Adsorption of phenol and it's derivatives from aqueous system by modified adsorbents

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The present research work has been divided into the following **seven chapters:**

Chapter 1: Introduction and objectives of the present work

This chapter introduces the applications and toxicity of phenolic compounds and the effect of their exposure on human beings. It also discusses the experimental and theoretical developments in the field of surface chemistry.

The operations of the chemical and pharmaceutical industries, the mineral (non-metallic) products sector, the steel and metal products sector, the pulp, paper, and wood products sector and petroleum refining sector are responsible for the presence of phenols into the environment. The substances enter ecosystems due to the penetration of the urban or industrial effluent to the surface water. Phenol and its derivatives are poisonous and corrosive chemicals that are categorized as priority pollutants by United States Environmental Protection Agency (USEPA). The unspecified toxicity associated with the phenolic compound's hydrophobicity and the production of free radicals is the two basic mechanisms underlying phenol toxicity.

The experimental development of adsorption started in 1773 when Scheele reported some experiments of the uptake of gases by charcoal and clays derived from various sources. In 1786, Lowitz, used charcoal for decolourization of tartaric acid solutions as result of organic impurities uptake. A variety of experiments for adsorption of various liquids and gases at solid surface including the use of active carbons as the adsorption medium in gas masks during World War I.

Since the start of the twentieth century, adsorption at varied interfaces has been of interest to scientists. The theoretical development of adsorption started in 1888, when the so-called Freundlich empirical equation was firstly proposed by van

Bemmelen. It is known in the literature as Freundlich equation, because Freundlich assigned great importance to it and popularized its use. In times, different theories such as Langmuir monolayer adsorption theory, BET surface area theory, TVFM (Theory of volume filling of micropores) etc. have been given for the interpretation of the mechanism of adsorption at various solid-liquid interfaces.

Chapter 2: Review of literature

This chapter discusses the recent developments in the field of the adsorptive removal of phenolic compounds by different classes of adsorbents. In the last decade, scientists have looked at a variety of natural adsorbents for this purpose. Their adsorption capabilities range from 1 to >1000 mg/g, depending on the adsorbent's surface area, pH, temperature, phenol and surface functional group concentrations, contact time, and other parameters. Carbonaceous adsorbents, clay and natural mineral adsorbents, polymer-based adsorbents, and new adsorbents are the four classes of adsorbents evaluated for the removal of phenol and its derivatives. Polymer-based adsorbents had the highest adsorption capabilities (>1000 mg/g), whereas natural clays and new adsorbents had lesser adsorption capacities when compared to carbonaceous adsorbents. The significant potential for phenol recovery and reuse is a major advantage of phenol adsorption over other applicable methods.

Chapter 3: Materials, methods and characterization techniques

This chapter describes the materials and experimental methods used throughout the research work. The characterization techniques used for the analysis of adsorbents are as follows:

- UV-Vis spectroscopy for concentration determination at a specific wavelength.
- Fourier Transform Infrared (FT-IR) spectroscopy for functional group analysis.

- Powder X-ray Diffraction (XRD) for phase analysis.
- Scanning Electron Microscopy (SEM) for surface morphology.
- Brunauer Emmett Taylor (BET) surface analysis for porosity and surface area analysis.
- Optical profilometry for surface profiling.

Chapter 4: Effective removal of 4-aminophenol from aqueous environment by pea (*Pisum sativum*) shells activated with sulfuric acid

This chapter describes the synthesis and characterization of pea shells activated with sulfuric acid and its use to remove 4-aminophenol from an aqueous medium. The goal of the current work was to create an inexpensive adsorbent (pea shells activated with sulfuric acid, PSASA) from agricultural waste (pea shells), and to use it to remove hazardous 4-aminophenol effectively (4-AP). SEM, FT-IR, and XRD studies supported the new PSASA's substantial 4-AP adsorption behaviour. The surface topography of the PSASA surface revealed its high degree of unevenness, and BET analysis verified the PSASA's macroporous characteristic.Multiple tests were conducted to determine the effects of adsorbent dosage, temperature, pH, PZC, the addition of KCl and urea, and the starting concentration of 4-AP on adsorption. As the temperature rises from 25°C to 45°C, a decrease in 4-AP adsorption uptake is seen. At an ideal pH of 7.0 and 25ºC, the maximum adsorption uptake (q_{max}) was found to be 106.11 mg/g. The Langmuir isotherm provided the best explanation for the experimental data, with high R^2 values, out of all the examined adsorption isotherm models. The kinetics of adsorption were discovered to be well explained by the pseudo-first-order model.

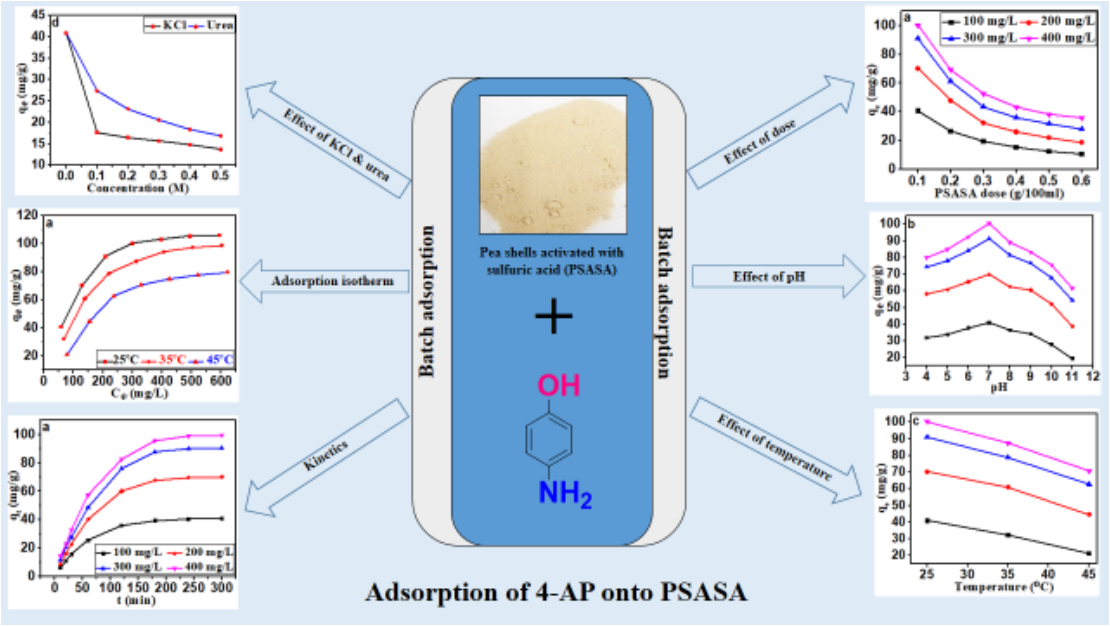

Fig. 1: Graphical representation of the 4-AP Adsorption onto PSASA.

The thermodynamic result supports the physical and exothermic nature of the adsorption phenomenon. Electrostatic interaction, hydrogen bonds, and the π-π exchange process were the main factors controlling the adsorption of 4-AP. As a result of the current research's successful findings, we can use the PSASA as a low-cost adsorbent to remove phenolics from aqueous stream.

Chapter 5: Adsorption, kinetics and thermodynamics of phenol removal by ultrasound-assisted sulfuric acid-treated pea (*Pisum sativum*) shells

This chapter describes the synthesis and characterization of ultrasound-assisted sulfuric acid-treated pea shells and its use to remove phenol from aqueous medium.Waste pea shells were utilised in the current investigation to create an effective adsorbent (ultrasound-assisted sulphuric acid-treated pea shells, USAPS) that was employed to remove phenol. SEM-EDS, FT-IR, XRD, optical profilometry, BET, and PZC techniques were used to characterise the USAPS sample. The

adsorption characteristics were greatly improved by the application of ultrasound during the chemical activation. By adjusting the pH (2–9), temperature (25–45°C), USAPS dose (0.1–0.6 g/100 ml), phenol concentration (50–500 mg/L), and addition of inorganic salts, the adsorption of phenol was investigated (0.1 M KCl and 0.1 M $CaCl_2$). With 0.1 g/100 ml of the USAPS dosage, the maximal phenol absorption (q_{max}) was determined to be 125.77 mg/g for 500 mg/L of phenol at pH 7 and 25°C. Temperature rise and the USAPS dose had a negative impact on adsorption, but the addition of 0.1 M KCl and 0.1 M $CaCl_2$ reduced the maximum phenol adsorption (q_{max}) from 125.77 mg/g to 103.45 mg/g and 84.11 mg/g, respectively.

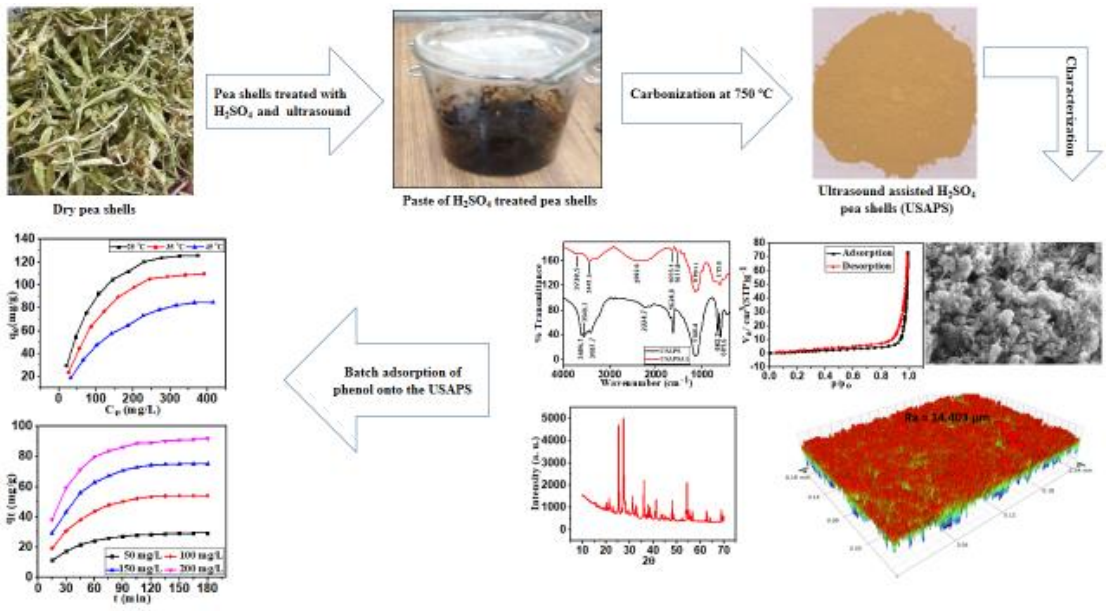

Fig. 2: Graphical representation of the phenol adsorption onto USAPS.

The equilibrium data were best explained by the Langmuir model, whereas the time-dependent phenol elimination was best explained by the pseudo-second-order kinetic model. The thermodynamic analysis showed that there was no structural change at the adsorbent-adsorbate interface, demonstrating the physical character of adsorption.

Chapter 6: Adsorption of phenol onto pea peels biochar derived at three different pyrolysis temperatures: A comparative study

This chapter describes a comparative study of the synthesis and characterization of biochars-derived pea shells at different pyrolysis temperatures and their use to remove phenol from an aqueous medium. Pea (*Pisum sativum*) peels were employed as a precursor for the production of biochar at three distinct temperatures (250ºC: PP250, 500ºC: PP500, and 750ºC: PP750) utilising moderate pyrolysis for one hour in order to remove phenol from an aqueous medium effectively. SEM, XRD, and FT-IR were used to characterize the samples of biochar.

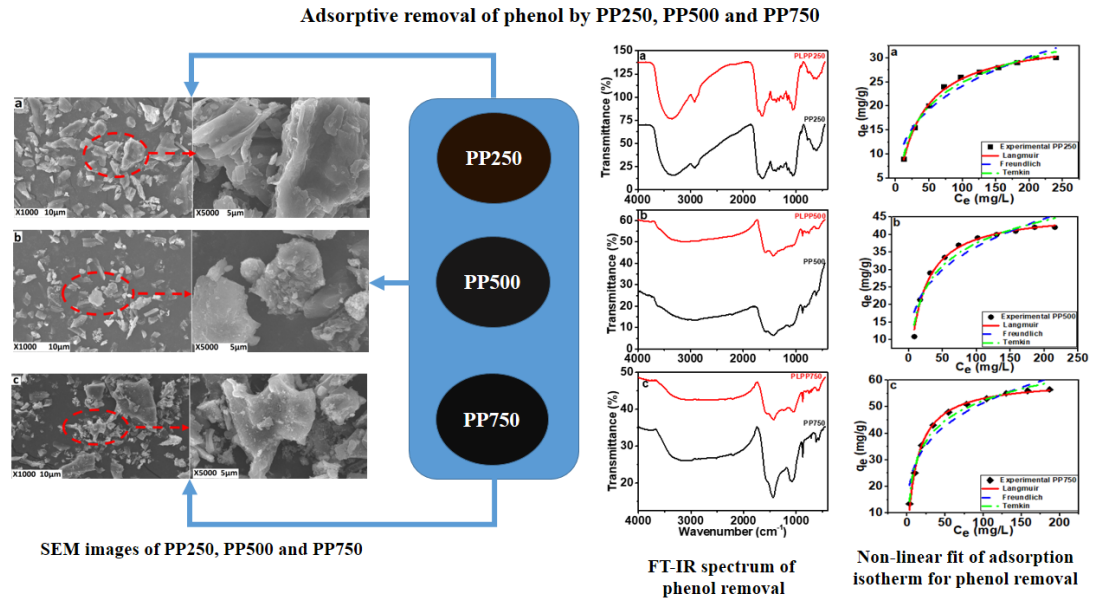

Fig. 3: graphical representation of the phenol removal by PP250, PP500 and PP750.

Temperature and solution pH were used as function to check the removal of phenol. It was discovered that 6.0 pH and 25ºC were the ideal conditions. The adsorption capacity of PP250 is primarily influenced by the presence of NaCl and urea in the solution, while PP500 and PP750's adsorption potential is only marginally influenced. The adsorption data were best explained by the Langmuir isotherm. The q_{max} was

determined to be 34.63, 46.70, and 60.10 mg/g for the PP250, PP500, and PP750, respectively. The kinetic data were most successfully explained by a pseudo-second-order model. The physical and exothermic nature of adsorption was supported by thermodynamic parameters. PP750 can preferably be used for phenol removal than PP500 and PP250.

Chapter 7: Conclusion & future prospects

This chapter describes the conclusions and future prospects of the present research work. The removal of phenol by USAPS and PS biochars (PP250, PP500 and PP750) and 4-AP by PSASA from an aqueous solution is highly dependent on the pH of the solution which affects the surface charge of the adsorbent and the degree of ionization of the adsorbate. The adsorbed amount of phenol and 4-AP decreases when the pH value is greater than 7. It seems that the phenol and 4-AP removal capabilities with USAPS and PSASA were increased at pH value 7, respectively, whereas, for PS biochars (PP250, PP500 and PP750), phenol removal capabilities increased at pH 6 under the given test conditions. The adsorption equilibrium of phenol by USAPS and PS biochars (PP250, PP500 and PP750) and 4-AP by PSASA are described by the Freundlich, Langmuir and Temkin adsorption isotherm. Out of these isotherm models Langmuir adsorption isotherm successfully explained the adsorption of phenol and 4-AP onto PS modified adsorbents used in the experiments. It concludes the applicability of Lagmuir theory i.e. the formation of monolayer during the adsorption. The maximum phenol uptake by USAPS, PP250, PP500 and PP750 were found to be 125.77, 34.63, 46.70, and 60.10 mg/g respectively, whereas maximum 4-AP uptake by PSASA was found to be 106.11 mg/g. The removal of phenol by USAPS and 4-AP by PSASA took place through electrostatic interactions, hydrogen bonding and π-π interactions among adsorbent and adsorbate interfaces. The removal of phenol by

PP250 took place through electrostatic interactions, hydrogen bonding and π-π interaction, whereas by PP500 through π-π interactions with some extent of hydrogen bonding and by PP750 through π-π interactions only.

The usage of low-cost adsorbents has introduced a new area of research for water/wastewater treatment, and it also brings more opportunities in producing a better way of management. The future perspectives of low-cost adsorbents can be determined to explore the possibilities, functionalization/modifications/pre-treatment of agro-waste-based materials to improve their adsorption potential.

1. **Prashant Mishra**, Kaman Singh, Utkarsh Dixit, Adsorption, kinetics and thermodynamics of phenol removal by ultrasound-assisted sulfuric acid-treated pea (Pisum sativum) shells; *Sustainable Chemistry and Pharmacy, Elsevier;* 22 (2021) 100491. (**I.F. 5.464**)
2. **Prashant Mishra**, Kaman Singh, Utkarsh Dixit, Ankita Agarwal, Rayees Ahmad Bhat; Effective removal of 4-Aminophenol from aqueous environment by pea (Pisum sativum) shells activated with sulfuric acid: Characterization, isotherm, kinetics and thermodynamics; *Journal of the Indian Chemical Society, Elsevier;* 99 (2022) 100528. (**I. F. 0.243**)
3. **Prashant Mishra**, Kaman Singh, Gajanan Pandey; A comparative study of phenol removal by Pisum-sativum peels biochars derived at different pyrolysis temperatures: Isotherm, kinetic and thermodynamic modelling; 2022, *ChemistrySelect; 7 (2022)* e202202856. doi.org/10.1002/SLCT.202202856.
4. Rayees A. Bhat, Kaman Singh, D. Kumar, Ashok Kumar, **Prashant Mishra**; Antimicrobial studies of the Zn(II) complex of S-benzyl-β-(N-2-methyl-3-phenylallylidene)dithiocarbazate; *Journal of Coordination Chemistry, Taylor & Francis;* (**I.F. 1.869**) *doi.org/10.1080/00958972.2022.2083962*
5. Kaman Singh, K.K. Sharma, R.K. Singh, **Prashant Mishra**, Ankita Agarwal, Anita Suman, Pankaj Singh; Sugar solutions colour measurement : Problems and Prospects; *Asian Sugar Journal*, Vol. 1, No. 1, Jan-Apr, 2021 : 32-67. (**I.F. NA**)
6. Kaman Singh, **Prashant Mishra**; The influence of different qualities of mops reagent on the measured sugar colour in solution; e - *Proceed. Sug. Tech. Assoc. India*, 79, 361-364, 2021. (**I.F. NA**)
7. Kaman Singh, **Prashant Mishra**, Ashok Kumar; Selection of pH for measurement of sugar solution colour; *Proceed. Sug. Tech. Assoc. India*, 77, 461-480, 2019. (**I.F. NA**)
8. **Prashant Mishra**; Alternative uses of sugarcane to mitigate green house gases generation; *Proceeding of GCGHGSPCT*, 62-63, 44, 2019; ISBN: 978-93-88237-65-9 (**I.F. NA**)