.9760	4.82	0.9877
C-ph	0.459	0.9906	9.97	0.9940	0.344	0.9815	6.76	0.9944	0.290	0.9777	6.21	0.9957
4-Nph	0.490	0.9923	10.89	0.9962	0.375	0.9834	7.47	0.9951	0.345	0.9852	6.88	0.9944

TABLE 7. Thermodynamic parameters for the adsorption of phenols onto the PMS-based AC.

	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol.K)	R^2	ΔG^0 (kJ/mol)		
				293 K	308 K	323 K
Phenol	-21.51	-23.91	0.9785	-14.50	-14.15	-13.79
C-ph	-22.49	-20.04	0.9993	-16.62	-16.32	-16.01
4-Nph	-31.53	-44.30	0.9930	-18.55	-17.89	-17.22

**Figure 8.** Fitting results for modeling of phenols adsorption kinetics onto the PMS-based AC (C_0 : 300 mg/l; T : 20°C; pH: 7).**Figure 9.** Adsorption of phenol onto the PMS-based and commercial AC ($C_0=330$ mg/l, adsorbent dosage = 1 g/l, pH= 7, $T=20^\circ\text{C}$).

The negative value of calculated ΔS^0 indicates the irregularity and randomness of the adsorption of phenols on the prepared AC surfaces. Low values of the ΔH^0 of the adsorption revealed that the adsorption of phenolic compounds onto the PPMS-based AC is dominated by the physisorption mechanism [34, 35].

4. COMPARISON IN ADSORPTION PERFORMANCE OF PPMS-BASED AND COMMERCIAL AC

The commercial activated carbon was produced from charcoal provided by Merck (Darmstadt, Germany).

According to data presented in Figure 9, the adsorption capacity achieved using PPMS-based AC was remarkably higher than the amount gained by the commercial AC. This superior adsorption performance can be attributed to the high textural characteristics of the PPMS-based AC, such as higher total and micro-pore volume, very higher surface area and smaller average pore diameter, compared to the commercial one as reported in Table 3.

5. CONCLUSION

PPMS was used as a low cost carbonaceous precursor for the synthesis of high characteristic AC which was efficiently employed for the removal of phenol and two of its chloro and nitro derivatives from aqueous solution. The characterization results revealed the porous structure of the prepared AC with numerous heterogeneous active sites in which the micro pores had a major contribution. The effect of solution pH, concentration and temperature on the adsorption capacity of each adsorbate was investigated. It was found that neutral pH (7.0) was the optimum pH. This provides an opportunity for the treatment of polluted waste waters by the phenolic compounds using the PPMS-based AC without preconditioning for any pH adjustment. The adsorption capacity achieved by the produced adsorbent for adsorption of different phenolic compounds followed the order of 4-NPh > 2-Cph > Ph. It is concluded that the difference in adsorption capacities of various phenolic compounds cannot be simply explained based on the difference in molecular size. The adsorption capacity of the prepared AC for uptake of phenolic compounds was attributed to the chemical nature of substituent groups in the chemical structure of phenol. Amongst the different model isotherms used to describe the adsorption behavior of the phenolic compounds onto the PPMS-based AC, the best match was that of Sips isotherm which indicates the heterogeneous nature of the AC surface. The kinetic study was carried out to determine the rate constant for

adsorption process using the experimental transient data. Thermodynamic analysis was performed using the adsorption data obtained at different temperatures. Based on the results of thermodynamic analysis, the negative values obtained for free Gibbs of energy, enthalpy and entropy revealed the spontaneous, exothermic and randomness nature of the adsorption process. Finally, the adsorption performance of the PPMS-based AC was compared with the commercial one. The comparative study for the adsorption of phenol proved the higher performance of the PPMS-based AC compared to the commercial one owing to its higher textural properties. The results obtained by using low cost PPMS-based AC prepared at the present study is promising in terms of both economic and environmental aspects and could improve the adsorption economy for the removal of hazardous materials such as phenolic compounds from industries effluents.

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Adsorption of Phenolic Compounds onto the Activated Carbon Synthesized from Pulp and Paper Mill Sludge: Equilibrium Isotherm, Kinetics, Thermodynamics and Mechanism Studies

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نوع جدیدی از کربن فعال با استفاده از لجن حاصل از کارخانه های چوب و کاغذ به عنوان یک پیش ماده ارزان قیمت از طریق فعال سازی با کلرید روی تولید گردید. سپس کربن فعال تولید شده با موفقیت برای جذب فنل و دو نمونه از مشتق هایش یعنی ۲-کلرو فنل و ۴-نیترو فنل از محلول های آبی مورد استفاده قرار گرفت. آنالیز کربن فعال تهیه شده بیانگر خواص ساختاری بالائی برای آن بوده که باعث عملکرد جذبی برتر آن نسبت به کربن فعال تجاری گردیده است. تاثیر پارامتر های مهم مانند pH، زمان تماس، غلظت حل شونده و دما بر روی جذب ترکیبات فنلی بر روی کربن فعال تهیه شده به طور تجربی در سیستم ناپیوسته مورد مطالعه قرار گرفت. ترتیب ظرفیت های جذب به دست آمده در آزمایشات عبارت بودند از: فنل > ۲-کلرو فنل > ۴-نیترو فنل که این ترتیب به خواص گروه های استخلافی در ساختار شیمیائی آنها نسبت داده شد. در میان معادلات همدمای جذب مورد استفاده برای توصیف جذب تعادلی، بهترین برازش با استفاده از معادله Sips حاصل گردید که بیانگر ناهمگن بودن مراکز جذب بر روی سطح جاذب بوده است. مطالعه سینتیکی نشان داد که سینتیک جذب از معادله شبه درجه دوم تبعیت می کند. همچنین تحلیل ترمودینامیکی داده های جذب با توجه به مقادیر منفی به دست آمده برای انرژی آزاد گیبس، انتالپی و انتروپی جذب، به ترتیب بیانگر خود به خودی، گرماگیر و تصادفی بودن فرایند جذب سطحی بوده است.

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