Industrial Waste &
Wastewater Treatment &
Valorisation

Chromium (VI) removal from wastewater by acid-treated pyrolytic char derived from used rubber tires

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Disposal of waste tires

- disposal of waste tires has become a serious source of environmental pollution :
- accumulate in open dumps or landfill sites → hazardous (disease, accidental fires)

- *tires consist mainly of:*
- synthetic and natural rubber
- tire rubber additives (carbon black, sulfur and zinc oxide)

- *Ways of treatment :*

- tire recycling → valuable products used in various applications
- tire grinding → civil engineering applications
- retreading → reused of tires

- pyrolysis → results in the recovery of useful products from wastes

Pyrolysis

- **Pyrolysis:**

➢ an efficient, cost effective and product valorisation process

➢ thermal decomposition of waste tires at high temperatures (450–900^{o}C) under oxygen-free atmosphere

- **Products of pyrolysis**

▪oil fractions (as a source of chemical feedstock or a fuel)

▪ gas fractions (energy requirements off-side or heating of pyrolysis unit)

▪carbonized solid residue,

pyrolytic tire char (PC)

Pyrolytic Tire Char

- Pyrolytic char as a carbon - rich solid material can be used:
  - ✓ reinforcing filler for low-value rubber goods
  - ✓ printing ink pigment after appropriate treatment
  - ✓ for filling polymers and vulcanizates
  - ✓ precursor for adsorbent materials (high carbon content)

- Tire pyrolytic recycling technology can be further exploited to produce:
  - added value products with catalytic and adsorptive capacities
  - low cost efficient adsorbent to remove hazardous organic – inorganic compounds, heavy metals → applications in wastewater treatment and waste valorization

Cr(VI) - Pyrolytic Tire Char

- Hexavalent chromium Cr (VI) is a highly toxic pollutant contained in various wastewater coming from:

• industrial processes (textile, leather tanning, electroplating)

- Adsorption → treatment technique for the removal of chromium from wastewaters because of:

✓ simple operation

✓ effectiveness

✓ low cost equipment

Aims of the study:

- to characterize the physicochemical properties of acid (HNO_3)-treated pyrolytic tire char

- to assess the ability of Char purified to remove the model organic pollutant, Cr (VI), from aqueous solution

- to evaluate the adsorption characteristics of Cr(VI) on the basis of equilibrium (isotherms) and kinetic studies

- to indicate the nature of pollutant adsorption from the calculated thermodynamic parameters

Experimental Section

Preparation of Char purified

- The Char was derived from the pyrolysis of used rubber tires at 450 ^{o}C in oxygen- free atmosphere under vacuum for 4 hours

The purification of pyrolytic char :

10 g of char was suspended in 1L of a HNO_3 2M solution

↓

24 h under vigorous stirring

↓

suspension filtration

↓

refluxed with 250ml HNO_3 2M solution for 48h

↓

Washing with double distilled water (pH 6-7)

Characterization of adsorbent

Characterization of Char purified was achieved by:

- **X-Ray powder Diffraction (XRD) mesuraments**

  Brüker Advance D8 instrument using Cu K_a radiation (λ = 1.5418 Å) in the 10° <2θ < 80° with a 2θ resolution of 0.02°

- **N_2 adsorption–desorption BET isotherms**

  Tristar Micrometrics Instruments and Brunauer–Emmett–Teller (BET) method at 77 K

Surface characteristics of adsorbent

- **Elemental analysis:** elemental analyzer Perkin Elmer (2400 Series II) at 1.100 ^{o}C for the determination of CHNO contents

- **Boehm titration:**

➢ mixing 100 mg of char purified with 40 ml solutions of 0.1 M of sodium bicarbonate (carboxylic groups), 0.05 M of sodium carbonate (carboxylic and lactonic groups), 0.1 M of sodium hydroxide (carboxylic, lactonic and phenolic groups) and 0.1 M of HCl

➢ 24h stirring

➢ filtering and titration of solutions

- **Point of zero charge (pH_{pzc})** → potentiometric mass titration (PMT)

Adsorption Studies

Kinetic experiments

- prepared in a series of 200 ml conical flasks
- 10 mg of adsorbent was added in 100 ml of aqueous solutions of Cr (VI) (C_o = 10 mg L^{-1})
- suspensions were kept in the dark under stirring at 600 rpm
- aliquots (≈ 2ml) were filtered through a 0.45 μm filter (HVLP, Millipore)

Adsorption Studies

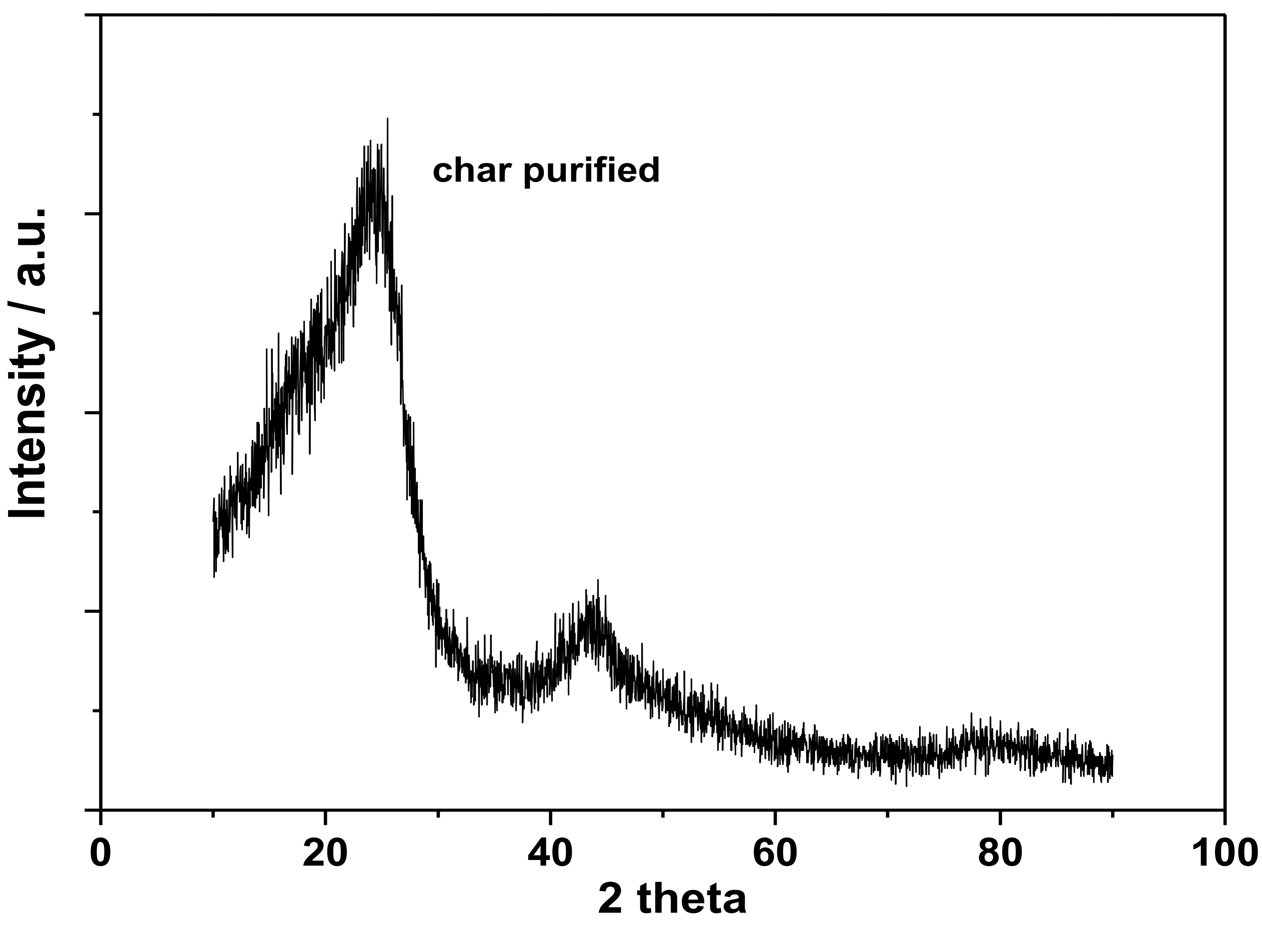
Isotherm experiments

- 5 mg of adsorbent was added in conical flasks of 100 mL
- 50 ml of aqueous solutions at varying concentrations $C_{Cr(VI)}$ = 5, 10, 20, 50, 100 mg L^{-1} were mixed with the adsorbent
- suspensions were kept in the dark for 60 min under stirring at 600 rpm
- aliquots (≈ 2ml) were filtered through a 0.45 µm filter (HVLP, Millipore)

- Concentration of Cr(VI) **:** diphenylcarbazide colorimetric method at a wavelength of 540 nm using a UV–Vis spectrophotometer (Hitachi, U-2000).

Results

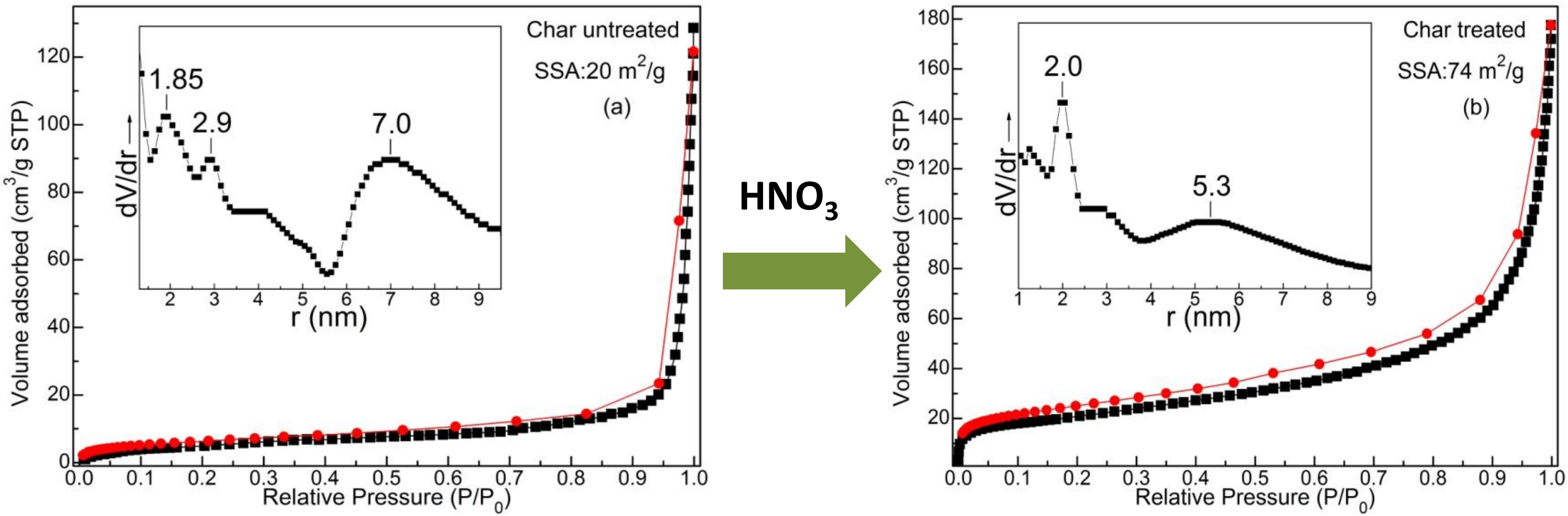
X-Ray Diffraction (XRD) characterization



❖ 2theta ≈26º → layered graphitic sheets

❖ According to JCPDS databank a Diamond like amorphous carbon (DLC) phase detected (broad background)

N_2-Porosimetry and BET analysis



- The isotherms, of characteristic **type IV** shape with a well-defined **type H3** hysteresis loop are characteristic of a **mesoporous** material.
- Type H3 loops are usually given by aggregates of plate-like adsorbents containing slit-shaped pores.
- Some adsorption, at low relative pressures, is attributed to the presence of **some degree of microporosity**.

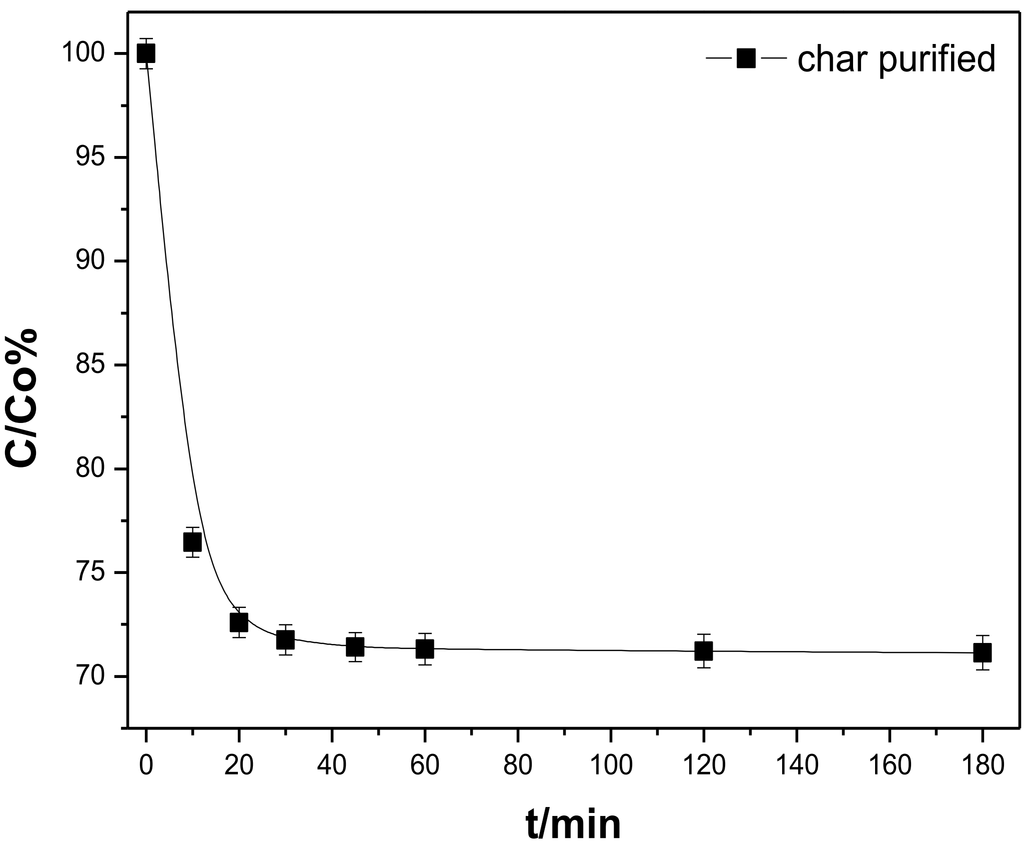
Surface Characterization

Adsorbent	XRD phase	pH $_{pzc}$	SSA(m^2 g^{-1})
Char purified	Graphite planes	3.5	74

	Elemental composition (% w/w)					Surface functional groups (mmol g^{-1})			
	C	**N**	**H**	**S**	**O**	**Carboxylic**	**Lactonic**	**Phenolic**	**Total acidic**
Char untrated	75.23	4.76	4.70	2.84	15.17	3.5	-*	6	9.5
Char purified	68.13	3.85	3.26	2.29	22.47	350	-*	100	450

* Not detected

Adsorption kinetics



Four kinetic models → describe the mechanism of the adsorption process:

- **pseudo first - order** :

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

- **pseudo second – order** :

$t/q_t = 1/k_2 q_e^{\ 2} + (1/q_e)\ t$

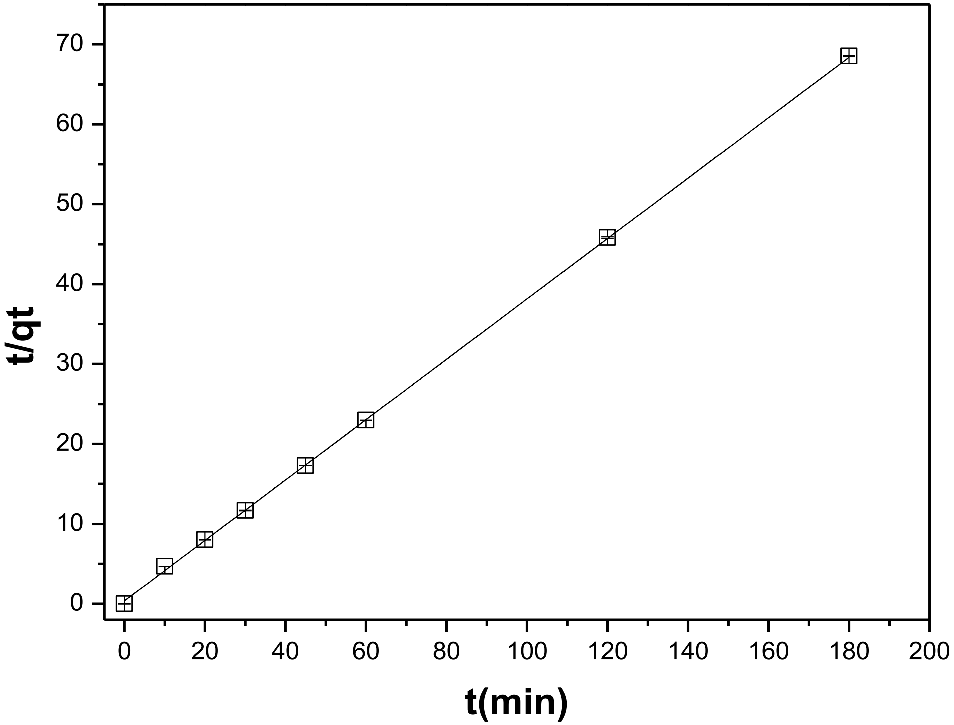
- **intraparticle diffusion**:

$q_t = K_p t^{\ ½} + Z$

- **Elovich**:

$q_t = (1/\beta)\ \ln\alpha\beta + (1/\beta)\ \ln_t$

Adsorption kinetics

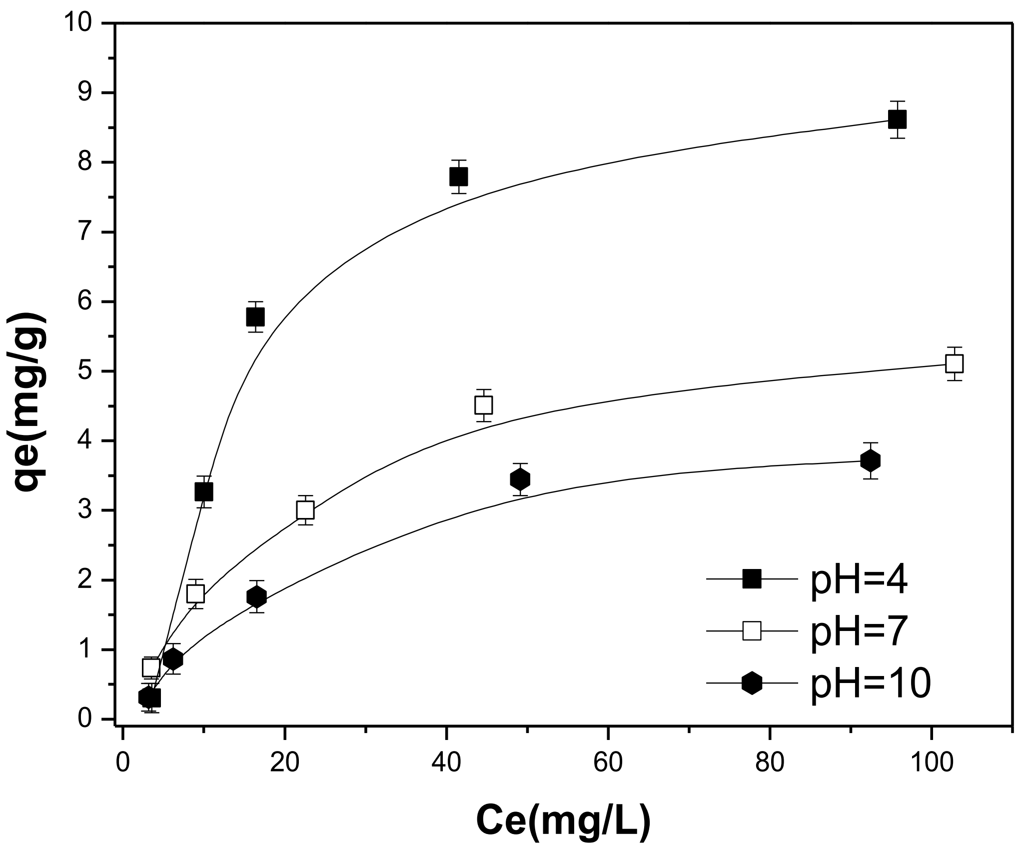


The kinetic experimental data were better fitted by **the pseudo-second order model :**

- the rate-limiting step may be the surface adsorption interactions
- adsorption capacity is proportional to the number of active sites of pyrolytic char

Pseudo-first order				Pseudo-second order				Intraparticle diffusion			Elovich		
$q_{e,exp}$ (mgg^{-1})	k_1 (min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2 (ARE)	$q_{e,exp}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2 (ARE)	Z	K_p	R^2 (ARE)	α	β	R^2 (ARE)
2.61	0.12	1.86	0.9773 (3.59)	2.61	0.39	2.64	0.9998 (0.14)	1.24	0.14	0.4016 (1.38)	2479	7.21	0.5694 (3.83)

Adsorption isotherms



The experimental data were examined according to following isotherm models:

- **Langmuir** : $C_e q_e = (1/q_e) C_e + 1/K q_m$
- **Freundlich** : $\ln q_e = \ln K_f + 1/n \ln C_e$

Adsorption isotherms of Cr(VI)

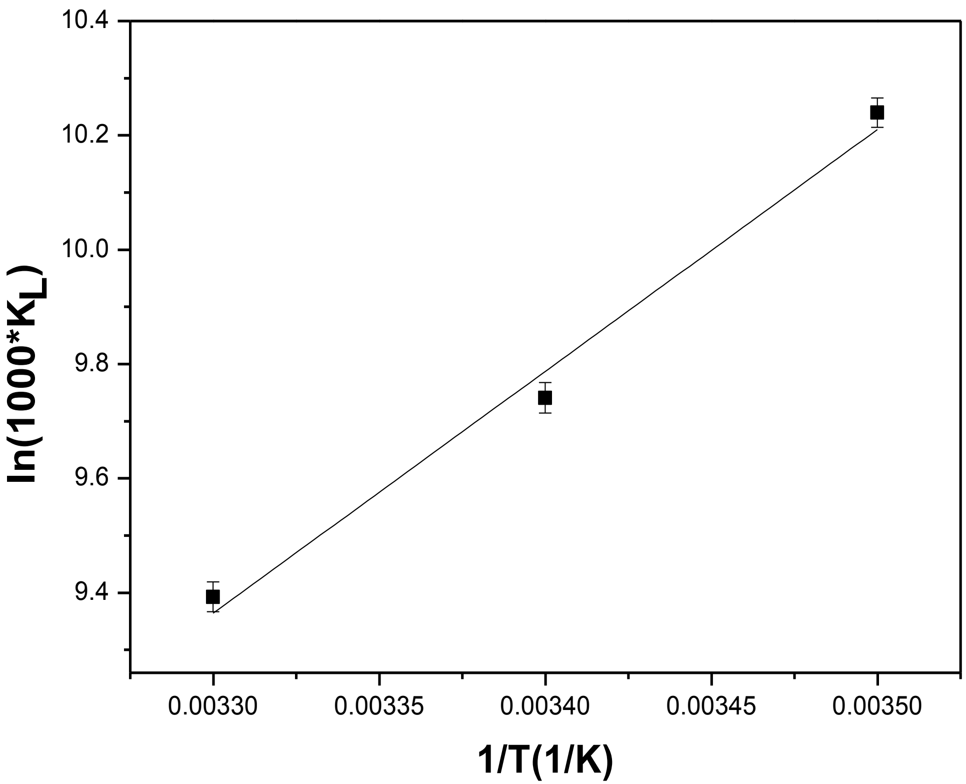
Catalysts	Freundlich			Langmuir		
	K_f (mg g^{-1})	1/n (mg L^{-1})	R^2	Q_m (mg g^{-1})	k_L (L mg^{-1})	R^2
Char purified pH=4	1.31	0.43	0.7692	10.98	0.049	0.9121
Char purified pH=7	0.73	0.43	0.9061	6.43	0.042	0.9864
Char purified pH=10	0.38	0.51	0.9176	5.12	0.033	0.9816

- **Langmuir isotherm** fits the adsorption equilibrium data
  - ✓ adsorption occurs uniformly on the active sites of the adsorbent
  - ✓ monolayer coverage of Cr(VI) onto char particles

- **The maximum percent removal of Cr (VI)** → obtained at acidic pH 4

Adsorbents	**Langmuir constants**			**SSA_{BET} (m^2g^{-1})**
	Q_m (mg g^{-1})	**k_L (L mg^{-1})**	**R^2**	
Waste tyre Activated carbon (TAC)	48.07	0.1503	0.9969	832
Activated carbon derived from olive bagasse	88.59	0.354	0.998	718
Modified activated carbon (MAC)	16.10	0.38	0.9977	853
Granular activated carbon (GAC)	6.40	0.72	0.9996	681
Oxidized Activated carbon- HNO_3	13.74	0.063	0.995	853
Commercial coconut activated carbon	7.61	0.034	0.9964	873
Powdered activated Carbon (PAC)	55.6	1.21	0.997	1.027
Present study	*10.98*	*0.049*	*0.9121*	*74*

Adsorption Thermodynamics - Van’t Hoff plot



$$\ln K_L = \Delta S^o/R - \Delta H^o/RT$$

- negative **ΔG°** → spontaneous nature of the adsorption process at all temperatures
- negative **ΔH°** → exothermic character of the adsorption process.
- negative **ΔS°** → decrease of randomness at the solid-solute interface during the adsorption process.

	ΔH° (kJ/mol)	ΔS° (kJ/mol)	ΔG° (kJ/mol)			R^2
			288 K	**298 K**	**308 K**	
Cr(VI)	-35.22	-0.038	-24.51	-24.13	-24.05	0.9791

Conclusions

☑ Tire rubber pyrolytic char was derived from pyrolysis method.

☑ The acid-treated pyrolytic char adsorbent is considerably efficient for adsorption of Cr (VI) from aqueous solutions.

☑ A graphitic structure with microporous-mesoporous characteristics and carboxylic-phenolic groups have been assessed for the Char purified.

☑ The kinetics of Cr (VI) adsorption on Char purified follows the pseudo-second order kinetic model

☑ Langmuir model provided the best fitting for Cr (VI) adsorption isotherms.

☑ The optimum pH value for the removal of Cr(VI) ions by Char purified is 4.

☑ The adsorption process was found spontaneous ($\Delta G<0$) and exothermic ($\Delta H<0$).

Acknowledgments

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η περιφέρεια στο επίκεντρο της ανάπτυξης

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Thank You
Σας Ευχαριστώ