

## ADSORPTIVE REMOVAL OF ORGANIC CHEMICALS FROM AQUEOUS SOLUTION BY SOIL EQUILIBRIUM STUDY

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### Abstract

The potential of soil, a low cost and abundantly available material with good sorption properties, for removing aromatic organic compound was investigated. Nitro-benzene, Chlorobenzene, Bromobenzene, Benzene, Phenol, O-chloro phenols, M-Chloro phenol, P-Chloro phenol, Benzaldehyde, Aniline, O-Chloro Aniline, M-Chloro aniline, P-Chloro aniline, Toluene, were selected for the studies. The effect of various factors such as adsorbent particle size, pH, phenol concentration and temperature on the sorption capacity was investigated. Langmuir adsorption isotherm constants were calculated and it was shown that the adsorption data for aromatic organic compound onto soil fitted the Langmuir model well. It was found that these low cost soil adsorbent demonstrated good removal capability of Nitro-benzene, Chlorobenzene, Bromobenzene, Benzene, Phenol, O-chloro phenols, M-Chloro phenol, P-Chloro phenol, Benzaldehyde, Aniline, O-Chloro Aniline, M-Chloro aniline, P-Chloro aniline, Toluene, hence can be used economically on large scale.

**KEYWORDS :** ; Soil; adsorption; Organic Chemicals, Equilibrium Study

### Introduction

The presence of organic chemicals in aqueous environments poses significant environmental and health risks. These compounds, which include pesticides, pharmaceuticals, and industrial pollutants, can contaminate water sources, affecting ecosystems and human health. Effective removal of these contaminants from water is critical, prompting research into various remediation techniques. One promising method is the adsorptive removal of organic chemicals using soil as a natural adsorbent. Soils possess unique properties that enable them to adsorb a wide range of organic compounds, driven by their complex composition, including minerals, organic matter, and microbial communities. Understanding the equilibrium interactions between organic contaminants and soil components is essential for optimizing remediation strategies. This study aims to explore the adsorption characteristics of different organic chemicals on various soil types, evaluating factors such as soil composition, pH, temperature, and concentration of contaminants. By conducting a systematic equilibrium study, we can gain insights into the adsorption mechanisms and capacity of soils, informing the development of effective water treatment processes. This research not only contributes to the scientific understanding of soil chemistry and contaminant

dynamics but also supports the implementation of sustainable environmental management practices. The contamination of water sources by chlorinated phenolic compounds, particularly para-chloro phenol (PCP), has raised significant environmental concerns due to its toxicity and persistence in the environment. PCP is widely used in various industrial applications, including the production of pesticides and as a wood preservative. Its presence in aqueous solutions can have detrimental effects on aquatic life and human health, necessitating effective removal techniques. (1-3)

Adsorption is a widely studied method for the removal of organic pollutants from water, and soils are recognized as potential adsorbents due to their complex matrix of minerals, organic matter, and biological activity. Sorption is a key process for the removal of organic contaminants from aqueous solutions, wherein pollutants adhere to soil particles. Soils composed of minerals, organic matter, and microbial communities, exhibit varying capacities for adsorbing different organic chemicals. Understanding the sorption behavior of PCP, phenol, nitrobenzene, and para-chloro aniline on various soil types is crucial for developing efficient remediation techniques. Adsorption, chemical oxidation, precipitation, distillation, solvent extraction, ion exchange, membrane processes, reverse osmosis, etc as a traditional methods have been mostly used for removal of phenols from aqueous solutions. Adsorption as removal of phenols is the most effective and efficient method due to high efficiency, easy handling, high selectivity, lower operating cost, easy regeneration of adsorbent and minimized production of chemical or biological sludge. Adsorption phenomena are affected strongly by the surface morphology as well as chemistry of the adsorbent. So various adsorbents like activated carbon, red mud, rubber seed coat and many more have been used for removal of organic compounds (4-8). Among them, activated carbon is mostly used for removal of organic compounds from industrial effluents due to its high removal efficiency. But due to its high cost, it is not applicable to industrial effluents containing low concentrations of contaminants. Hence, many more cheap materials have been tested for removal of organic compounds from water and wastewater. Recently much attention has been focused on the utilization of soil including flyash, peat, wheat shells, wood sawdust, and activated sludge, zeolite etc. for the removal of organics from water and wastewater. The potentiality of soil as a natural adsorbent has been investigated by various authors (9-12). In this study, soil is used as a low cost adsorbent to remove phenol, 2-Chlorophenol, 3-Chlorophenol and 4-Chlorophenol as a target pollutant from aqueous solution. The aim of this research is to study application of soil for removal of Nitro-benzene, Chlorobenzene, Bromobenzene, Benzene, Phenol, O-chloro phenols, M-Chloro phenol, P-Chloro phenol, Benzaldehyde, Aniline, O-Chloro Aniline, M-Chloro aniline, P-Chloro aniline, Toluene, from aqueous solutions using equilibrium experiments under such as particle size, pH, concentration and temperature.

## **MATERIAL AND METHODS:-**

Soil is obtained from the land of Balaghat in the Lohara district Balaghat of Madhya Pradesh. The sample is then particle sizes using a standard by sieve of lattice size having a geometric mean particle diameter of 75 $\mu$ m. After that, the 75 $\mu$ m fraction of the sample was divided, providing samples for XRF, XRD, FTIR and SEM analysis. The chemical constituents and LOI at 800 °C were determined by the Indian Standard Method<sup>(13)</sup> (Indian Standard Methods of Chemical Analysis of Fireclay and Refractory Materials 1960), the specific gravity, surface area and porosity and are shown in Table-1. The chemical compositions of fractions of soil are also determined by Indian Standard methods<sup>8</sup> and are shown in Table-2. The result indicate that silica and –alumina oxide are the major constituents of soil. The chemical analysis of data indicates that the sample consists of mullite (Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>), quartz (SiO<sub>2</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>), anhydrite (CaSO<sub>4</sub>), hematite (Fe<sub>2</sub>O<sub>3</sub>), and lime (CaO) as the major phase<sup>(14)</sup>.

### **Adsorbate:**

Nitro-benzene, Chlorobenzene, Bromobenzene, Benzene, Phenol, O-chloro phenols, M-Chloro phenol, P-Chloro phenol, Benzaldehyde, Aniline, O-chloro Aniline ,M-chloro aniline, P-chloro aniline, Toluene , (A.R. grade, all supplied by the Loba Company, Mumbai, India) were selected for this study because they represent the most commonly encountered pollutants and are readily analyzed using UV-VIS spectrophotometer (Shimadzu Model UV-1800) at wavelength of Nitro-benzene 252nm, Chlorobenzene 254nm, Bromobenzene 258nm, Benzene 255nm, Phenol 270nm, O-chloro phenols 274nm, M-Chloro phenol 280nm, P-Chloro phenol 280nm , Benzaldehyde 252nm, Aniline 230nm, O-chloro Aniline 230nm ,M-Chloro aniline 280nm, P-Chloro aniline 310nm, Toluene 253nm . Standard solutions of these organic chemicals (500 mg/dm<sup>3</sup>) are prepared by taking appropriate quantities and dissolving them in a minimum volume of acetone. Portions of these solutions are then diluted with distilled water to give the test samples.

### **Equilibrium Studies:**

Batch sorption experiments for determining equilibrium adsorption isotherms were carried out by agitating 1.0 g of the desired grade of soil with 35 cm<sup>3</sup> of a chosen concentration of a given Nitro-benzene, Chlorobenzene, Bromobenzene, Benzene, Phenol, O-chloro phenols, M-Chloro phenol, P-Chloro phenol<sup>(15)</sup>, Benzaldehyde, Aniline, O-nitro Aniline ,M-nitro aniline, P-nitro aniline, Toluene . Solutions were transferred in 100-ml conical glass-stoppered flasks and maintained in a temperature-controlled shaking thermostat for 120 min (the time required for equilibrium to be attained between the adsorbed phenol and that remaining in solution). Experiments were performed using particle sizes ( 75  $\mu$ m), pH values ( 6.5,) and temperatures (30°C,). The pH of the initial solution was adjusted with HCl or NaOH solution as monitored by a pH meter. At equilibrium, samples were taken from the flasks, centrifuged and filtered through a filter paper.

## RESULTS AND DISCUSSION

Equilibrium isotherm equations are used to describe experimental sorption data, with the equation parameters often providing some insight into the sorption mechanism, surface properties as well as the affinity of the sorbent. The Langmuir model is probably the best known and most widely applied sorption isotherm equation. The Langmuir isotherm is valid for monolayer sorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of sorption onto the surface and no transmigration of the sorbate over surface. The equilibrium data for the sorption of Nitro-benzene, Chlorobenzene, Bromobenzene, Benzene, Phenol, O-chloro phenols, M-Chloro phenol, P-Chloro phenol, Benzaldehyde, Aniline, O-nitro Aniline, M-nitro aniline, P-nitro aniline, Toluene (organic chemicals) on soil as measured at above specified size of particle, temperatures (30°C, ) and a pH value of 6.5 were well fitted by the rearranged Langmuir equation. The Langmuir isotherm has been employed successfully in many real sorption processes (16-17) and may be expressed. There are several models available in literature that shows equilibrium relationships between adsorbent and adsorbate.

Where,  $q_e$  is the amount adsorbed at equilibrium (mg g<sup>-1</sup>),  $Q_0$  (mg g<sup>-1</sup>) and  $b$  (L mg<sup>-1</sup>) are the Langmuir constants related to the maximum adsorption and energy of adsorption respectively from linear plots of  $C_e / q_e$  vs.  $C_e$  confirms the validity of the Langmuir model for the process. Organic chemicals at above specified size of particle, temperatures (30°C, ) and a pH value of 6.5 are found to be linear (correlation coefficient ranging from 0.995 to 0.999) indicating the applicability of the Langmuir model (18-20). The statistical significance of the correlation coefficient ( $R^2$ ) for  $C_e / q_e$  vs.  $C_e$  is the criteria by which the fitting of the data to Langmuir isotherm is tested. The parameters  $Q_0$  and  $b$  have been calculated from the slopes and the intercepts of the linear plots corresponding to the figures-1, 2 and 3 according as equation at different conditions shown in Figure-5 and the results are listed in table 3. The best fit of equilibrium data in the Langmuir isotherm predicted the monolayer coverage of Nitro-benzene, Chlorobenzene, Bromobenzene, Benzene, Phenol, O-chloro phenols, M-Chloro phenol, P-Chloro phenol, Benzaldehyde, Aniline, O-chloro Aniline, M-chloro aniline, P-chloro aniline, Toluene onto soil.

$$C_e/q_e = 1/Q_0b + C_e/Q_0 \text{-----} \quad \text{-- (1)}$$

Now the Langmuir Isotherm parameters  $Q_0$  and  $b$  for different conditions are listed in the table-3, can be summarized as follows

The variation among different organic chemicals is as follows:  $Q_0, b \text{ (PCP)} > Q_0, b \text{ (PCA)} > Q_0, b \text{ (PHL)} > Q_0, b \text{ (NBZ)}$ .

**Table – 1:- Proximate Analysis of Fraction of 75 $\mu$ m soil Samples.**

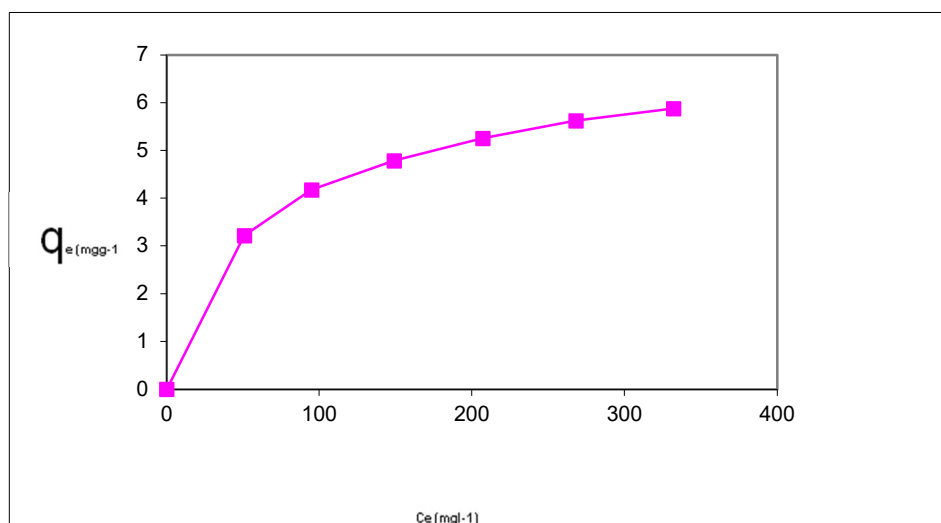
Element as oxide	Weight%
SiO <sub>2</sub>	74.47
Al <sub>2</sub> O <sub>3</sub>	8.97
Fe <sub>2</sub> O <sub>3</sub>	10.84
SO <sub>3</sub>	2.85
CaO	0.37
MgO	0.69
TiO <sub>2</sub>	1.09
LOI(800 <sup>0</sup> C)	4.3
Specific gravity	2.47
Moisture Contents(%)	4.60
Volatile Matter (%)	7.01
Fixed Carbon (%)	4.7
Surface Area	20.040s/g
OPore Volume	4.489e <sup>-</sup>

**Table – 2:- X-ray fluorescence (XRF) analyses for the soil sample**

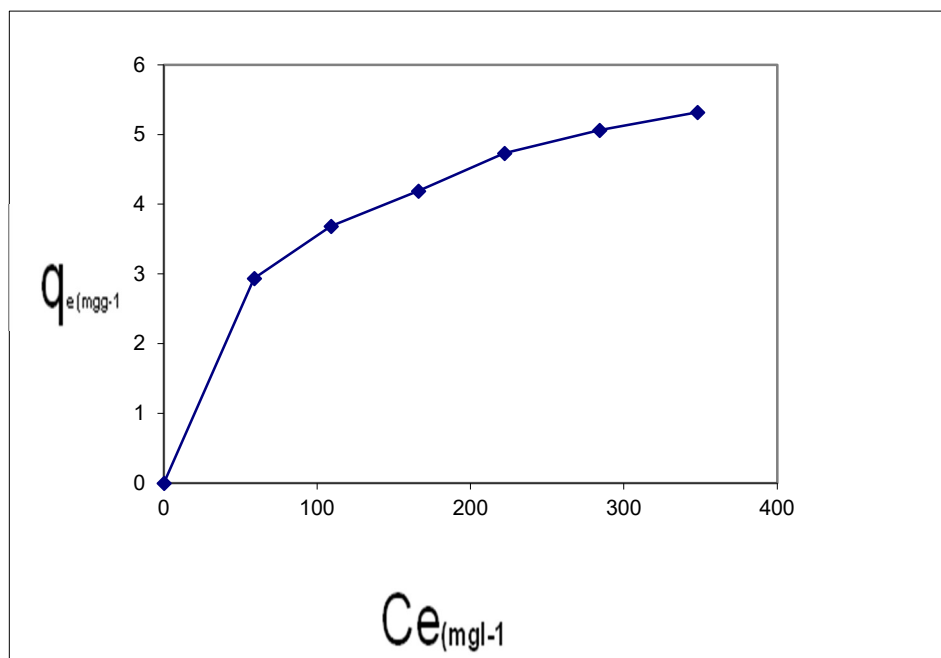
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SO <sub>3</sub>	2.85
CaO	0.37
MgO	0.69
K <sub>2</sub> O	0.60
MnO	0.15
TiO <sub>2</sub>	1.09

**Table 3:-** pseudo- first- order (Lagergren) rate constant of **Adsorbate** on soil

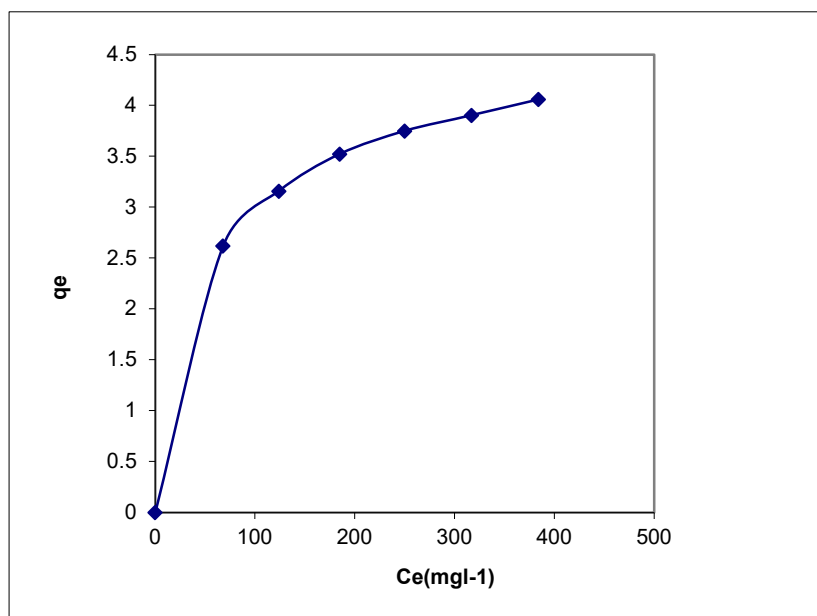
Adsorbate	Condition	Rate constant (min <sup>-1</sup> )		Langmuir Parameters		
		k (min <sup>-1</sup> ) x10 <sup>-2</sup>	R <sup>2</sup>	Qo(mmol g-1) x 10 <sup>-2</sup>	b (L mol-1 ) x 10 <sup>3</sup>	R <sup>2</sup>
Nitrobenzene	Particle Size 0.75(μm)	2.99	0.977	3.57	3.14	0.998
Clorobenzene		2.76	0.960	3.54	4.10	0.996
BromoBenzene		3.22	0.986	4.20	2.66	0.998
Benzene	pH6.5	3.45	0.991	4.901	2.84	0.998
Phenol		3.45	0.986	4.21	4.14	0.999
OCP		3.68	0.991	4.52	2..32	0.993
MCP		3.68	0.991	5.14	2.23	0.986
PCP		5.29	0.992	7.46	2.49	0.999
Benzaldehyde	Concentration 500(mg/L)	4.37	0.965	5.0	2.20	0.997
Aniline		4.60	0.946	5.61	2.573	0.997
OCIA		4.83	0.994	5.5	2.32	0.996
MCIA	Temperature 30C <sup>0</sup> .	5.06	0.994	6.25	2.58	0.998
PCIA		4.14	0.974	5.15	2.10	0.996
Toluene		4.83	0.966	6.802	2.75	0.998



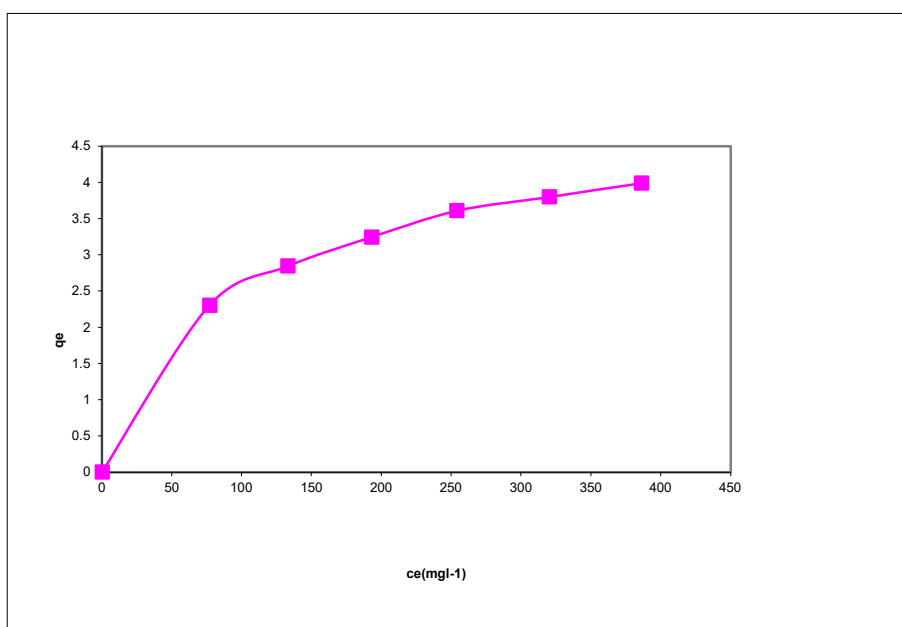
**Figure-1:- Adsorption Isotherm for p -chloro phenol on Soil condition: pH;6.5, Particle size 75 $\mu\text{m}$ ; Temperature 30°C,**



**Figure-2:- Adsorption Isotherm for p -chloro Aniline on soil condition: pH;6.5, Particle size 75 $\mu\text{m}$ ; Temperature 30°C,**

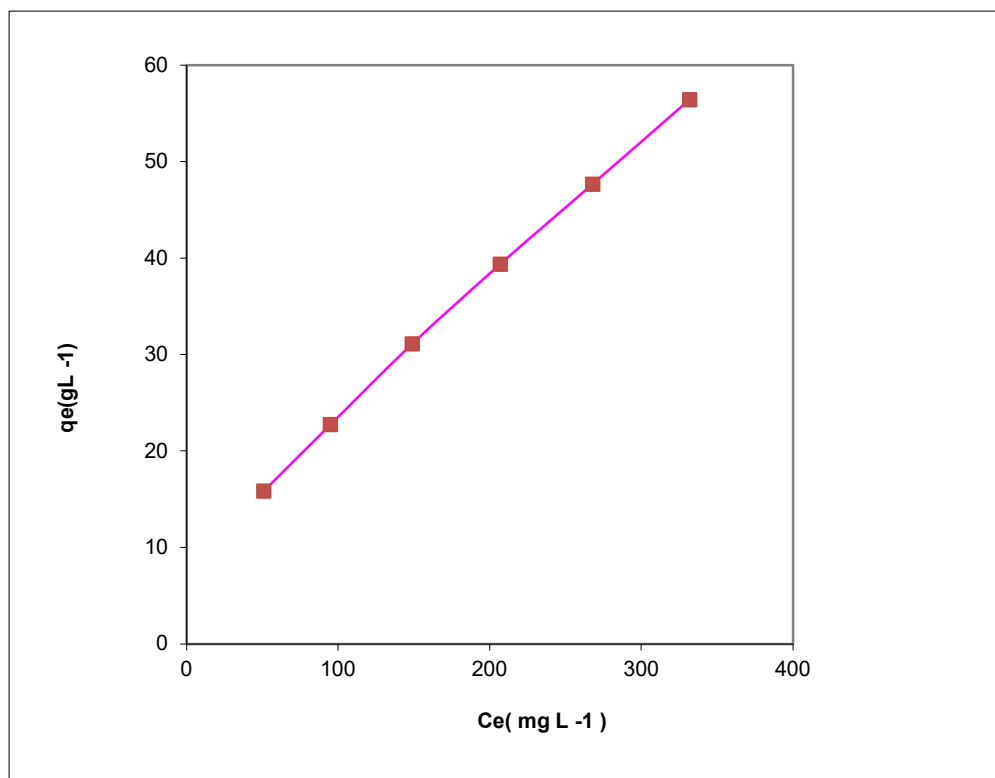


**Figure-3 :-Adsorption Isotherm for p -chloro Phenol on soil condition: pH;6.5, Particle size 75 $\mu$ m; Temperature 30°C,**



**Figure-4:- Adsorption Isotherm for Nitrobenzene on soil condition: pH;6.5, Particle size 75 $\mu$ m; Temperature 30°C,**





**Figure-5 :-Langmuir plot for the adsorption of p - chlorophenol on Soil Particle size 75  $\mu\text{m}$ ; pH 6.5 ;Temperature 30°C**

## CONCLUSIONS

From the above discussion, it is clear that the proposed system employed a simple and economical sorbent. Increasing the temperature and decreasing the particle size and pH increased the sorption capacity as well as the sorption rate constant of soil towards organic chemicals. These data would help in the design of treatment plants for organic chemicals effluents where continuous removal or recovery may be achieved on a large scale.

## Reffrence

1. H., Ma, X., & Luo, J. (2018). Removal of benzene from aqueous solution by natural soil: isotherm, kinetics, and thermodynamics. *Water, Air, & Soil Pollution*, 229(6), 186.
2. Pyrzynska K. Removal of cadmium from wastewaters with low-cost adsorbents. *J. Environ. Chem. Eng.* 2019;7:102795. doi: 10.1016/j.jece.2018.11.040.
3. Zhang H., Hu X., Li T., Zhang Y., Xu H., Sun Y. MIL series of metal organic frameworks (MOFs) as novel adsorbents for heavy metals in water: A review. *J. Hazard. Mater.* 2022;429:128271. doi: 10.1016/j.jhazmat.2022.128271.

4. Al-Musawi T.J., Mengelizadeh N., Al Rawi O. Capacity and Modeling of Acid Blue 113 Dye Adsorption onto Chitosan Magnetized by Fe<sub>2</sub>O<sub>3</sub> Nanoparticles. *J. Polym. Environ.* 2022;30:344–359.
5. Sordon W. Benzie, Vladimir I. Bakhmutov, Janet Blümel. Benzene Adsorbed on Activated Carbon: A Comprehensive Solid-State Nuclear Magnetic Resonance Study of Interactions with the Pore Surface and Molecular Motions. *The Journal of Physical Chemistry C* **2020**, 124 (39) ,
6. Diana Hernández-Monje, Liliana Giraldo, Juan Carlos Moreno-Piraján. Enthalpic and Liquid-Phase Adsorption Study of Toluene–Cyclohexane and Toluene–Hexane Binary Systems on Modified Activated Carbons. *Molecules* **2021**, 26 (10) ,2839
7. J. Tao, P. Huo, Z. Fu, J. Zhang, Z. Yang, D. Zhang, Characterization and phenol adsorption performance of activated carbon prepared from tea residue by NaOH activation, *Environ. Technol.* 40 (2019) 171–181.
8. Abdul Majid Channaa,b,d,\* ,Sıtkı Baytakb, Saima Qayoom Memonc, Muhammad Younis Talpur ,Equilibrium, kinetic and thermodynamic studies of removal of phenol from aqueous solution using surface engineered chemistry *Heliyon* 5 (2019) e01852.
9. Adewuyi, A., Göpfert, A., Adewuyi, O.A., Wolff, T., 2016. Adsorption of 2-chlorophenol onto the surface of underutilized seed of *Adenopus breviflorus*: a potential means of treating waste water. *J. Environ. Chem. Eng.* 4, 664–672.
10. Yang, Q., Gao, M., Zang, W., 2017. Comparative study of 2,4,6-trichlorophenol adsorption by montmorillonites functionalized with surfactants differing in the number of head group and alkyl chain. *Colloid. Surf. Physicochem. Eng. Asp.* 520, 805–816.
11. Afidah, A.R., Garba, Z.N., 2016. Efficient adsorption of 4-Chloroguaiacol from aqueous solution using optimal activated carbon: equilibrium isotherms and kinetics modeling. *J. Assoc. Arab Universities Basic Appl. Sci.* 21, 17–23.
12. Kakavandi, B., Jahangiri-rad, M., Rafiee, M., Esfahani, A.R., Babaei, A.A., 2016. Development of response surface methodology for optimization of phenol and p chlorophenol adsorption on magnetic recoverable carbon. *Microporous Mesoporous Mater.* 231, 192–206.
13. Indian Standard Methods of Chemical Analysis of Fire Clay and Silica Refractory Materials, IS: 1527 (**1960**)).

14. Olaseinde, A., Shongwe, M.B., Babalola, J. and Adisa, A.L. (2020) Instrumental Characterization of Pretoria Clay Soil by XRF, XRD and SEM. *Journal of Minerals and Materials Characterization and Engineering*, 8, 1-8.
15. Adsorption of 2,4-di chlorophenol on paper sludge/wheat husk biochar: process optimization and com parison with biochars prepared from wood chips, sewage sludge and hog fuel/de molition waste. *J. Environ. Chem. Eng.* 5, 2222–2231.
16. F. Mahmoodi, P. Darvishi, B. Vaferi. Prediction of coefficients of the Langmuir adsorption isotherm using various artificial intelligence (AI) techniques. *Journal of the Iranian Chemical Society* **2018**, 15 (12) , 2747-2757.
17. Nayak P., S., Singh B.K. And Nayak S., Equilibrium, Kinetic and Thermodynamic Studies on Phenol Sorption to Clay, *Journal of Environmental Protection Science*, Vol. 1, 83 – 91 (2007).
18. H. Koyuncu, A. RızaKul, Removal of aniline from aqueous solution by activated kaolinite: kinetic, equilibrium and thermodynamic studies, *Colloids Surf A Physicochem Eng Asp* 569 (2019) 59–66.
19. Kalderis, D., Kayan, B., AkaKakavandi, B., Jahangiri-rad, M., Rafiee, M., Esfahani, A.R., Babaei, A.A., 2016. Development of response surface methodology for optimization of phenol and p chlorophenol adsorption on magnetic recoverable carbon. *Microporous Mesoporous Mater.* 231, 192–206. Kalderis, D., Kayan, B., Akay, S., Kulaksız, E., Gözmen, B., 2017.
20. y, S., Kulaksız, E., Gözmen, B., 2017. Adsorption of 2,4-di chlorophenol on paper sludge/wheat husk biochar: process optimization and com parison with biochars prepared from wood chips, sewage sludge and hog fuel/de molition waste. *J. Environ. Chem. Eng.* 5, 2222–2231.