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Thermodynamics and kinetics studies of Phenol adsorption on to Anchote peel activated carbon adsorbent

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Abstract

Thermodynamic ($\Delta G, \Delta H, \Delta S$) and kinetics (pseudo first, pseudo second) of phenol adsorption were investigated. Anchote peel (coconia Abysinica peel) was carbonized and activated by treating with KOH solution followed by heating in an electrical furnace at 800℃ for 2 hrs. Kinetic studies of the data showed that the adsorption follows the pseudo-second-order kinetic model. Thermodynamic parameters showed that adsorption on the surface of APAC was feasible, spontaneous in nature, and exothermic. The equilibrium data better fitted the Freundlich isotherm model. Maximum adsorption efficiencies of Phenol were 97% at optimum pH 6 and optimum contact time 210 min., adsorbent dose 0.25 g and initial conc. 0.025 mg/l respectively. Maximum adsorption capacity of APAC was observed to 43.75 mg/g of Phenol at 25 ℃ and 5 mg/L.

Keywords: *Thermodynamic and kinetic study, phenol, Adsorption, carbonization, adsorption isotherms*

Organic compounds can be considered as water pollutants if their concentration exceeds allowed level in drinking water. Phenol is an aromatic organic compound with the molecular formula C_6H_5OH. It is a white crystalline solid that is volatile. It is a component of industrial paints strippers used in the aviation industry and other chemically resistant coatings. Phenol derivatives are also used in the preparation of cosmetics. It has also wide spread application in the pharmaceutical, dyes, paper, pesticides and petrochemical industries etc. Phenol is essential as well as has disadvantage due to its toxicity nature. Water containing phenol (toxicity nature) is characterized as bad odour and taste which causes Vomiting and nausea, increased respiratory rate, Anorexia, liver and kidney damage, and headache. Sources of Phenolic compounds are petrochemical, oil refinery, plastic, explosives, azo dyes, pigments, leather, paint, pharmaceutical, coking plant, steel and pesticides industries (Uberoi et al., 1997; Srivastava et al., 2006). The improper discharge of these compounds in water bodies over a long period can cause the deterioration of water environments, while its intake by both human and animals causes liver and kidney damage, central nervous system impairment, diarrhoea and excretion of dark urine (Sarkar and Acharya, 2006). They may be present in waste waters and natural environmental waters. Phenols are introduced to the environment in variety of ways: wastes from paper manufacturing, agriculture, petrochemical industry, coal processing or as municipal wastes [1].The phenolic micropollutants generally include phenol derivatives [2]. Due to its toxicity at higher concentration, phenol considered as water pollutants. Concentration of phenolic compounds can possibly get increased in drinking water. Therefore, an easily applied, sensitive and selective method is required for monitoring of phenolic compounds concentration in environmental waters. In the past decade a variety of analytical methods were proposed for determination of phenol in natural environmental waters and waste waters. The most widely used are gas chromatography [5-7], high performance liquid chromatography [8-10]. These methods are important to determine phenolic compounds, however they often considered complicated and expensive equipment. Many efforts have been made to develop the simple and effective methods for determination of phenols [3, 16]. UV-visible spectrophotometer instrument used in determination of the total concentration of phenol. There are many methods available for the removal of pollutants from polluted water. The most important are chemical and physical methods involves coagulation combined with flotation and filtration, electro flotation, electro kinetic coagulation, irradiation and electro chemical processes. The application of such methods is cost expensive and is unaffordable for large scale treatment of water. Therefore, more economical means adsorption for the removal of pollutant has been required because it is an effective and simplicity of design. In this study adsorption capacity and adsorption efficiency of Anchote (Coccinia abyssinica) peel activated carbon adsorbent was studied.

EXPERIMENTAL SECTION

MATERIALS AND METHODS

MATERIALS

Analytical reagent grade chemicals were used. Phenol (C_6H_5OH), Isobutyl acetate, 4-aminoantipyrine ($C_{11}H_{13}N_3O$), ferric cyanide ($[Fe(CN)_6]^{3-}$), chloroform ($CHCl_3$), & sodium sulphate ($NaSO_4$), glacial acetic acid (CH_3COOH), sodium acetate ($NaCH_3COO^-$), concentrated ammonia (NH_3), and ammonium chloride (NH_4Cl).

APPARATUS

Glass bottles, thermometer, volumetric flask, Measuring cylinder, Boiling tube.

INSTRUMENTS

pH meter (HANNA instruments, pH 211), Electronic balance (Model AFP-110L, ADAM, China), Fourier Transform Infrared(FTIR) Spectroscopy, UV-ViS Spectro photometry (Model DR 5000, Hach USA).

ADSORPTION STUDIES

3.1. PREPARATION OF ADSORBENT

The Adsorbent, Anchote peel were collected and cut into small sizes and allowed to be air dried. The dried adsorbent was washed by distilled water and allowed to be dried and further Oven dried at 105 °C. The well dried sample was grinded and then sieved. The sieved adsorbent was soaked in 25% (W/V) of KOH solution. The mixture was stand for 3 hr for agitation. Then oven dried for 12 hr at 105 °C.The dried sample was carbonized at a temperature of 800°C for two hr and the carbonized sample was cooled. The activated carbon product was treated with 5%HCl solution followed by washing with distilled water until the pH of the washing solution become neutral. Then the carbonization product “activated carbon” was kept in plastic container and from which applied for adsoption study. [10]

Proximate analysis of APAC adsorbent [11, 12]

Table 1. Proximate analysis of APAC adsorbent

parameter	Moisture content (%)	Ash content (%)	Volatile matter (%)	Fixed carbon **(%)**	pH
% Yield	2.23	8.7	5.5	83.57	7

Fourier Transform Infrared (FTIR) Characterization of Adsorbent

The FT-IR spectroscopic characteristics of the Activated carbon Anchote peel (Activated carbon coconia abysinica peel) and Phenol sorbed Anchote Peel activated carbon are shown in Table 2. The type and net charge of functional groups bonded to the carbon surface is important in understanding the mechanism of adsorption of ionic adsorbate on activated carbons. FT-IR spectrum is an essential tool to identify the surface functional groups which can contribute significantly to enhance adsorption efficiency of the activated carbon.

Table 2: Activated carbon Anchote peel,AP (Activated Carbon Coconia abysinica peel) and Phenol sorbed Anchote Peel activated carbon

S.No	Before Adsorption cm^{-1}	AC Phenol Adsorption cm^{-1}	Difference	Assignment
1	3479	3485	6	O-H band
2	3033	2960	73	C-H Stretching absorption band
3	1673	1670	3	C=C Stretching
4	1409	1410	1	C-O stretching of phenol
5	1079	1080	1	C-C stretching

4. Preparation of stock solution

Stock solution of Phenol with a concentration of 100 mg/l were prepared from Phenol by dissolving 0.94 g of Phenol in 100 ml volumetric flask. From 100 mg/l of Phenol solution, Phenol solution with a concentration of 5 mg/l were prepared and by dilution method a number of standards (solutions of less concentration) were prepared.

5. Adsorption and study of parameters influence adsorption

Study of the adsorption of Phenol on adsorbent (activated carbon prepared from Anchote peel (coconia Abysinica peel) have been performed. Adsorption parameter pH, contact time, initial metal ion concentration, adsorbent dosage, and temperature were studied.

Effects of pH

This is an important parameter on which the adsorption of Phenol is strongly depended. It was carried out by varying a pH between (1-12) and by contacting 0.25 g of adsorbent with 0.025 mg/l Phenol solution.

The mixture was shaken for 210 min. Then was filtered using whatman No 42 filter paper. The filtrate was analyzed using UV-Vis spectrophotometry.Then the optimum pH was determined as the pH with the highest adsorption efficiency of phenol. As it is shown in Figure 1, maximum adsorption was observed at pH 6 of phenol.

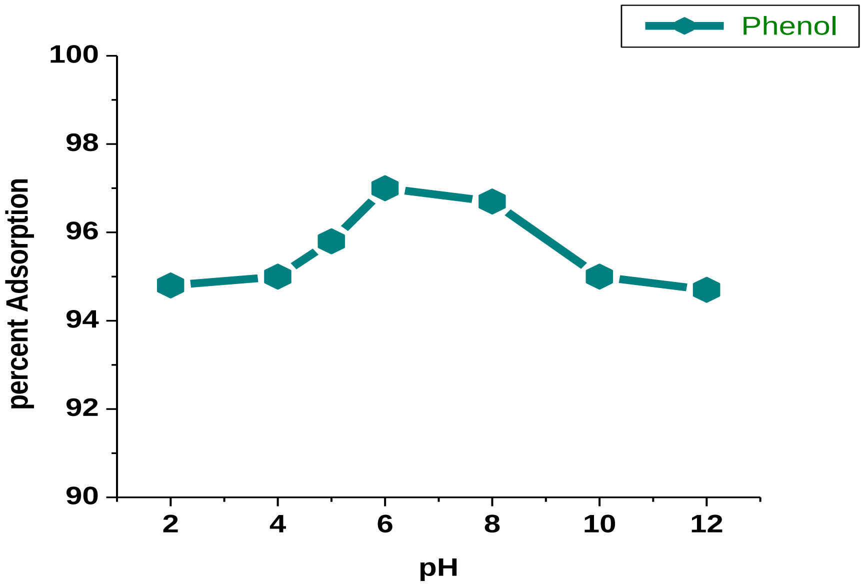


Figure1: Effect of pH on adsorption of Phenol onto APAC respectively.

The adsorption efficiencies of adsorbents were slightly decreased from lower pH values to higher pH. More adsorption at acidic pH indicates that the increase in H^+ ions on the adsorbents surface that results in strong electrostatic attraction between positively charged adsorbent surface and adsorbate ions.

Lower adsorption of adsorbents at maximum pH values may be due to the competition of the adsorbate ions and OH^- to be adsorbed on the surface of the adsorbents.

7.2. Effects of contact time

Adsorption of Phenol was studied at various adsorption times (35, 70, 105, 140, 175, 210 and 245 min) at optimum pH and keeping other variables constant. Then the solutions were filtered and analyzed using UV-Vis spectrophotometer.

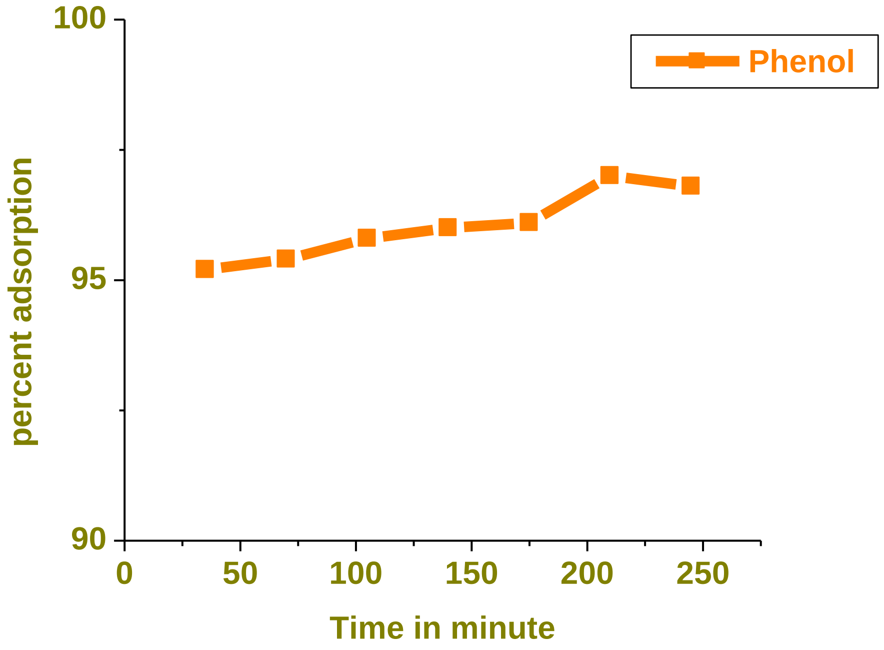


Figure 2: Effect of contact time on phenol adsorption

The adsorption efficiencies of phenol increases with increase in contact time and maximum efficiency occurred at 210 min then it becomes decreases. The initial rapid rate of adsorption may be due to the availability of Vacant surfaces of the adsorbents. The later slow adsorption rate could be due to the electrostatic hindrance caused by already adsorbed adsorbate species and the slow pore diffusion of the ions.

7.3. Study of effect of initial concentration and adsorbent dose

Was done by introducing Phenol concentration (0.00625, 0.0125, 0.025, 0.05, 0.1mg/L) and then mixed with 0.25 g APAC and shaken for 210 min at optimum temperature 25 ℃ keeping other variables constant. After adsorption time was completed the AC were removed from the solution and the final concentration of metal ion in each solution was determined using UV-Vis spectrophotometer.The adsorption of phenol ion at different adsorbent doses in the range of 0.15 - 0.55 g was investigated. This was carried out by adding a weighed mass of

AC adsorbent to 0.025 mg/L Phenol at optimal pH and contact time by keeping other variables constant. After adsorption time was completed, the solution was filtered and concentration of residual metal ion in each solution was determined using UV-Vis Spectrophotometer. Then the effect of adsorbent dose on the adsorption of adsorbate ion is shown in Figure 5 below. The adsorption efficiencies increase with increase in adsorbent dose. Because, contact surface of adsorbent particle increase for adsorbate and reach a saturation level at high doses. Then mass transfers of phenol ion from bulk liquid to the surface of the solids become resisted.

Phenol

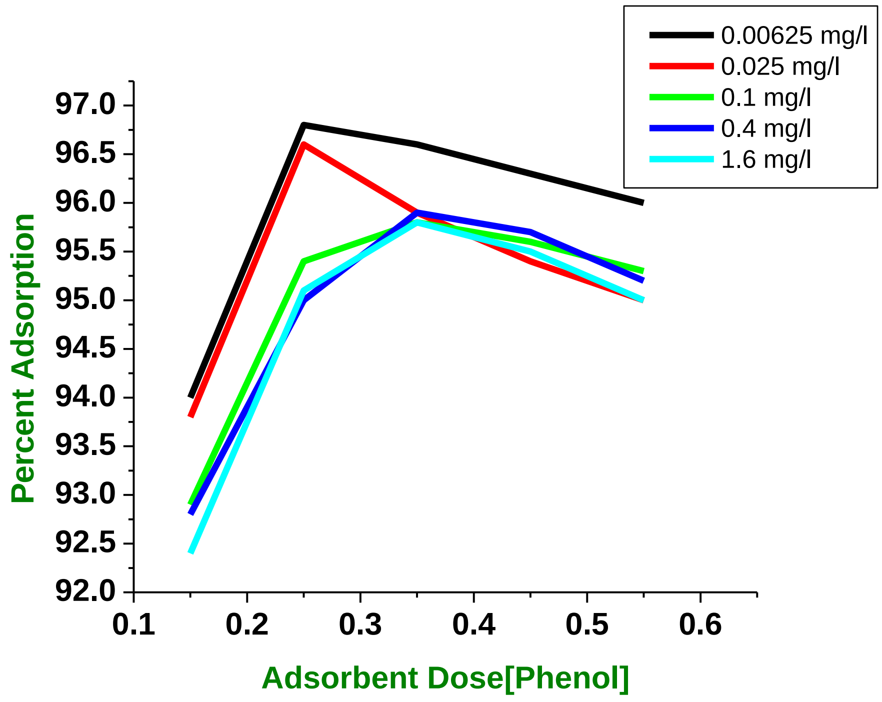


Figure 3: Effect of initial concentration & adsorbent dosage on the adsorption of Phenol

Adsorption was decreased with increasing initial concentration because at lower concentration there are sufficient active sites that the sorbate can easily occupy. But at higher concentrations, active sorption sites are not sufficiently available. Hence, absorbate ions were not completely adsorbed for the saturation of binding sites.

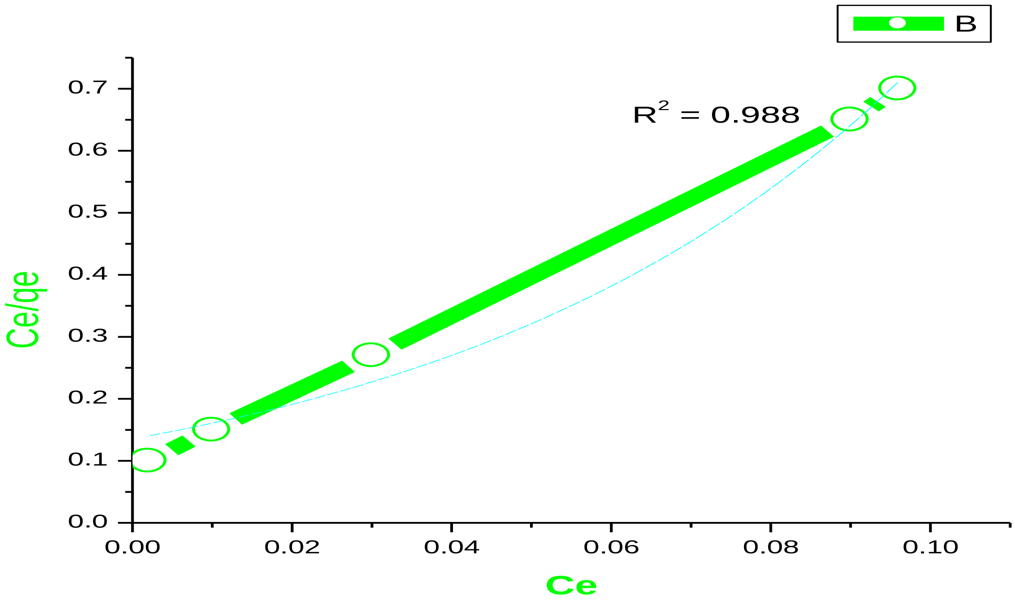
7.4. Effect of temperature

Adsorption efficiency increased with increasing temperature commonly 20 °C - 40 °C. Because of the chemical interaction between adsorbate and adsorbents and the increased rate of intra particle diffusion of ions into the pores. But it was shown decreasing after 40 °C because of desorption caused by an increase of the available thermal energy that may damage the active binding sites of adsorbents. Higher temperature induces higher mobility of the adsorbate causing desorption.

8. Adsorption Isotherms

Indicate how the adsorbed molecules distribute between the liquid and the solid phases when the adsorption process reaches an equilibrium state.

Langmuir and Freundlich isotherms have been widely used to explain the phenomena of adsorption. Langmuir isotherm is based on the principle that only a single adsorption layer exists on adsorbents.



Phenol

Fig.4. Langmuir plot of Phenol

Freundlich isotherm is an indicator of the extent of heterogeneity of the adsorbents surface. In this work, the experimental data was fitted to both isotherms. However, it well fitted to the

Freundlich isotherm as indicated by the higher R^2 values (Table 3). This show the heterogeneity of the adsorbent surface.

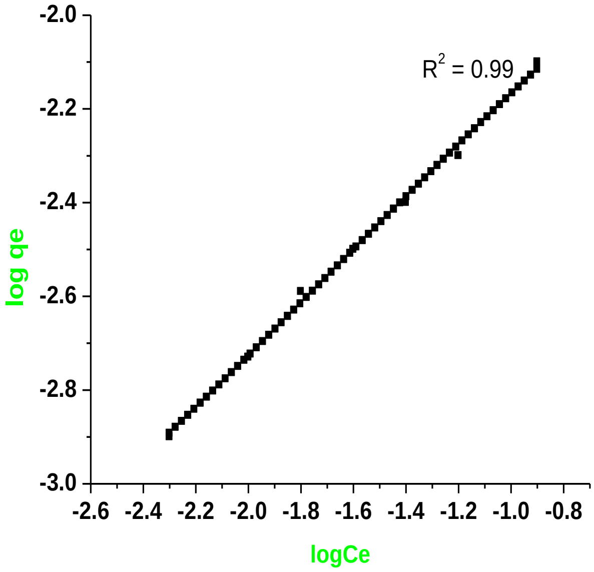


Fig.5 Freundlich plot of Phenol

Table 3: Results of isotherm models for the adsorption of Phenol onto APAC at 298 K.

	Phenol
Langmuir constants	
q_m(mg/g)	0.34636
b_L(mg/g)	6.124
R^2	0.988
R_L at 0.025 mg/L	0.975
Freundlich constants	
K_f	0.10875
n	2.493
R^2	0.99

The adsorption is favorable since n values are more than unity and the values of RL are between zero and one.

9.1. Adsorption Kinetic Studies

Pseudo-first and pseudo-second order kinetics are used to explain mechanism of adsorption. Experimental results showed rapid initial adsorption rate followed by a slower rate because initially, adsorption sites are open and metal ions interact easily with the sites. Slow adsorption was due to slower diffusion of adsorbate into the interior of the adsorbent.

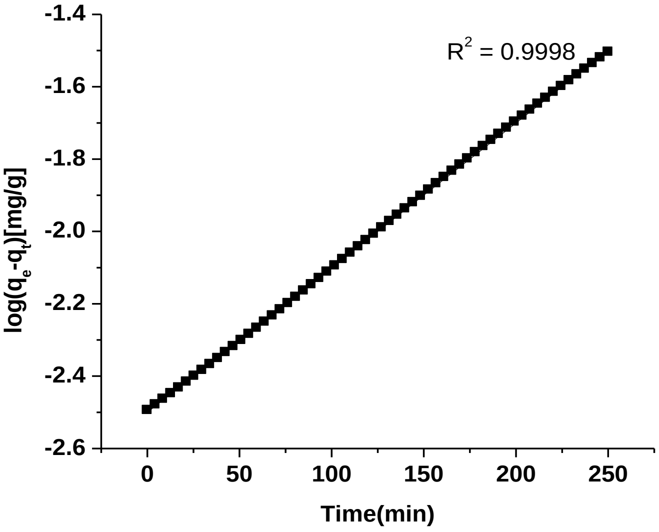


Fig.6. Pseudo first order of Phenol

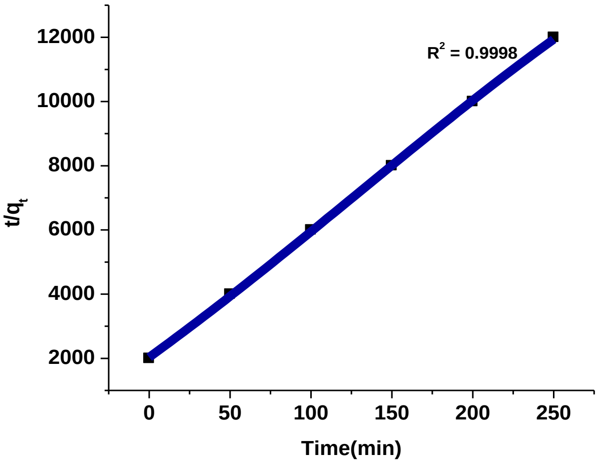


Fig.7 Pseudo second order of phenol

As R^2 (Table 4) below showed, pseudo-second order fits better to experimental data than pseudo-first order

Table 4: Kinetics parameters for the adsorption of Phenol onto APAC at 298 K

Kinetic parameters	
Pseudo-first order constants	Phenol
q_e (mg/g)	37.29
K_1(min^{-1})	0.008
R^2	0.9998
Pseudo-second order constants	
q_e (mg/g)	43.75
K_2 (g/mg. min)	3.16
R^2	0.9998

9.2. Adsorption thermodynamic study

The thermodynamic parameters that help us to understand the nature of the adsorption are ΔG, ΔH and ΔS. Their calculated results are indicated in Table 5 below.

Table 5: Thermodynamic Parameters for the Adsorption of Phenol ion onto adsorbent

Organic compound	ΔH(J/mol)	ΔS(J/mol.K)	ΔG(kJ/mol)				
			293 K	298 K	303 K	308K	3013K
Phenol	-16	18.56	-12	-15	-10	-17	-18

Negative values of ΔG and ΔH indicate the feasibility, spontaneous and exothermic nature of the adsorption process.Positive values of ΔS show the increased randomness at solid-liquid interfaces during the adsorption.Negative values of ΔG confirm the adsorption process is spontaneous, which becomes more negative with an increase in temperature. This indicates that a higher adsorption is actually occurred at higher temperatures. At higher temperature, ions are readily desolvated and thereby their adsorption becomes more favorable.

APPLICATION OF DEVELOPED METHOD FOR REAL SAMPLE

Collection of water sample

The study was conducted at Wollega University Chemistry laboratory, East Wollega Figure 8, Shows the overall view of the Gimbi town in West Wollega, and the sampling sites.

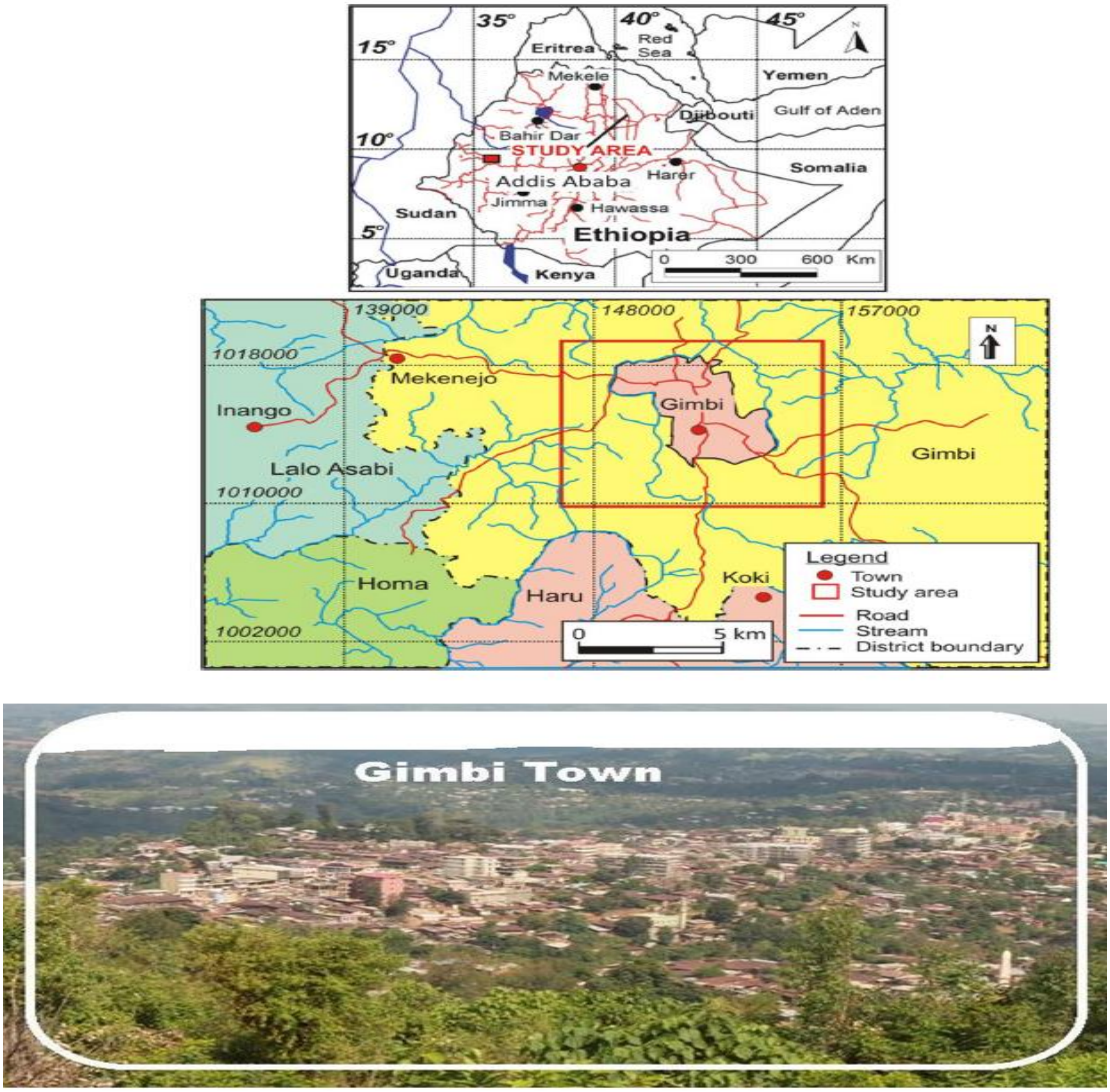


Fig 8: Overall view of Gimbi town
Sample site: Sarxe, Medini, Malifu, Bus station, Isaksi (Colli)

Analysis of Phenol

Study was conducted at wollega University Chemistry laboratory, East Wollega.

Water samples were distilled using simple distillation and distillate was collected. The distillate was quantitatively transferred to a separately funnel; extracted using isobutyl acetate yield orange colour distillate. The absorbance of the extract was measured at a wavelength of 510 nm using UV-Visible spectrophotometer. Stock solution (Standard) and blank were analyzed by exactly the same procedure for calibration and accuracy.

Concentration of phenol in analyzed water sample

Study has been conducted and concentration level of total phenol was determined. The analysis were done as mean ±SD of three replicates.

Table 6. The concentration level of phenol (μg/l) ± SD, in studied site

sample site	SW	DSTW	STW	1SWTS	SSTWS	SSTWS	RW	RW+Al	RW+Cl	DWIS1	DWIS2	DWABS	DWMA	DWMA	DWM1	DWM2	DWME	DWME	DWS1	DWS2
Total phenol conc. (μg/l)	0.39±0.1	0.3±0.23	0.62±0.13	0.31±0.24	0.39±0.15	0.63±0.3	0.4±0.2	0.31±0.23	0.41±0.25	0.87±0.1	0.42±0.13	0.74±0.3	0.85±0.3	0. 94±0.4	0. 93±0.5	0. 99±0.1	0. 87±0.4	0. 92±0.2	0. 94±0.6	0. 93±0.3

MPL for total phenol concentration(μg/l) in drinking water is 200.

Where MPL (µg/l) represents Maximum permissible limit in drinking water

SW: Surface water *DW: Drinking water* *STW: Stream water*

Table 6: Shows that surface water, Raw water, treated water, and Stream water in Gimbi town had phenol contents within acceptable level as WHO, guide line. Concentration of phenol in the samples analyzed are found in the Range: Phenol (0.3 μg/l – 0.99 μg/l). Concentration level of Phenol in analyzed samples is very small. Thus, adsorption study was conducted by preparing aqueous solution from stock solution of Phenol as depicted above.

Conclusion

In this study, locally available, less costly and environmentally friendly adsorbent Anchote peel (*Cocinia abysinica peel*) were investigated for its efficiency and suitability in removing Phenol at low concentrations by preparing activated carbon from Anchote peel (*Coccinia abyssinica peel*) by chemical activation method. Parameters pH, contact time, adsorbent dose, initial concentration, and temperature were investigated. Maximum adsorption efficiency was 97% for phenol at pH 6 and optimum contact time 210 min., adsorbent dose 0.25 g and initial conc. 0.025 mg/l respectively. Maximum adsorption capacity of APAC was observed to 43.75 mg/g of Phenol at 25 ^{o}C and 5 mg/L.

The adsorption was found to be strongly influenced by contact time and pH, and initial metal ion concentration. The adsorption kinetic data were modeled using the pseudo-first order and pseudo-second order kinetic equations. Pseudo second order model gave better R^2 values confirming suitability of the model for describing the adsorption system. Both Freundlich and Langmuir models can be used to fit the data and estimate model parameters, but the overall data is slightly better fitted by Freundlich isotherm reflecting surface heterogeneity of APAC. Thermodynamic parameters (ΔH, ΔS and ΔG at 293 k, 298 k, 303 k, 308 K and 315 K have also been calculated and it has been found that the adsorption was favorable, spontaneous and exothermic in nature. The positive values of the entropy change suggest that the increased randomness at solid-liquid interfaces during the adsorption of metal ions and Phenol onto adsorbent.

The method was simple, cost effective and environmental friendly. Therefore, it will help to enable us to use adsorbent environmentally friendly and in easily operational methods.

Acknowledgement

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References

[1] Uberoi, V., Bhattavhaya, S.K. and Mingo, Q. (1997). Toxicity and degradability of nitrophenols in anaerobic systems. *Water Environment Research*. Vol. 69(2): 146.

[2] Srivastava, S.K., R., Pal, N., and Mohan, D., (1997). Process development for removal of substituted phenol by carbonaceous adsorbent obtained from fertilizer waste. Environment Engineering, Vol. 123, 842-851.

[3] Sarkar, M., Acharya, K.P. (2006). Use of fly ash for the removal of phenol and its analogues from contaminated water. Waste Management, Vol. 26, 559-570.

[4] Adamski J, Nowak P, Kochana J. Simple sensor for determination of phenol and its derivatives in water based on enzyme tyrosinase. Electrochim Acta. 2010;55:2363-2367. DOI: 10.1016/j.electacta.2009.11.099.

[5] Kim K-R, Kim H. Gas chromatographic profiling and screening for phenols as isobutoxycarbonyl derivatives in aqueous samples. J Chromatogr A.2000;866:87-96.

[6] Padilla-Sanchez JA, Plaza-Bolanos P, Romero-Gonzalez R, Barco-Bonilla N, Martinez-Vidal JL,Garrido-Frenich A. Simultaneous analysis of chlorophenols, alkylphenols, nitrophenols and cresols inwastewater effluents, using solid phase extraction and further determination by gas chromatography-tandem mass spectrometry. Talanta. 2011;85:2397-2404. DOI: 10.1016/j.Talanta.2011.07.081.

[7] Sanchez-Avila J, Fernandez-Sanjuan M, Vincente J, Lacorte S. Development of a multi-residue method for the determination of organic micropollutants in water, sediment and mussels using gas chromatography-tandem mass spectrometry. J Chromatogr A. 2011;1218:6799-6811. DOI:10.1016/j.chroma.2011.07.056.

[8] Kovacs A, Mortl M, Kende A. Development and optimization of a method for the analysis of phenols and chlorophenols from aqueous samples by gas chromatography-mass spectrometry, after solid-phase extraction and trimethylsilylation. Microchem J. 2011;99:125-131. DOI: 10.1016/j.microc.2011.04.007.

[9] Alcudia-Leon MC, Lucena R, Cardenas W, Valcarcel M. Determination of phenols in waters by stir membrane liquid - liquid - liquid microextraction coupled to liquid chromatography with ultraviolet detection. J Chromatogr A. 2011;1218:2176-2181. DOI: 10.1016/j.chroma.2011.02.033.

[10] Tanigawa T, Watabe Y, Kubo T, Hosoya K. Determination of bisphenol a with effective pretreatment medium using automated column-switching HPLC with fluorescence detection. J Sep Sci.2011;34:2840-2846.

[11] Segovia-Martinez L, Moliner-Martinez Y, Campins-Falco P. Direct capillary liquid chromatography with electrochemical detection method for determination of phenols in water samples. J Chromatogr A. 2010;1217:7926-7930. DOI: 10.1016/j.chroma.2010.10.078.

[12] Maya F, Estela JM, Cerda V. Flow analysis techniques as an effective tools for the improved environmentalanalysis of organic compounds expressed as total indices. Talanta. 2010;81(1-2):1-8. DOI:10.1016/j.talanta.2010.01.028.