ADSORPTION OF INDOLE AND ORTHO-PHENYLENEDIAMINE ON ACTIVATED CARBON

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CERTIFICATE

This is to certify that the dissertation entitled, **"Adsorption of Indole and Ortho-phenylenediamine on Activated Carbon"** is an authentic record of my own work carried out as requirement for the award of degree of Master of Technology in Chemical Engineering from Thapar University, Patiala, Punjab under the supervision of Dr. J.P. Kushwaha, Assistant Professor, Department of Chemical Engineering and Dr. V.K. Sangal, Assistant Professor, Department of Chemical Engineering.

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ABSTRACT

Indole is a nitrogenous hetrocyclic compound has the bicyclic structure consisting of 6-member benzene ring fused with the 5- member nitrogen containing pyrrole ring has the formula C_8H_7N. It occurs naturally in human feces and has an intense fecal odor. Indole also get released from the meat industry during the fermentation of tryptophan. It is commonly used in industries such as agrochemicals, pesticides, cosmetics. Ortho-phenylenediamine (OPD) is an endocrine disrupting chemicals, and are widely distributed in environment. OPD is an aromatic amine, used as a component of polymers, pesticides, drugs, and dyeing intermediate compounds.

In the present study adsorptive removal of Indole & OPD on activated carbon from aqueous solution have been investigated. For this, dosage study was carried out by varying the adsorbent dosages in the range of 0.5-5 g/100 ml at natural pH = 5.5 at 303 K. The adsorption of Indole & OPD was studied over a initial pH range of 2-9 at 303 K with optimum adsorbent dosage of 3 g/100 ml. Optimum conditions for the adsorptive treatment of Indole and OPD by activated carbon were found to be $pH_{i\text{-}opt}$ = 5.5, adsorbent dose of $m_{ad\text{-}opt}$=30 g/l and contact time = 4 hour, and at this optimum condition Indole and OPD removal were found up to 92.35% and 89.4%, respectively.

To explore the effect of time on the adsorption process, kinetic study were performed at various $\mathbf{C_o}$ values (25-50 mg/l) at optimum dosage of adsorbent $m_{ad-opt} = 30\ g/l$ and optimum pH ($pH_{i-opt} = 5.5$), and experimental data were tested for their validation with pseudo-first-order and pseudo-second-order model with non-linear regression. Isothermal experiments were performed at 303 K, 313 K and 323 K with $\mathbf{C_o}$ values of 10-100 ppm both for Indole and OPD with pH_{i-opt} and m_{ad-opt} of ACC. Various isotherms such as Freundlich, Langmuir and Redlich-Peterson (R-P) and Temkin were used to represent the adsorption equilibrium data.

It was found the pseudo-second-order kinetic model best fitted the experimental kinetic data, whereas, isothermal study showed that the process is endothermic in nature, and Temkin isotherm best fitted the experimental equilibrium data onto ACC at all temperatures.

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ABBREVIATIONS

ACC	Activated Carbon
MPSD	Marquardt's Percent Standard Deviation
GAC	Granular activated carbon
OPD	Ortho-phenylenediamine
R-P	Redlich-Peterson

CHAPTER - 1

INTRODUCTION

1.1 Background

. Rivers, lakes and other water bodies are being contaminated due to effluent discharge from industrial activities. Aniline compounds such as OPD often appear in industrial wastewaters, where they have a high potential toxicity to humans and other organisms they are regarded as priority pollutants by the US Environmental Protection Agency and the Occupational Safety and Health Agency (Sun et al., 1998). In the present study removal of Indole and OPD by adsorption method onto commercial activated carbon. It has been estimated that about 0.5 million tons of wastewater containing OPD is produced in China each year, Similarly the removal of aqueous orthophenylene diamine (OPD) has been an issue in the wastewater treatment because of its non-biodegradable nature. Indole is a nitrogenous hetrocyclic compound occurring from some flower oils, such as jasmine and orange blossom, in coal tar, and in fecal matter (Srivastava et al., 2014). Indole are toxic organic pollutants in the wastewaters discharged from the coking plants, pharmaceutical factories. The mixture of Indole and OPD is appear in sewage wastewater. They have been listed as priority pollutants by US Environmental Protection Agency.

1.2 PROPERTIES, USES AND TOXIC EFFECTS OF INDOLE & OPD

Indole is a nitrogenous hetrocyclic compound has the bicyclic structure consisting of 6-member benzene ring fused with the 5- member nitrogen containing pyrrole ring. The main function of indole as a popular component of fragrances indicator of some diseases and the signal molecule in plant, animal and microorganism respectively. Indole is widely distributed in the natural environment and can be produced by a variety of bacteria. Indole is a solid at room temperature. It also occurs in the coal tar. It occurs naturally in human feces and has an intense fecal odor. At very low concentrations, however, it has a flowery smell, and is a constituent of many flower scents (such as orange blossoms) and perfumes (Srivastava et al., 2014). Indole with chlorine disinfection containing wastewater leads to formation of carcinogenic chlorinated aromatic products. Indole also get released from the meat industry during the fermentation of tryptophan. Indole along with pyridine derivatives during coal processing such as gasification, carbonization, and liquification, are produced highly toxic compounds. It is soluble in hot water.

Unlike most amines, indole is not basic. The bonding situation is completely analogous to that in the pyrrole. Various adsorption studies have been carried out adsorption of indole from aqueous solution onto GAC effect of initial pH_i from 2-11. The pH of indole in aqueous solution alone is near about 5.7. It is commonly used in industries such as agrochemicals, pesticides, cosmetics, pharmaceuticals, and dyestuffs for different applications. (Mitome et al., 2013). More details of properties of indole are given in Table 1.1.

Ortho-phenylenediamine (OPD) is an Endocrine disrupting chemicals are widely distributed in environment. It is unstable in the solid state and even so as liquid and in the solution. Brown coloured products are formed particularly in the light or the presence of oxygen. In aqueous solution with increase in pH value the oxidizability of ortho-phenylenediamine increases as result of deprotonation of amino acids. Endocrine disrupting chemicals are now regarded as the most dangerous pollutants by environmental protection agencies around the world. OPD is an aromatic amine, used as a component of polymers, pesticides, drugs, and dyeing intermediate compounds. It is Store in tablets at 2-8 °C. Protect from heat, light and moisture. Solutions should be freshly prepared, Allow to reach room temperature before use. It has sparingly soluble in cold water and high solubility in hot water. OPD aqueous solution with a pH of 9.0 (range 8.5 - 9.5). The background absorbance of this solution cannot be more than 0.04. Adjust the pH to 5.0, if necessary Alternatively, use phosphate citrate buffer capsules containing sodium perborate. If phosphate citrate buffer capsules is used then, it is not necessary to use the H_2O_2 to as the substrate solution since sodium perborate is treated as the substitute for the hydrogen peroxide Despite its industrial applications, the hazardous nature of OPD to liver, kidney, nervous, skin and hormone systems demands the complete removal of OPD (Kodak et al., 1970) from the environment Ortho-phenylenediamine condenses with aldehydes and ketones to give rise to a variety of useful products. This chemical intermediate is used in the synthesis of insecticides, dyestuff, fungicides, corrosion inhibitors and pigments (Wang et al., 2003). More details of properties of OPD are given in Table 1.2.

Table 1.1 Properties of Indole

Parameters	**Indole**
Synonyms	1-H-Benzo[b]pyrrole, Benzazole
Physical state	Solid
Molecular formula	C_8H_7N
Molecular weight	117.15 g/mole
Colour	White crystals
Melting point	$51 - 54℃$
Boiling point	$253 - 254℃$
Solubility	Soluble in hot water
Density	1.17 g/Cm^3

Source: *http://pubchem.ncbi.nlm.nih.gov*

Table 1.2 Properties of Ortho-phenylenediamine

Parameters	**Ortho-phenylenediamine**
Synonyms	1,2-Diaminobenzene, 1,2-Phenylenediamine
Physical state	Solid
Molecular formula	$C_6\ H_8\ N_2$
Molecular weight	108.14 g/mol
Colour	Reddish brown
Melting point	$102 - 104℃$
Boiling point	252℃
Density	$1.03g/Cm^3$
Solubility	Soluble in hot water

Source: *http://pubchem.ncbi.nlm.nih.gov*

1.3 VARIOUS METHODS FOR REMOVAL OF INDOLE & ORTHO-PHENYLENEDIAMINE

For the treatment of Indole and OPD containing wastewater, various physical-chemical and biological methods are reported. In physical-chemical methods, adsorption, coagulation membrane separation and biological methods are used.

Table 1.3 Comparative study of the different process for removal

Process	Definition	Advantages	Drawbacks	References
Adsorption	Adsorption may be defined as selective concentration or retention of one or more components of a mixture on a solid surface. The solid that's adsorbs a component is called adsorbent & the component adsorbed is called adsorbate	Potential for significant heavy metals removal	Required prediction knowledge of the process	Wang et al., 2003
Coagulation	Coagulation is the process of decreasing or neutralizing the negative charge on suspended particles or zeta potential. This allows the force (vander Waals) of attraction to encourage initial aggregation of colloidal and fine suspended	High efficiency	Proess is not effective in removing low molecular disinfection by products	Koohestanian et al., 2008

	materials to form microflock			
Membrane separation	Membrane is a thin barrier, placed between two phases or medium which allows one or more constituents to selectively pass from one medium to another medium in the presence of an appropriate driving force while retaining the rest.	Clean Technology, Energy saving	Fouling, Low selectivity	Chakraborty et al., 2014
Biological method	This method consist of ensuring contact between the water to be treated and bacteria, which feed on the organic materials in the wastewater, thereby reducing its Biological Oxygen Demand (BOD) content.	Biological methods can remove 30-50% dissolved organic matter and avoid using chemicals.	Complex treatment, Very expensive	Sekaran et al., 2010

Adsorption is known to be simplest and cheap method for the treatment of organic compounds in waste water. Adsorption of carbon is an extremely versatile technology. It has proved to be the least expensive treatment option from many water treatment applications. Adsorption is particularly effective in treating low concentration waste streams. Its ability to remove a wide variety of toxic organic compounds to non-detectable levels (99.99%) is the one of the major attributes of activated carbon treatment, its suitability on a specific application will normally depend on costs as they relate to the amount of carbon consumed. From all of the technologies, adsorption is the most common for removing pollutants from wastewater with high efficiency and simple operating conditions.

1.4 ACTIVATED CARBON AS AN ADSORBENT

Adsorption on to activated carbon is one of the most important methods for removal of dissolved organic matter. It is microcrystalline non-graphitic form of carbon. It is also used in decolourising solutions of sugar, water purification, textile, clothing, drugs. Activated carbon is also used in filter tobacco smoke, decolourising sugar solution, gas purification, decaffeination, water purification, medicine, gold purification, sewage treatment, air filters in gas mask. Adsorption capacity of an activated carbon depends on the characteristics of activated carbons like surface area, pore size distributions, surface chemistry, structural strength and stability, ash content. Proximate analysis showed the presence of moisture content, volatile matter, ash and fixed carbon for ACC. Adsorption capacity also depends on adsorbate characteristics like molecular weight, polarity, molecular size, and functional groups. The adsorption capacity can be affected by adsorptive concentration, pH and presence of other possible adsorptive contaminants. The three important parameter attributes of an adsorbent make it suitable and effective for the separation of a mixture. (1) selectivity (2) reversibility of adsorption, (3) adsorption capacity. Selectivity is the difference in the rate of diffusion and adsorption. The adsporption capacity depends only the affinity of adsorption and specific surface area, with the repeated use and regeneration its adsorption capacity decreases. Reversibility of adsorption is necessary if the selectively adsorbed substance is to be recovered or the adsorbent is to be reused

or regenerated. Commercial grade of activated carbon surface area range between 300 and 2000 m^2/g (Baker et al., 1997). Some have high surface areas as 5000 m^2/g. Size compared to powdered activated carbon & Granular activated carbon has a relatively larger particle consequently, presents a smaller external surface of powdered activated carbon. The adsorbate Diffusion is an important factor. These carbons are suitable for absorption of gases and vapors, because they diffuse rapidly. For water treatment, deodorization and separation of components of flow system Granulated carbons are used.

Scanning electron microscope (SEM) was used to examine the morphologies of GAC and found to have an heterogeneous surface morphology (Mishra et al., 2006). Activated Carbons are a very versatile group of adsorbents, with capability for selectively adsorbing thousands of organic, and certain in- organic, material. After indole and opd adsorption surface of GAC to be smooth as compared to that before adsorption.

Fig. 1.1: Granular activated carbon

Table 2.1. Adsorption capacities of various adsorbents.

Adsorbent	Adsorption capacity (mg/g)
Commercial activated carbon	980.3
Activated carbon produced from New Zealand coal	588
Filtrasorb 400	476
Activated carbon	400
Activated carbon produced from Venezuelan bituminous coal	380
Peat	324
Coal	323.68
Filtrasorb 400	299
Norit	276
Picacarb	246
Filtrasorb 300	240
Activated carbon	238
Coal	230
Commercial activated carbon	200
Bituminous coal	176
Charcoal	62.7
Activated carbon	9.81
BFA	6.46
Red mud	2.49
Spent tea leaves	300.5
Zeolite	10.82
Papaya seeds	555.55
Pineapple stem	119.05

CHAPTER- 2

ADSORPTION THEORY

2.1 GENERAL

Adsorption occurs due to the imbalance of forces at the surface of a material. This lead to formation of bonds (Covalent, ionic, Vander Waals, Hydrogen bonds etc.) between the surface molecules (adsorbents) and the molecules in the fluid phase (adsorbate). One way of classification of adsorption is based on how strong the interaction between the adsorbent and adsorbate is. If the interaction is rather weak, then the type of adsorption is called physical adsorption (also called physisorption). The physical adsorption forces are vander waal's force (or dispersion force), hydrogen bonding and electrostatic force. On the other hand, if the interaction is very strong between adsorbate and adsorbent, a chemical bond may be formed between them. This is called chemical adsorption (also called chemisorption). The heat of chemisorptions is considerably larger than that of physical adsorption. Physical adsorption is reversible, but chemisorption is irreversible in nature. Other criteria, which are helpful in distinguish between these two type of adsorption, are electrical conductivity and FTIR spectroscopy. Under proper conditions, physical adsorption can forming multiple layers result in adsorbed molecules. Chemisorption, is therefore a single-layer process in the typical case, only proceeds as long as the adsorptive can make direct contact with the surface. As the temperature is raised and is generally very small above the critical temperature of the adsorbed component the amount of physical adsorption decreases. The energy of activation for physical adsorption is not more than 1 kcal/g mol. Chemisorption however, is highly selective and occurs only between certain adsorptive and adsorbent species and only if the chemically active surface is cleaned of previously adsorbed molecules. If the adsorption has higher activation energy or the heat of adsorption is very large than the latent heat of evaporation, then the adsorption is clearly chemisorption. If the heat of adsorption is about 40-50 KJ/mol. In this case, it is very difficult to determine whether the adsorption is chemical or physical. The chemisorptions name for describing this second type of combination of gas molecules with solid surfaces, because the energy possessed by chemisorbed molecules can be substantially different from that of molecules alone, and also high heat of adsorption.

2.2 PROCESS OF ADSORPTION

The adsorption rate is predicted by the rate of transfer of the adsorbate from the bulk to the surface of adsorbent. The following steps: film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, can control transport of components from the solution phase into the pores of the adsorbent particles. It is necessary to calculate the slowest step involved among these steps to identify the controlling step during the adsorption process (Srivastava et al., 2014). To understand the transport of adsorbate from the exterior surfaces to the pores of adsorbent is better understand by intraparticle diffusion model. The steps for the external mass transfer control for the adsorption process are: poor mixing, small particle sizes of adsorbent and higher affinity of adsorbate for adsorbent, dilute concentration of adsorbate.

As the adsorbate concentration increases, adsorption occurs in three stages. First, a single layer of molecules builds up over the surface of the solid. This monolayer may be chemisorbed and is associated with a change in free energy that is a characteristic of the forces that hold it. Second, as the fluid concentration is further increased, second, third etc., (layer form by physical adsorption). The numbers of layers will be formed this is decided by the size of the pores. Finally, for adsorption from the gas phase, capillary condensation may occur in which capillaries become filled with condensed adsorbate, when its partial pressure reaches a critical value relative to the size of the pore.

The parameters that affect the adsorption process are initial pH (pH_i), adsorbent dose (m), contact time (t), initial concentration (C_o) and temperature (T).

2.3 ADSORPTION KINETICS

Pseudo-first-order model: Pseudo-first order kinetic model was first applied by Lagergren 1898. Assuming a non-dissociating molecular adsorption of adsorbate molecules on adsorbent, the sorption phenomenon can be described as the diffusion controlled process. The adsorption of adsorbate onto adsorbent is considered as a reversible process.

Using first order kinetics it can be shown that with no adsorbate initially present on the adsorbent, the uptake of the adsorbate by the adsorbent at any instant t is given as (Srivastava et al., 2014)

$$q_t = q_e [\ 1- \exp (- k_f t\ )] \quad (2.1)$$

where, q_e is the amount of the adsorbate adsorbed on the adsorbent under equilibrium condition, k_f is the pseudo-first order rate constant, t is the time, q_t is the amount of the adsorbate adsorbed on the adsorbent in time t.

Pseudo-second-order model: This is represented as (Ho and McKay, 1999):

$$q_t = \frac{tk_S q_e^2}{1 + tk_S q_e} \quad (2.2)$$

The initial sorption rate, h (mg/g min), at t –> 0 is defined as

$$h = k_S q_e^2 \quad (2.3)$$

Where k_s (g $mg^{-1}min^{-1}$) is the rate constant for pseudo second order adsorption

2.4 Adsorption Isotherm

Chemical as well as physical adsorption may govern the final isotherm step. An increase in temperature by overcoming the activation energy barrier the mobility of adsorbate into the adsorbent increases. Therefore it is important to establish the most appropriate correlation for the equilibrium isotherm curves have discussed the theory associated with the most commonly used isotherm models (Abdullah et al., 2004). Various isotherms namely Freundlich, Langmuir, Redlich-Peterson (R-P), Temkin and are widely used Table 3.1.

The R-P isotherm incorporates three parameters and can be applied either in homogenous or heterogeneous systems. The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface, whereas in the Langmuir theory the basic assumption is that the sorption takes place at specific homogeneous

sites within the adsorbent. The Temkin isotherm can be applied for heterogenous surface having maximum adsorbate adsorbent binding energy.

2.4.1 Langmuir Isotherm

The Langmuir isotherm (1918) is based on the simplest model of physical adsorption which assumptions that (Zhang et al., 2013)

(i) The molecules are adsorbed at discrete active sites on the surface.

(ii) Each active sites adsorbed one molecule only (monolayer adsorption).

(iii) There is no interaction among the adsorbed molecules.

(iv) The adsorbing surface is energetically uniform.

2.4.2 Freundlich Isotherm

Freundlich (1906) give an empirical equation which representing the isothermal variation of adsorption of a quantity adsorbate adsorbed by unit mass of solid adsorbent.

This equation is known as Freundlich Adsorption Isotherm (Hassan et al., 2008). The following assumptions are used in this method.

(i) This isotherm represents adsorption on a surface that is energetically non-uniform

(ii) The heat of adsorption at different sites is not the same.

2.4.3 Redlich-Peterson Isotherm

Jossens and co-workers modified the three parameter isotherm first proposed by Redlich and Peterson (1959) to incorporate features of both the Langmuir and Freundlich equations. At low concentration the Redlich-Peterson isotherm approximates to henry's lawand at high concentration its behavior approaches that of the Freundlich isotherm.

2.4.4 Temkin Isotherm

The Temkin isotherm model assumes that the adsorption energy decreases linearly with the surface coverage due to adsorbate interactions. It is not suitable for the prediction of liquid phase adsorption, only suitable for the prediction of gas phase equilibria.

Table 3.1. Various isotherm equations for the adsorption process

Isotherm	Equation	Reference
Freundlich	$q_e = K_F C_e^{1/n}$	(Freundlich, 1906)
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	(Langmuir, 1918)
R-P	$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$	(Redlich and Peterson, 1959)
Temkin	$q_e = B_T \ln (K_T C_e)$	(Temkin and Pyzhev, 1940)

K_R: R–P isotherm constant (l/mg), a_R: R–P isotherm constant (l/mg), β: Exponent which lies between 0 and 1, C_e: Equilibrium liquid phase concentration (mg/l), K_F: Freundlich constant (l/mg), 1/n: Heterogeneity factor, K_L: Langmuir adsorption constant (l/mg), q_m: adsorption capacity (mg/g). K_T =Temkin isotherm equilibrium binding constant (L/mg), B_T = Temkin isotherm constant.

In this chapter, various adsorption studies for Indole and Orthophenylene diamine on varieties of adsorbent available in open literature, have been discussed.

Adsorption Studies for Indole:

Abdullah et al., (2004) studied the adsorption of indole and 2-methylindole on ligand-exchange matrix. The adsorbent such as cobalt (II)-CDAE-sporopollenin that was modified with a carboxylated diaminoethyl cobalt complex used as a ligand exchanger material. Adsorption showed that concentration range was increased with increasing external ligand concentration capacities for indoles on cobalt (II)-CDAE-sporopollenin. The adsorption equilibrium were well represented by Langmuir & Freundlich isotherm. However, the Langmuir model in the case of 2-methylindole the experimental data did not fit, especially when the high ligand concentration range was used this was probably due to the nonspecific interactions between the methyl group present and ligand exchange matrix. The methyl group was played the predominant role in its hydrophobic interaction with the ligand exchange matrix.

Mishra et al. (2008) studied the Indole sorption from aqueous solution by rice husk ash (RHA) and granular activated carbon (GAC). The adsorption of Indole onto (GAC) and (BFA) were the function of such as adsorbent dose (m), initial pH, contact time (t), initial concentration (C_0) & temperature. The indole removal was increases with increasing temperature. The thermodynamic calculations indicate that the adsorption process was endothermic in nature.The equilibrium data were well represented by Toth and Redlich–Peterson isotherm equations. The uptake of Indole on RHA and GAC was found to be in the order of GAC> RHA. For the removal of heavy metals from wastewaters RHA was found be a very effective adsorbent. The pore volume and the pore size were calculated by Brunauer-Joyner-Halenda (BJH) method. The maximum indole adsorption was occur at the pH 6.2 by RHA 90% at time 5 hour and a pH 6.5 by GAC 91% at time 6 hour both at temp 303K.

Zhang et al. (2012) studied the mechanistic aspects of nitrogen-heterocyclic compound such as pyridine, indole, and quinoline adsorption on bamboo charcoal. Bamboo charcoal (BC) was a porous carbonaceous materials. The main objective of bamboo charcoal was (1) To characterize surface properties of BC and modified BC and the porous structure; (2) To evaluate nitrogen-heterocyclic compounds (NHC) adsorption performance on BC; (3) To measure the relative contribution of each interaction to develop an adsorbent–adsorbate derived model. The nonlinear isotherm models, Freundlich model, Langmuir model was commonly used for fitting the adsorption isotherms of organic compounds, including BC. The BC mechanism of NHC adsorption were mainly regulated in the sequence of surface area > hydrophobic interaction > electrostatic interaction > $\pi - \pi$ electron-donor-acceptor EDA interaction. $By\ HNO_3$ & NaOH treatment as well as by microwave (MW) radiation different structures and surface properties of BC was created. The maximum adsorption capacities for pyridine, indole and quinoline were reach 42.92, 93.24, and 91.74 mg/g respectively, at an initial concentration of 200 mg/l.

Mitome et al. (2013) studied the adsorption of indole on KOH-activated mesoporous carbon. The adsorbent such as mesoporous carbons were synthesized by a soft-templating Method. To improve their porosity the mesoporous carbon were activated by using KOH. After KOH activation the surface area and micropore volume were increased for the mesoporous carbons. Gases such as carbon dioxide and carbon monoxide were generated during KOH activation. The adsorption equilibrium was well represented by Langmuir isotherm model. In the buffer solution KOH activated carbon was showed high adsorption rate because of the 3D-interconnected mesopore structure and the large mesopore volume. For developing a high performance adsorbent for indole was the main suggest that the precise mesopore size tuning as well as the increase in the micropore surface area was required.

Srivastava et al. (2014) investigated the comparative studies were performed for the adsorptive removal of Indole by granular activated carbon (GAC) and bagasse fly ash (BFA) in the batch system. The adsorption of Indole on GAC and BFA were the function of contact time, pH, adsorbent dose, and temperature. The equilibrium adsorption data was well represented by Redlich-Peterson isotherm. The adsorption kinetics of Indole was followed pseudo-second order model. The adsorbent dose and equilibrium time for BFA were found to 7 g/l and 3 hour and for GAC were 20 g/l and 7 hour. The adsorption of Indole was found to predominately occur in the mesoporous of the adsorbent. It was concluded that GAC exhibited lower adsorption capacity

than BFA for adsorptive removal of Indole. In thermal desorption cycle were showed that the GAC can be used for more than five cycles whereas it was better to use fresh BFA during the adsorption process because adsorption capacity decreases sharply during repeated desorption-adsorption cycle. If BFA was used in single stage adsorption then it showed higher adsorption capacity. Under optimum condition were found to be at initial pH = 5.7, Indole removal were found to be 95% for both GAC and BFA. Table 3.2 shows the comparative assessment of various adsorption studies with Indole & OPD.

Adsorption Studies for OPD:

Wang et al. (2003) studied the effect of ortho-phenylenediamine on Cu adsorption and desorption in red soil and its uptake by paddy rice. The adsorbent such as paddy rice seeds were first immersed in cold water for 24 hour, and then soaked in warm water of $52\,℃$ for 10 min and $40-45\,℃$ for 5 min. The effect of pH on Cu adsorption in red soil was studied and the results that the quantity of Cu adsorbed increased with increasing pH at pH > 6.0. An Cu complex was formed only when Cu reacted with OPD and solution have pH greater than 5. This means that no Cu complex was formed in the soil solution at pH < 5.0., with increasing pH the percentage of Cu desorption from red soil was decreased. The equilibrium isotherm data was well represented by the Freundlich isotherm equations. The wet weight of paddy rice was obviously decreased with increasing Cu concentration. When the external Cu concentration in the red soil was 50 mg/kg, the biomass of paddy rice were increased by 40.7%, 98%, and 114.7% in the presence of 1.0, 2.0, and 4.0 mmol/kg OPD, respectively.

Lataye et al. (2008) studied the adsorption of orthophenylene diamine onto bagasse fly ash from aqueous solution. The adsorption of OPD onto BFA were the function of such as contact time (t), pH, adsorbent dose (m), initial concentration (C_0), temperature. The adsorption of OPD on bagasse fly ash was follows second order kinetics & the equilibrium adsorption rate was increases with increasing initial concentration. The equilibrium isotherm data were well represented by the Langmuir and Redlich–Peterson isotherm equations. The total surface area of the carbons was calculated by the Brunauer-Emmett-Teller (BET) method. The increase in the equilibrium uptake of OPD on BFA the isosteric heat of adsorption was decrease. The maximum adsorption capacity was 91% at pH 6.45, 303K temperature for 6 hour. Adsorption was found to be very fast in the initial 5 min of contact between BFA.

Peldszus et al. (2008) studied the adsorption of selected pharmaceuticals and an endocrine disrupting compound by granular activated carbon. The main objective was to investigate preloading effects by natural organic matter (NOM) on adsorption capacity and concentration relevant for drinking water treatment, & kinetics under condition. In lower adsorption capacity the granular activated carbon (GAC) with the wider pore size distribution was greater resulting NOM loading. The equilibrium isotherm data was well represented by the Freundlich isotherm equations. In this method virgin and preloaded carbon was used. The preloaded carbon (various time up to 16 weeks) were freeze dried for at least 48 h, and then sieved to obtain 30 × 40 U.S. mesh fraction used for the isotherm test. The increase in the preloading time short fixed bed SFB depth was increases. For the nonylphenol (EDC) mass transport was controlled by both the film and surface diffusion. During the first five weeks and then slowly thereafter the film diffusion coefficients for all three compounds on both carbons were rapidly decreased. To control mass transport the Biot number was greater than 50-100 for the pore diffusion. Comparison of (scanning electron microscope) SEM between virgin and preloaded carbon, the preloading were effects both the adsorption capacities and mass transfer and for the very low concentration of contaminants.

Sekaran et al. (2010) studied the biodegradation of endocrine disrupting chemical-orthophenylene diamine using intracellular enzymes from citrobacter freundii. There was no report about enzymatic degradation of OPD there is only studies on photocatalytic and biological degradation of OPD. Zn^{+2} ion was used to increase the degradation efficiency of mixed intracellular enzyme. The degradation was best represented by pseudo-second order model (0.987) as observed greater R^2 values than the first order rate kinetic model (0.960). The peak at λ420 nm was corresponds to OPD. The peak λ420 nm was disappeared & new peak at λ290 nm was appeared after the degradation. Maximum degradation of OPD by MIE were concentration of OPD, 5 mg in 100 ml; reaction; Time, 2 hour; temperature, 30 ºC; pH, 7.0; and enzyme concentration, 0.2% (w/v). The degrading efficiency using MIE was enhanced by Zn^{+2} to about 95.87%.

Table 3.2 Various adsorption studies of Indole and OPD

Adsorbate	Adsorbent	Isotherm	Model	Results/Conclusion	Reference
Indole	Granular activated carbon & bagasse fly ash	Redlich-Peterson	Pseudo-second-order	Adsorption of indole was found to more occur in the mesopores. GAC exhibited lower adsorptive capacity than BFA for adsorptive removal of indole. GAC was used for more than five cycles as shown by the Thermal desorption-adsorption cycle.	Srivastava et al., 2014
Indole	Activated mesoporous carbon	Langmuir	_	By using KOH activation the micropore volume and surface area of the mesoporous carbons were significantly increased. The KOH-activated carbons was showed high adsorption capacity for indole	Mitome et al., 2013
Indole & 2-methylindole	Ligand-exchange matrix	Langmuir and Freundlich	_	In the case of 2-methylindole, the Langmuir model, experimental data did not fit especially when a high ligand concentration range is used; this is due to the nonspecific interactions between the methyl group present & the ligand exchange matrix.	Abdullah et al., 2004
Indole, Pyridine & Quinoline	Bamboo charcoal	Langmuir and Freundlich	_	Different structures and surface properties of bamboo charcoal are created by $HNO_3$and $NaoH$ treatment as well as by microwave (MW) radiation.	Zhang et al., 2012
Indole	Rice husk ash (RHA) & Granular activated	Redlich – Peterson & Toth	Pseudo-second - order	The adsorption of Indole on RHA and GAC was found to be in the order of GAC>RHA.	Mishra et al., 2008

	carbon (GAC)				
Orthophenylene diamine	Bagasse fly ash	Langmuir and Redlich – Peterson	Pseudo-second - order	Adsorption is found to be very fast of OPD removal was achieved in the initial 5 min of contact between BFA. Adsorption of OPD from an aqueous solution onto BFA was exothermic process, whereas the diffusion of the OPD molecules into the pores of the BFA was endothermic process.	Lataye et al., 2008
Endocrine disrupting compound	Granular activated carbon	Freundlich	_	Both on adsorption capacities & mass transfer the preloading was effect. For very low concentration the film diffusion was the primary controlling mass transfer mechanism. For pore diffusion was predominantly control mass transport when the Biot number should be greater than 50-100.	Peldszus et al., 2008
Orthophenylene diamine	Paddy rice	Freundlich	-	Cu adsorption was directly affected, by OPD which suggests that the presence of OPD enhanced Cu adsorption in soil. When solution pH was greater than 5, Cu reacted with OPD & formed a Cu complex only. In the soil solution at pH < 5.0, this means no Cu complex was formed.	Wang et al., 2003
Mixed intracellular enzyme	Orthophenylene diamine	-	Pseudo-second - order	Maximum removal of 93% in the degradation rate of OPD by MIE was achieved. Degrading efficiency was enhanced by Zn^{+2} using MIE to about 95.87%. Pyruvic acid was the final degraded product of OPD by MIE.	Sekaran et al., 2010

1.5 OBJECTIVES

The following aims and objectives have been set for the present work.

1. To study the effect of the initial pH, adsorbent dose, contact time, initial concentration, and temperatute on the removal of Indole and OPD from the aqueous solution in the batch study.

2. To perform the equilibrium adsorption and the kinetics of adsorption of Indole and OPD onto ACC and to analyze the experimental data using various kinetic and isotherm models.

CHAPTER-4

MATERIAL AND METHODS

4.1 Wastewater

Aqueous solution of Indole and orthophenylene diamine (OPD) was taken as wastewater to make the solution of different concentrations. Initially 50 mg/l of stock solution was prepared which was used in working solution of desired concentration as per the experiment requirement. The experimental details of the study have been presented in this chapter. These details include preparation of adsorbent, batch study for adsorption

4.2 Adsorbent and its BET surface area

Coconut-based granular ACC was supplied by Pneumatic Engineers Spares & Service, New Delhi, India. It was used as procured. Pores sizes are classified in accordance with the classification of International Union of Pure and Applied Chemistry (IUPAC) [IUPAC 1982], that is micro-pores (diameter (d) < 20 Å), meso-pores (20 Å <d <500 Å) and micro-pores (d > 500 Å). For larger sizes of liquid molecules, the adsorbents for liquid phase adsorbates should have predominantly meso-pores in the structure. The BET surface area of ACC was found to be 222.33 m^2/g, whereas the BET average pore diameter of ACC is found to be 26.56 Å (Singh et al., 2014).

4.3 Analytical Methods

To determine the concentration of Indole and orthophenylene diamine (OPD) were analysed by finding out the absorbance characteristics wavelength using UV/VIS spectrophotometer (Perkin Elmer, Schimadzu, Japan). The wavelength for Indole and OPD solution corresponding to maximum absorbance ((λ_{max}) was found to be at 270 nm and 285 nm. The calibration curve was plotted (Fig. 4.1 and 4.2) between the absorbance and concentration of Indole and OPD solution.

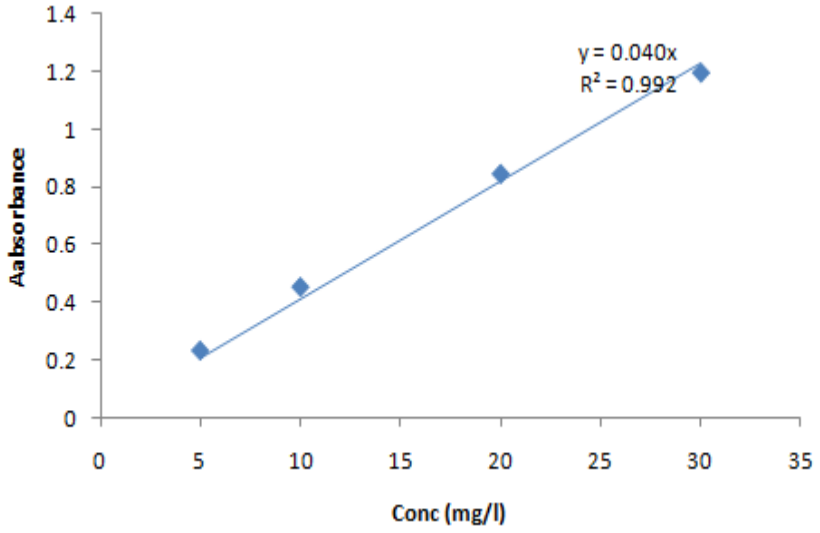

Fig 4.1. Calibration curve for Indole

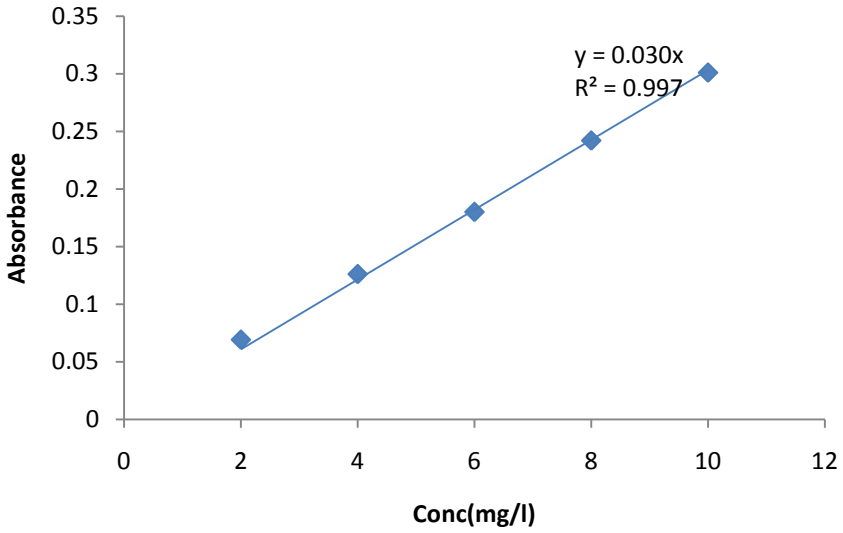

Fig 4.2. Calibration curve for OPD

4.4 Experimental programme

For each experiment, 100 ml of known indole and OPD mixture solution was taken in 100 ml stoppered conical flask with pre decided amount of adsorbent and pH. This was kept in a temperature controlled shaker at a constant speed of 150 rpm at pre-decided constant temperatures such as 303K, 313K, 323K to attain the equilibrium. After the desired times, samples were withdrawn from the incubator and the adsorbate and adsorbent was separated by filtration. Then after, the absorbance was measured with the help of UV-VIS spectrophotometer, and the residual concentration was calculated form Indole and OPD calibration plot. Percent removal of Indole & OPD was calculated using the following relationship.

$$\text{Percent removal} = \frac{(C_0 - C_e)100}{C_0} \qquad (4.1)$$

Where, C_0 is initial concentration and C_e is the equilibrium concentration (mg/l).

The adsorption of Indole and OPD was studied over an initial pH (pH_i) range of 2-9 at 303K. HCl and NaOH solutions of 1 N were used to adjust the initial pH of the solution. The adsorbent dose is kept constant at 3 g/100 ml during pH study. Dosage study was carried out by varying the adsorbent dosages (m_{ad}) in range of 0.5-5 g/100 ml for ACC at optimum (pH_i) and 303K.

4.5 Kinetics of adsorption

Kinetic parameters were calculated by using pseudo-first-order and pseudo-second –order model at various C_0 values (25-50 mg/l) at optimum mass of activated carbon as adsorbent and optimum pH at 303 K. The amount of adsorbate adsorbed, q_t (mg/g), at any time t was calculated as:

$$q_t = \frac{(C_0 - C_e)}{m_{ad}} V \qquad (4.2)$$

Where C_t is the Indole and OPD concentration at time t, V is the volume of solution in litre.

Nonlinear regression was used to check the validity of adsorption experimental data for these kinetics models. The best model for kinetic model is the Marquardt's percent standard deviation (MPSD) (Marquardt's 1963) to represent the experimental data. The equation of the error function is given as.

$$\text{MPSD} = 100 \sqrt{\frac{1}{n-p} \sum_{i=1}^{n} \frac{(q_{t,exp} - q_{t,calc})^2}{(q_{t,exp})^2}} \qquad (4.3)$$

Where 'n' is the number of measurements and 'p' is the number of parameter in the model. The subscript "exp" and "calc" represent the experimental and calculated values.

4.6 Isothermal study

An increase in temperature the mobility of adsorbate increases. In adsorption process it is necessary to study the effect of temperature on the adsorption process and isotherm equations at equilibrium. Equilibrium data in for the present work were performed at 303K, 313K, 323K, with C_0 value 10, 20, 30, 40, 50, 60, 80, 100 ppm both for Indole and OPD with initial pH 5.5 and constant value of optimum activated carbon m_{ad-opt} of ACC. Various isotherm such as Freundlich, Langmuir, Temkin and Redlich-Peterson (R-P) were used to fit Indole and OPD equilibrium adsorption data.

The equilibrium was reached after 4 hour. The Equilibrium adsorption uptake, q_e (mg/g), were calculated using the following relationship.

$$q_e = \frac{(C_0 - C_e)V}{w} \qquad (4.4)$$

Where w is the mass of adsorbent, C_0 & C_e are the initial and equilibrium concentration, V is the volume of the solution.

To find out best fit isotherm model Sum of Square error analysis function was used. It is given as:

$$SSE = \sum_{i=1}^{n} (q_{e,exp} - q_{e,cal})^2 \qquad (4.5)$$

CHAPTER-5

RESULTS AND DISCUSSION

5.1 GENERAL

Adsorptive removal of Indole and OPD from wastewater in batches using ACC is reported. Results obtained during the treatment of wastewater containing Indole and OPD, and interpretations have been discussed.

5.2 Effect of initial pH (pH_i)

In the adsorption process, the solution pH plays an important role, and is one of the most important parameter. At higher pH, concentration of H^+ ion is very low, where as it increase at lower pH. The surface charge of the adsorbent as well as degree of ionization affects the pH of the solution. The Fig 5.1. shows the effect of pH_i on the removal of indole and opd from aqueous solution by ACC at T = 303K, t = 4 hour, C_0 = 50 ppm of each Indole and OPD, adsorbent dose (m_{ad}) = 3 g/100 ml. It can be seen in Fig. 5.1 that increasing pH_i increases the % removal giving maximum removal of 92.4% and 89.34% at pH_i=5.5 for Indole and OPD, respectively. Increasing pH_i after pH_i=5.5 did not much improve the removal. Therefore pH_i = 5.5 was chosen as optimumpH_{i-opt} . The natural pH value of Indole and OPD solution was found to be 5.5 approximately. For the experiment with C_0 = 50 ppm Indole and 50 ppm OPD mixture, the final pH values (pH_f) of the adsorption process are shown as a function of pH_i in Fig 5.1. The pH_f values are greater than the pH_i except range for pH_i values 6-9.

5.3 Effect of Adsorbent Dosage (m_{ad})

The effect of adsorbent dosage (m_{ad}= 0.5 – 5 g/100 ml) on the adsorption of Indole and OPD by ACC was studied at C_0 = 50 ppm of each Indole and OPD, T = 303K, $pH_{i\text{-}opt}$ = 5.5 and t=4 h. From Fig. 5.2., it is clear that an increase in ACC dosage resulted in an increase in Indole and OPD removal up to 92.35% and 89.4%, respectively, at m_{ad}=3g/100ml, Thereafter, the removal efficiency remained almost constant. Therefore, optimum m_{ad} was chosen as m_{ad-opt}

=3 g/100 ml. The increase in m_{ad} increased the removal due to availability of more adsorption sites and greater surface area. The removal is nearly constant for $m_{ad} \geq m_{ad-opt}$ because the removal is limited by the concentration of the solution not by the dose m_{ad}.

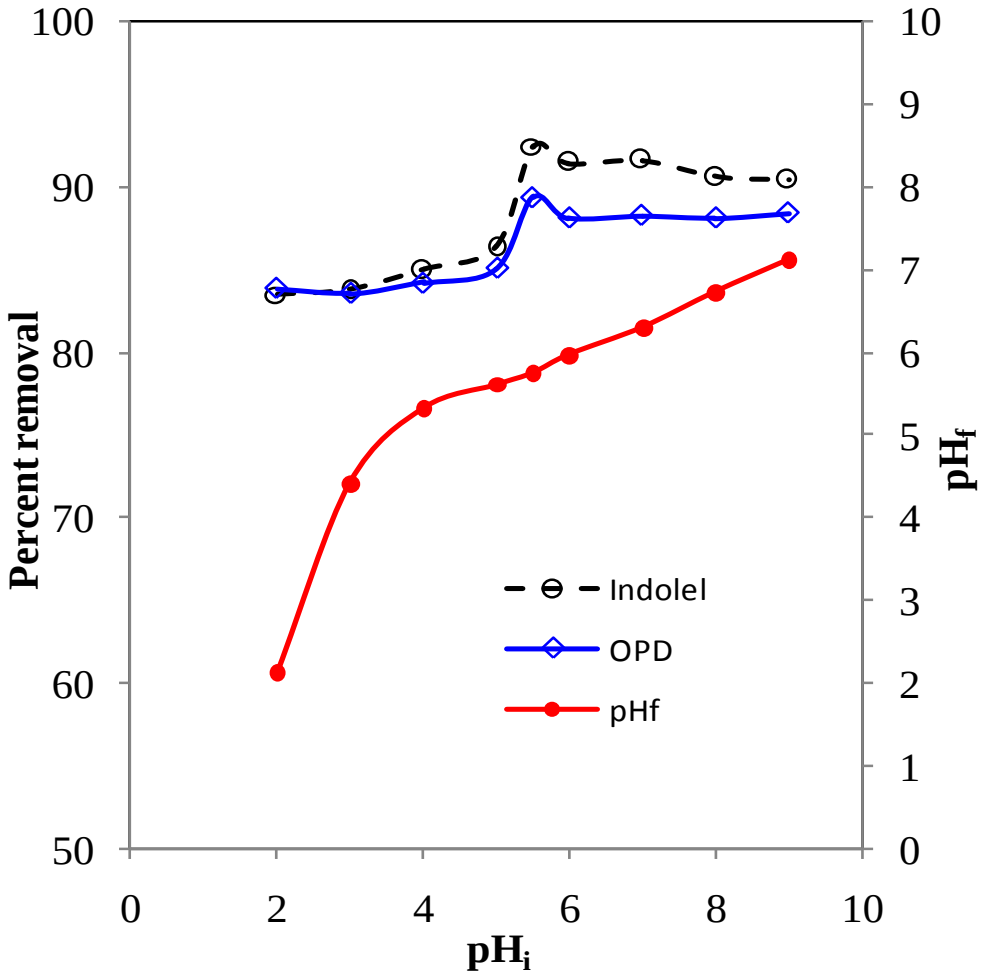

Fig. 5.1. Effect of pH_i on the Indole and OPD removal by ACC (T = 303K, t = 4 h, C_0 = (50, 50) mg/l, adsorbent dosage (m_{ad-opt}) = 3 g/100ml, RPM = 150)

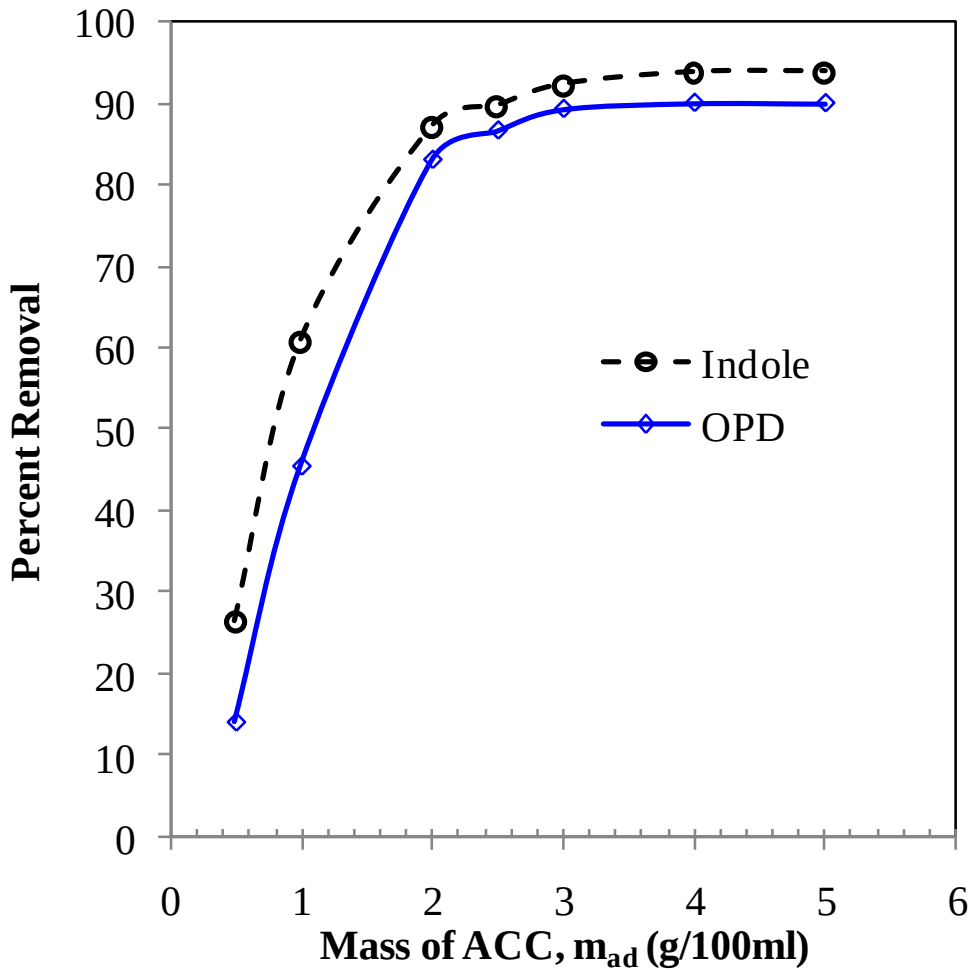

Fig 5.2. Effect of adsorbent dosage on the Indole and OPD removal by ACC (T = 303K, pH_{opt} = 5.5, t=4 h, RPM = 150, C_0 = (50, 50) mg/l)

5.4 Adsorption Kinetics

Pseudo-first-order and pseudo-second-order kinetic models were used to test their validity with the experimental kinetic adsorption data. Correlation coefficients with model parameters and MPSD error values for the best fit pseudo-first-order and pseudo-second-order kinetics models are given in Table 5.1 and 5.2, and Fig 5.3 and 5.4 shows the fitting of pseudo second-order model with kinetics experimental data shown by solid line for Indole and OPD, respectively. It can be seen that the Correlation coefficient values for each of fitted model is nearly same, but the MPSD error values are smaller for pseudo-second-order kinetics model.

Therefore, it can be concluded that pseudo-second-order kinetics model is suitable for the experimental kinetic data fitting.

It was observed that the q_e and k_s values increases with an increase in the $\mathbf{C_o}$ of Indole & OPD**,** showing that the uptake is limited by the concentration.

Generally, the adsorption rate is limited by $\mathbf{C_o}$ of Indole & OPD, affinity to the adsorbent, the pore size distribution of the adsorbent, degree of mixing and diffusion coefficient of the Indole and OPD in the bulk and solid phases (Mitome et al., 2013; Wang et al., 2003). Increase in the extent of all these factors increases the driving force to the adsorbate to be adsorbed on to surface of adsorbent. The increase in $\mathbf{C_o}$ value increases the driving force, and hence, the rate of adsorption increases with the increase in $\mathbf{C_o}$

Table 5.1. Kinetic parameters for the removal of Indole by Activated carbon (t = 5 hour, $\mathbf{C_o}$ = 25-50 mg/l, m = 3g/ml, pH_i = 5.5 , T = 303K).

Pseudo-first-order model					
C_o (mg/l)	**$q_{e,exp}$(mg/g)**	**$q_{e,cal}$(mg/g)**	**$k_f(min^{-1})$**	**R^2(non-linear)**	**MPSD**
50	1.526	46.0526	0.0144	0.984	101.58
25	0.787	24.666	0.0104	0.968	103.51
Pseudo second order model					
C_o (mg/l)	**$q_{e,cal}$(mg/g)**	**k_s (g/mg min)**	**h (mg/g min)**	**R^2(non-linear)**	**MPSD**
50	1.795	0.01016	0.03276	0.978	60.01
25	1.196	0.00702	0.00880	0.972	53.86

Table 5.2. Kinetic parameters for the removal of OPD by Activated carbon (t = 5 hour, C_o = 25-50 mg/l, m = 3g/ml, pH_i = 5.5 , T = 303K).

Pseudo-first-order model					
C_o (mg/l)	**$q_{e,exp}$(mg/g)**	**$q_{e,cal}$(mg/g)**	**$k_f(min^{-1})$**	**R^2(non-linear)**	**MPSD**
50	1.529	1.651	0.007	0.997	99.71
25	0.766	0.908	0.006	0.992	72.94
Pseudo second order model					
C_o (mg/l)	**$q_{e,cal}$(mg/g)**	**k_s (g/mg min)**	**h (mg/g min)**	**R^2(non-linear)**	**MPSD**
50	5.058	0.00034	0.009	0.994	79.76
25	1.1780	0.00461	0.0064	0.992	72.20

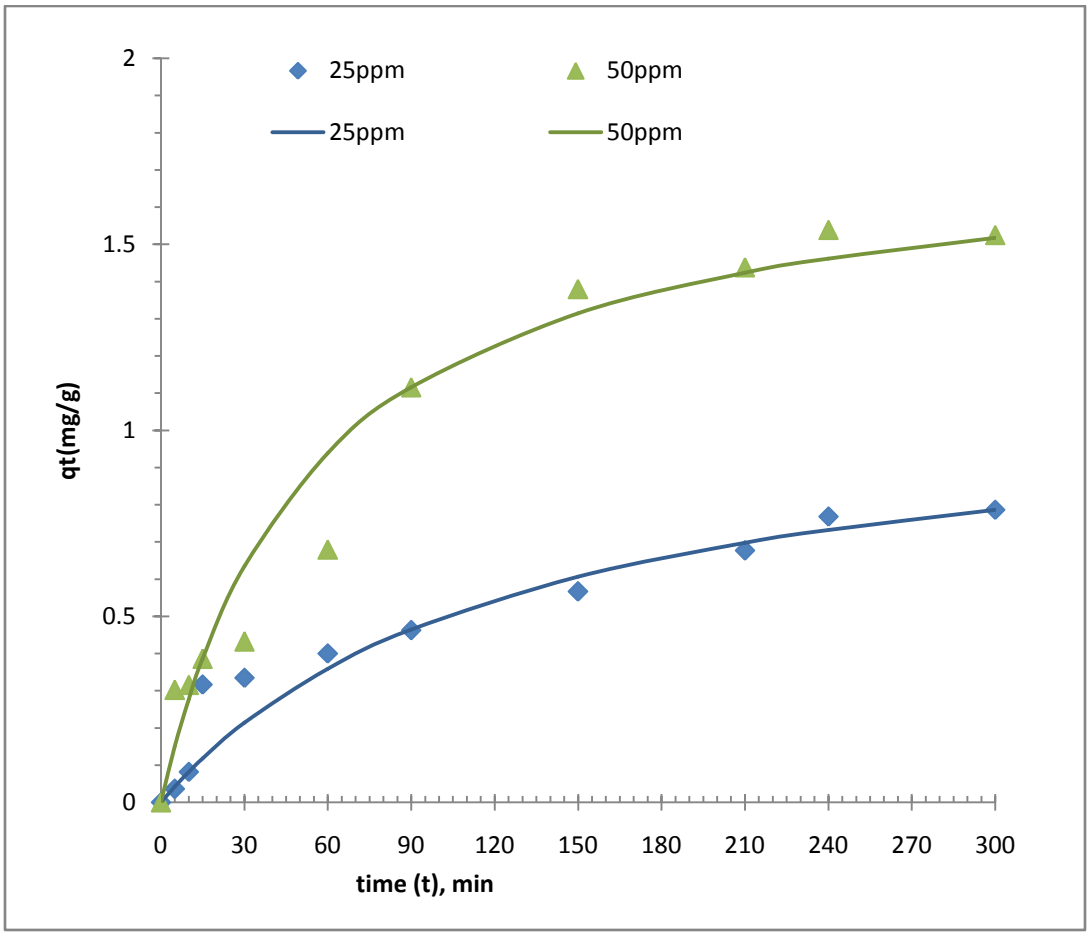

Fig 5.3. Effect of contact time on the Indole removal by Activated carbon. Experimental data points given by the symbols and the lines predicted by the pseudo-second-order model. T = 303 K, $m_{ad-opt} = 3g/100\,ml$

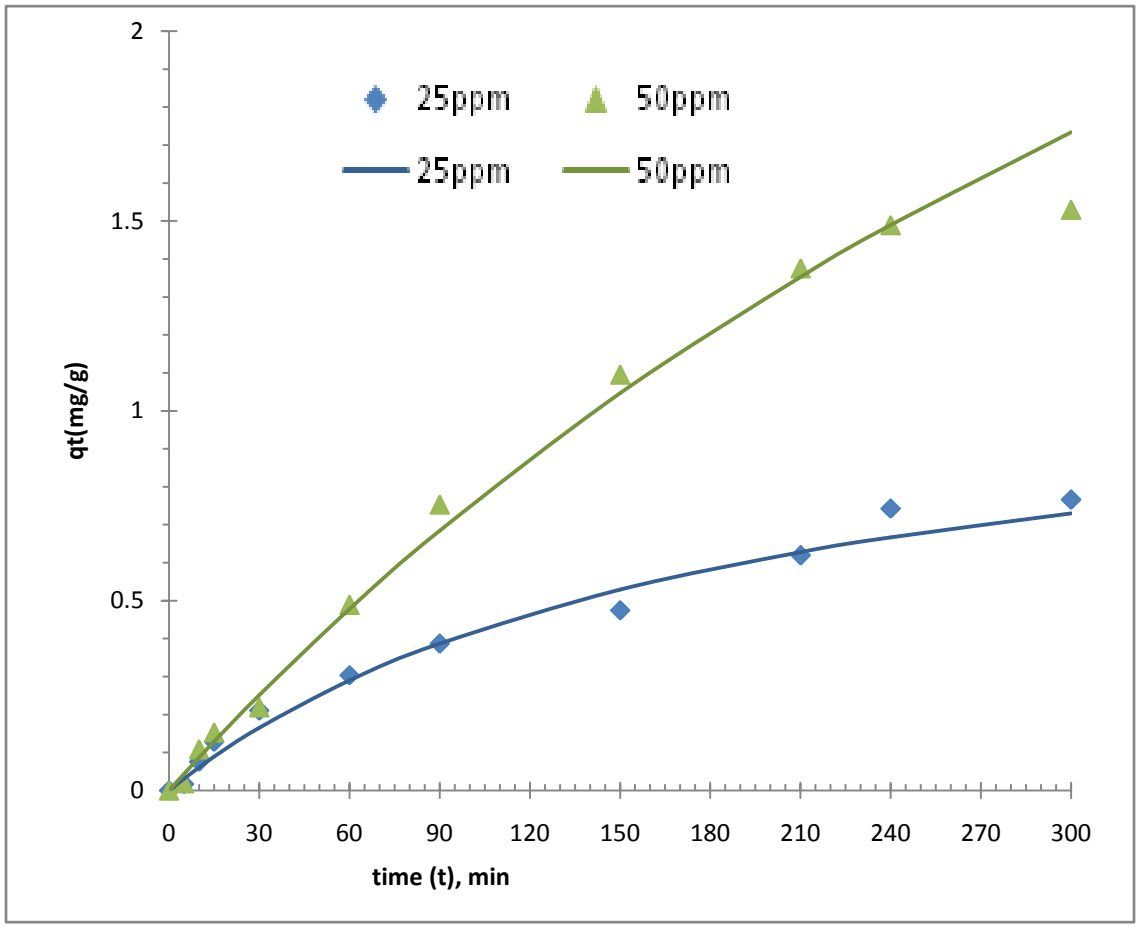

Fig 5.4. Effect of contact time on the OPD removal by Activated carbon. Experimental data points given by the symbols and the lines predicted by the pseudo-second-order model. T = 303 K, $m_{ad-opt} = 3g/100\ ml$

5.6 ADSORPTION ISOTHERM

5.6.1 Effect of temperature

Temperature significantly affect the adsorption capacity of the adsorbents. To study the effect of temperature on Indole and OPD adsorption onto ACC, experiments were conducted at different temperature ranging from 303-323 K, and the result is shown in Fig. 5.5 and 5.6 for Indole and OPD, respectively. It was found that adsorption onto ACC increases with increase in temperature. Therefore, it can be concluded that Indole & OPD adsorption onto ACC is an endothermic in nature. Generally adsorption is not an endothermic, but it is an exothermic process (kushwaha et al., 2010). However, if the adsorption process is controlled by intraparticle transport-pore diffusion the adsorption capacity will increase with an increase in temperature. The increase in molecular mobility of Indole & OPD with increased temperature, resistance decreases and adsorptive capacity of adsorbent increases. It can also be concluded that adsorption of Indole & OPD is chemisorptive in nature, because adsorption capacity increases with increase in temperature.

5.6.2 Isotherm Modeling

For isotherm modeling, various isotherms like Freundlich, Langmuir, R-P isotherm and Temkin have been tested for their validity with the experimental equilibrium adsorption data. Table (5.3, 5.4) shows the values of various isotherm parameter, R^2 and SSE for the fitting to the experimental data. It may be concluded that Temkin isotherm best fits the equilibrium adsorption of Indole & OPD onto ACC at all temperature. The validation of various isotherm studied with experimental data points is shown in Fig 5.5 and 5.6 by solid lines. K_F and 1/n indicates the adsorption intensity and adsorption capacity, respectively. Higher value of 1/n indicates the higher affinity between the adsorbate and adsorbent, and heterogeneity of the adsorption sites.

K_T value indicates the adsorption capacity. K_T value increases with increase in temperature, showing adsorption capacity is increasing with temperature. This indicates the endothermic nature of adsorption of Indole & OPD onto ACC. The q_m value indicates the affinity of the Indole and OPD with the ACC. A high q_m value indicates a higher affinity. At higher temperature showing higher affinity because q_m was found to increased with increase in temperature.

Table 5.3. Parameter of isotherm models for Indole (t = 5 hour, C_o = 10-100 mg/l, m = 3g/ml)

Freundlich $q_e = K_F C_e^{1/n}$

T (K)	$K_F((mg/g)/(l/mg)^{1/n}$	1/n	R^2	SSE
303	0.600	0.576	0.969	0.330
313	0.832	0.602	0.961	0.466
323	1.165	0.490	0.967	0.413

Langmuir $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$

T (K)	K_L(l/mg)	q_m(mg/g)	R^2	SSE
303	0.11853	4.366	0.990	0.117
313	0.20046	4.653	0.977	0.296
323	0.36367	4.120	0.976	0.324

Redlich-Peterson $q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$

T(K)	K_R(l/mg)	$a_R(l/mg)^{1/\beta}$	β	R^2	SSE
303	0.525	0.1279	0.980	0.989	0.121
313	0.999	0.2741	0.900	0.975	0.313
323	1.718	0.5730	0.850	0.972	0.358

Temkin $q_e = B_T \ln (K_T C_e)$

T(K)	K_T(l/mg)	B_T(kJ/mol)	R^2	SSE
303	1.239	0.9303	0.9896	0.105
313	1.818	1.073	0.9894	0.124
323	3.075	0.976	0.9833	0.203

Table 5.4. Parameter of isotherm models for OPD (t = 5 hour, C_o = 10-100 mg/l, m = 3g/ml)

Freundlich $q_e = K_F C_e^{1/n}$

T (K)	$K_F((mg/g)/(l/mg)^{1/n}$	1/n	R^2	SSE
303	0.368	0.766	0.989	0.117
313	0.583	0.667	0.980	0.225
323	1.014	0.598	0.974	0.335

Langmuir $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$

T (K)	K_L(l/mg)	q_m(mg/g)	R^2	SSE
303	0.0444	7.141	0.992	0.085
313	0.0527	8.230	0.981	0.283
323	0.1026	8.330	0.963	0.527

Redlich-Peterson $q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}}$

T(K)	K_R(l/mg)	$a_R(l/mg)^{1/\beta}$	β	R^2	SSE
303	0.298	0.0197	1.248	0.992	0.083
313	0.513	0.0609	1.170	0.988	0.140
323	0.902	0.0453	1.617	0.978	0.284

Temkin $q_e = B_T \ln (K_T C_e)$

T(K)	K_T(l/mg)	B_T(kJ/mol)	R^2	SSE
303	1.061	0.795	0.9819	0.186
313	1.068	1.196	0.9935	0.071
323	1.208	1.946	0.9900	0.124

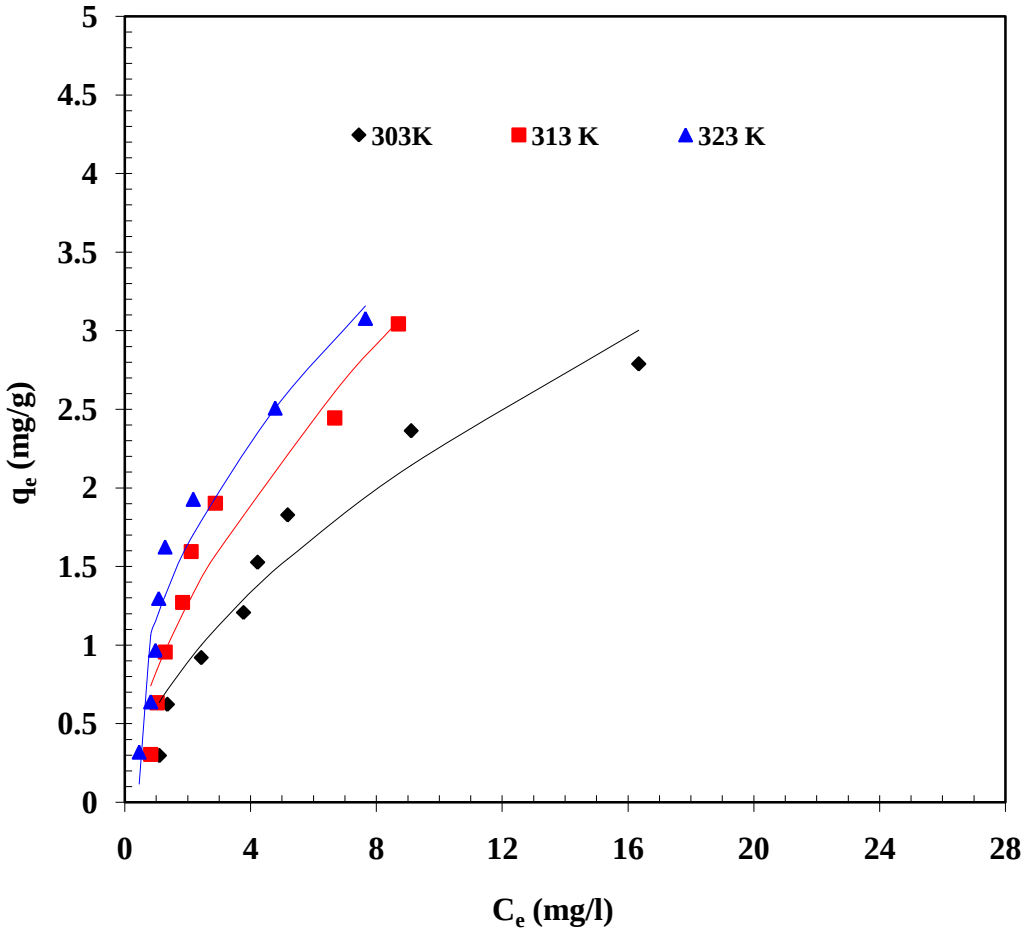

Fig 5.5a. Equilibrium adsorption isotherms at different temperature for the Indole removal by ACC. Experimental data points given by symbols and the lines predicted by Freundlich isotherm model, t = 5 h, C_o = 10-100 mg/l, $m_{ad-opt} = 3g/ml$.

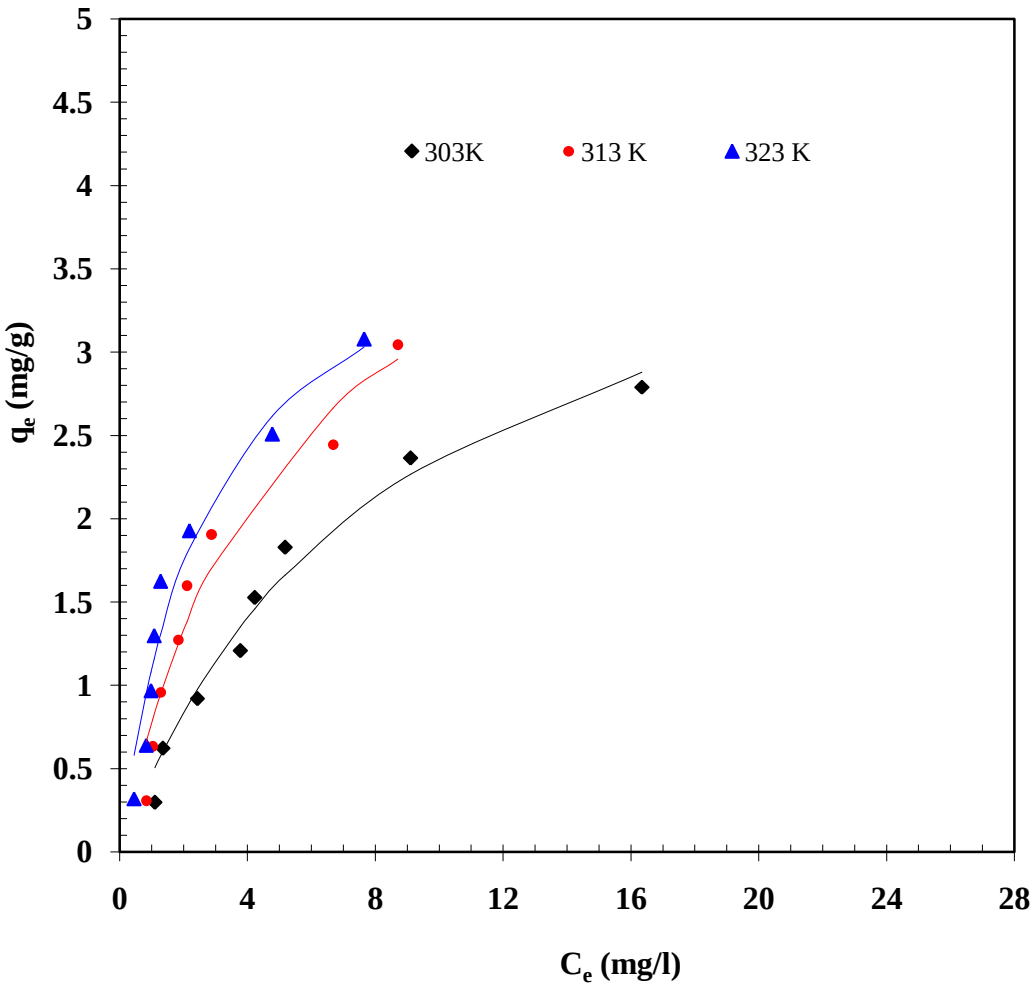

Fig 5.5b. Equilibrium adsorption isotherms at different temperature for the Indole removal by ACC. Experimental data points given by symbols and the lines predicted by Langmuir isotherm model, t = 5 h, C_o = 10-100 mg/l, $m_{ad-opt} = 3g/ml$.

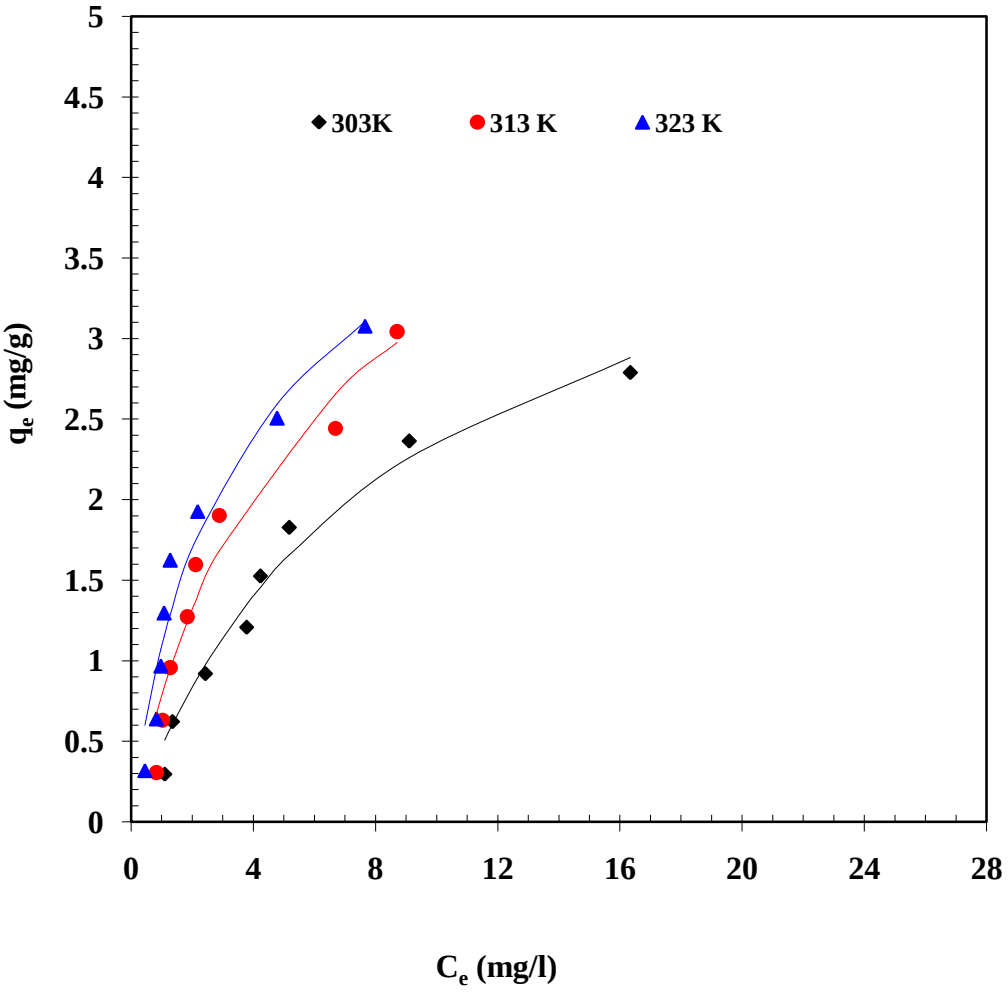

Fig 5.5c. Equilibrium adsorption isotherms at different temperature for the Indole removal by ACC. Experimental data points given by symbols and the lines predicted by Redlich-Peterson isotherm model, t = 5 h, C_o = 10-100 mg/l, $m_{ad-opt} = 3g/ml$.

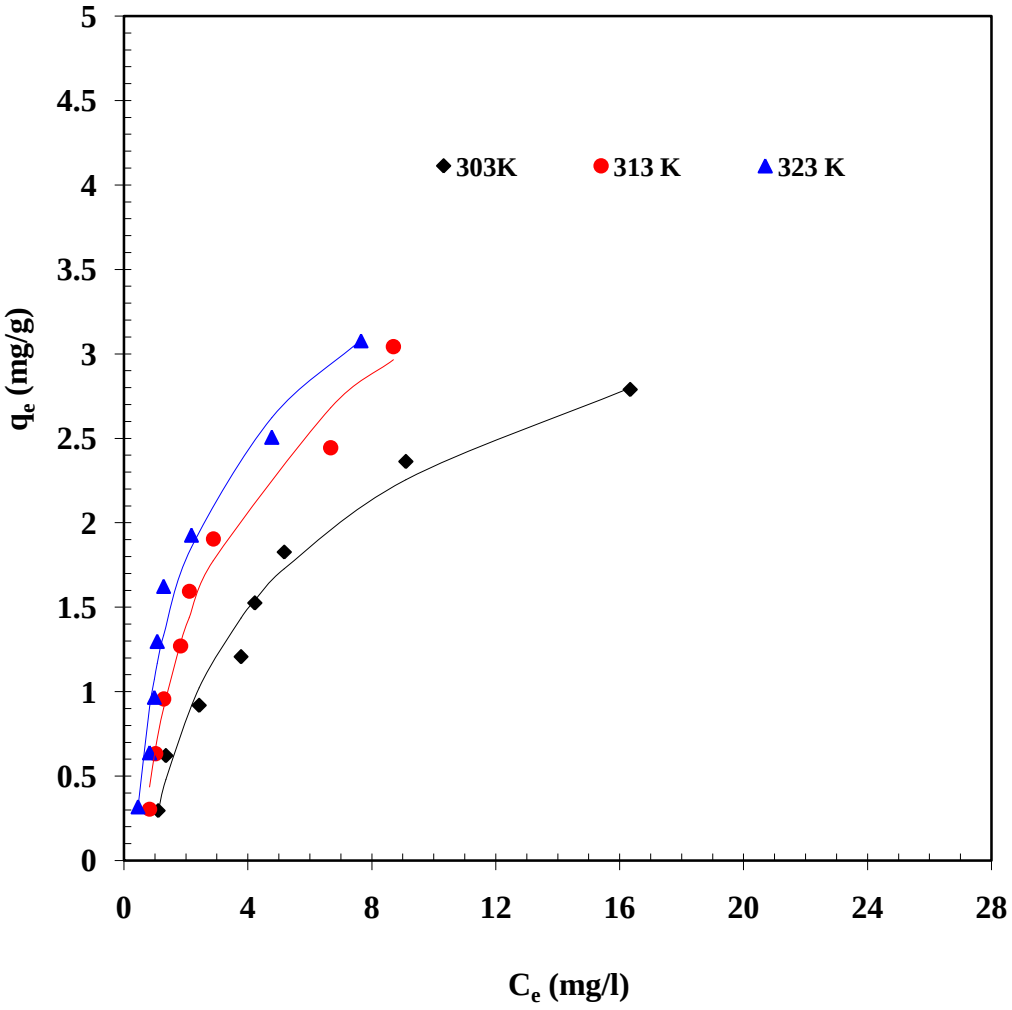

Fig 5.5d. Equilibrium adsorption isotherms at different temperature for the Indole removal by ACC. Experimental data points given by symbols and the lines predicted by Temkin isotherm model, t = 5 h, C_o = 10-100 mg/l, $m_{ad-opt} = 3g/ml$.

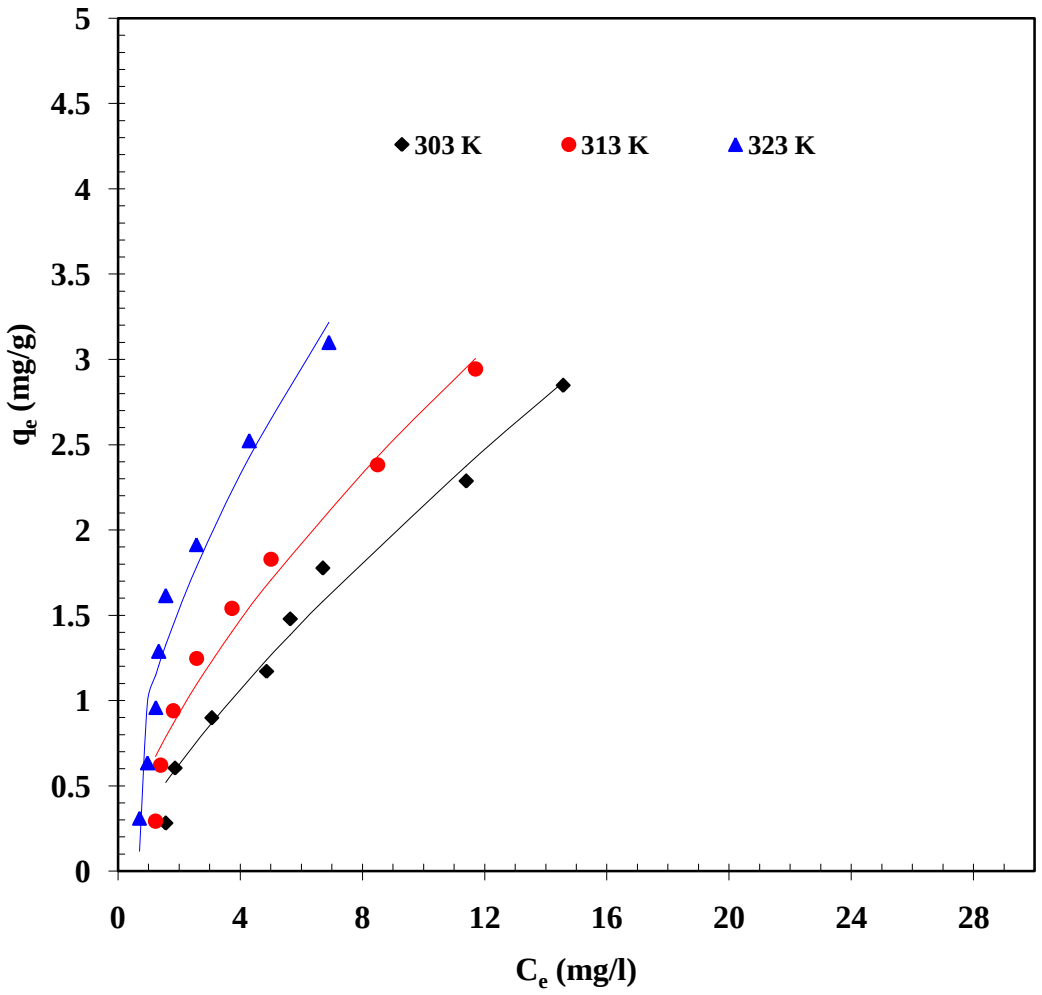

Fig 5.6a. Equilibrium adsorption isotherms at different temperature for the OPD removal by ACC. Experimental data points given by symbols and the lines predicted by Freundlich isotherm model, t = 5 h, C_o = 10-100 mg/l, $m_{ad-opt} = 3g/ml$.

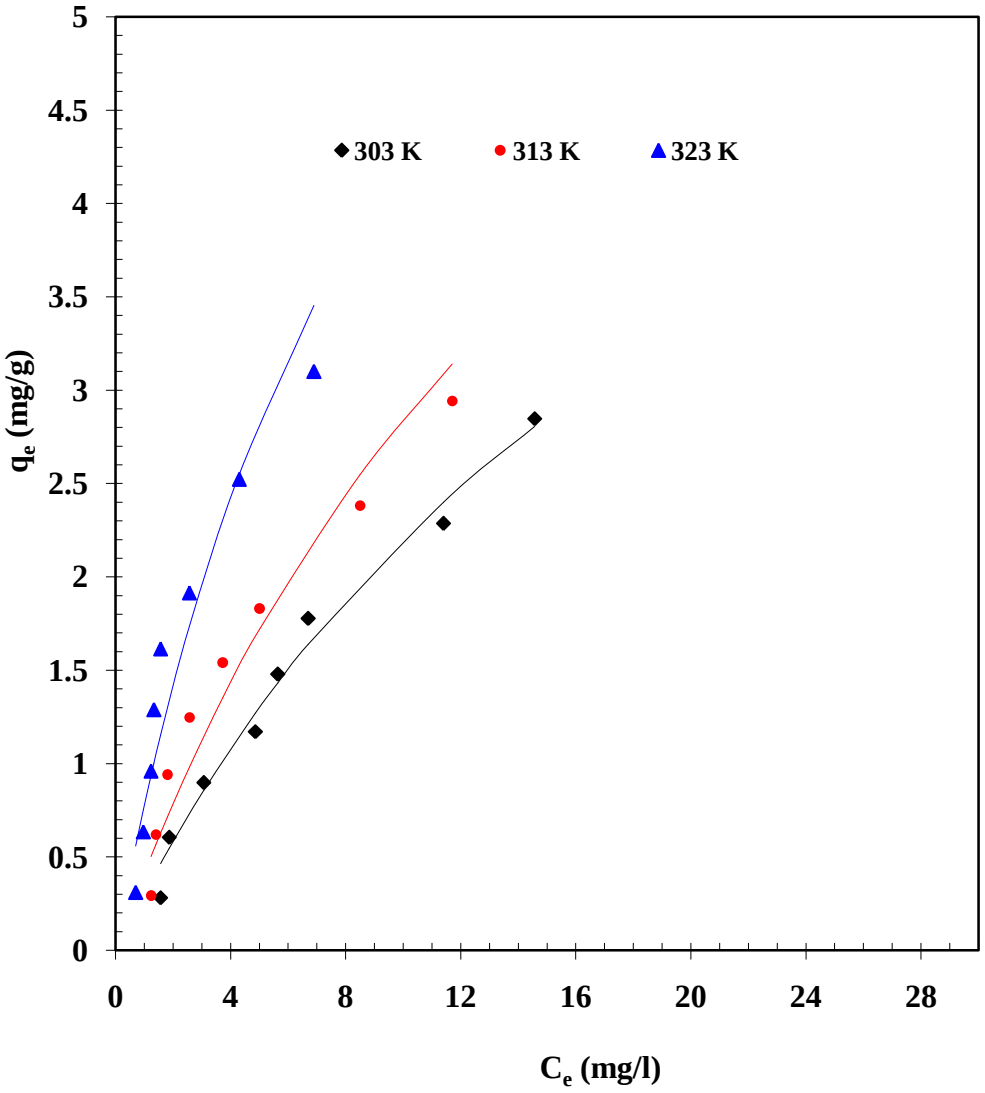

Fig 5.6b. Equilibrium adsorption isotherms at different temperature for the OPD removal by ACC. Experimental data points given by symbols and the lines predicted by Langmuir isotherm model, t = 5 h, C_o = 10-100 mg/l, $m_{ad-opt} = 3g/ml$.

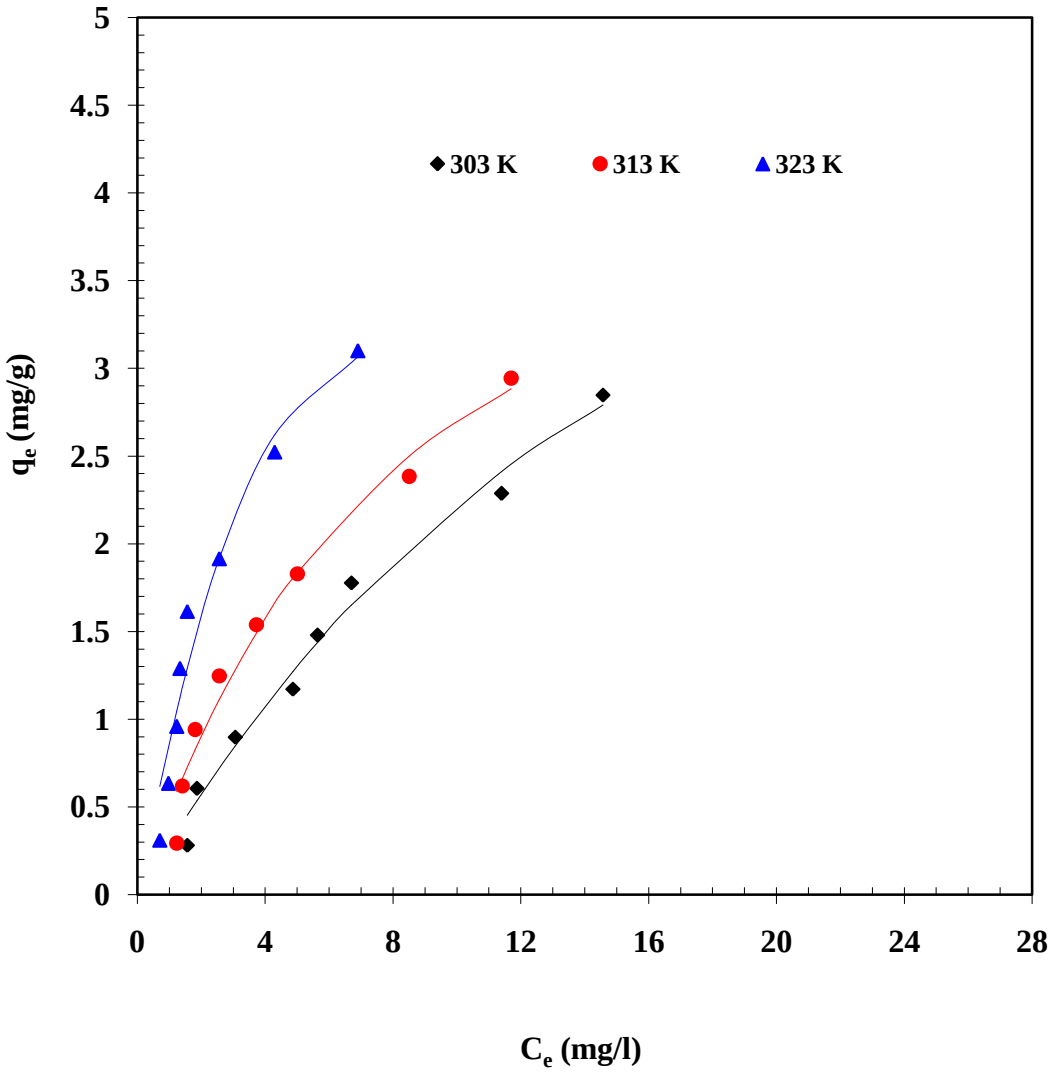

Fig 5.6c. Equilibrium adsorption isotherms at different temperature for the OPD removal by ACC. Experimental data points given by symbols and the lines predicted by Redlich-Peterson isotherm model, t = 5 h, C_o = 10-100 mg/l, $m_{ad-opt} = 3g/ml$.

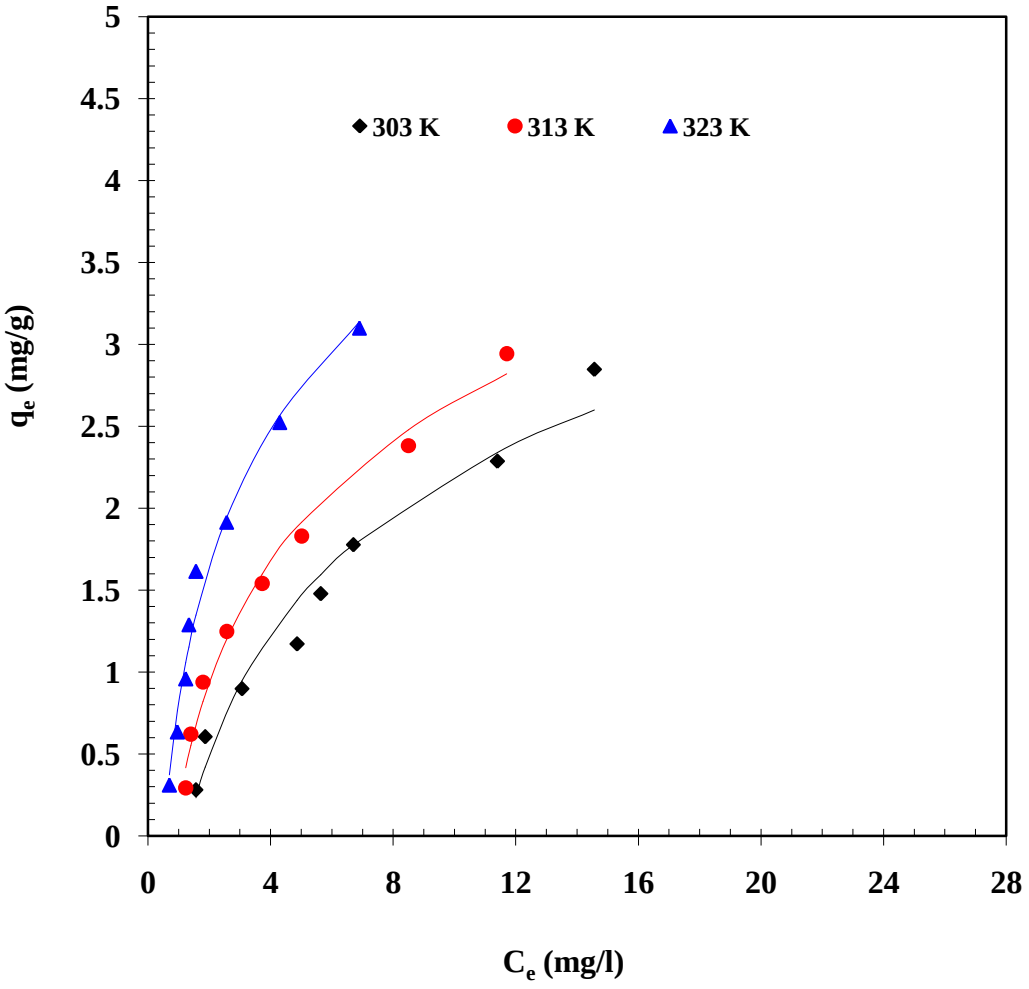

Fig 5.6d. Equilibrium adsorption isotherms at different temperature for the OPD removal by ACC. Experimental data points given by symbols and the lines predicted by Temkin isotherm model, t = 5 h, C_o = 10-100 mg/l, $m_{ad-opt} = 3g/ml$.

CHAPTER-6

CONCLUSION

On the basis of the experiment, results and discussion presented for the adsorptiove removal of Indole & OPD onto activated carbon, following conclusions can be drawn:

- Optimum conditions for the adsorptive treatment of Indole and OPD by activated carbon were found to be $pH_{i\text{-}opt}$ = 5.5, adsorbent dose of $m_{ad\text{-}opt}$=30 g/l and contact time = 4 hour, and at this optimum condition Indole and OPD removal were found up to 92.35% and 89.4%, respectively.
- Pseudo-second-order model was found to best fit the kinetic experimental data.
- It was found that q_e values increases with increase in C_o therefore, the uptake of Indole & OPD is limited by the $C_{o.}$
- Adsorption is chemisorptive in nature, because adsorption capacity increases with increase in temperature.
- Adsorption process was found to be endothermic in nature and Temkin isotherm model was generally found to best represent the equilibrium data.
- K_F value indicates the adsorption capacity. K_F value increases with increase in temperature, showing adsorption capacity is increasing. This also confirms the endothermic nature of adsorption of Indole & OPD onto adsorbent.
- K_T value increases with increase in temperature, showing adsorption capacity is increasing with temperature. This indicates the endothermic nature of adsorption of Indole & OPD onto ACC.

REFERENCES

Ahmaruzzaman M., (2008), "Adsorption of phenolic compounds on low-cost adsorbents", Advances in Colloid and Interface Science 143, 48-67.

Baker F.S., Miller C.E., Repik A.J., Tolles E.D., (1992), "Activated carbon", Kirk-Othmer Encyclopedia of Chemical Technology 4, 1015-1037.

Brasquet C., Roussy J., Subrenat E., Cloirec P.E., (1996), "Adsorption of micropollutants onto fibrous activated carbon association of ultrafiltration and fibers", Water Science Technology 34, 215-222.

Burdock G.A., (1997), "Encyclopedia of Food and Color Additives", Boca Raton: CRC.

Chakraborty A., Sun B., (2014), "An adsorption isotherm equation for multi-types adsorption with thermodynamic correctness", Applied Thermal Engineering 324, 1-10.

Erciyes N., Gurten A.A., Abdullah M.I., Ayar A., (2004), "Adsorption of indole and 2-Methylindole on ligand-exchange matrix", Journal of Colloid and Interface Science 278, 91-95.

Hassan L.G., Abdulrahman F.W., Itodo A.U., Maigandi S.A., (2008), "Freundlich Adsorption Isotherms of Adsorbent from H_3PO_4 and $ZnCl_2$ Treated Irish potato peels" Nig. J. Basic Appl. Sci. 16(2), 263-268.

Hiwarkar A.D., Sirvastava V.C., Mall I.D., (2014), "Comparative Studies on Adsorptive Removal of Indole by Granular Activated Carbon and Bagasse Fly Ash", Environmental Progress & Sustainable Energy.

Ho Y.S., McKay G., (1999), "Pseudo-second order model for adsorption processes", Process Biochemistry 34, 451-465.

Johnson R.D., Arnold F.H., (1995), "The Temkin isotherm describes heterogeneous protein adsorption", Biochimica et Biophysica Acta 1247, 293-297.

Khalfaoui M., Knani S., Hachicha M.A., Lamine A.B., (2003), "New theoretical expressions for the five adsorption type isotherms classified by BET based on statistical physics treatment", Journal of Colloid and Interface Science 263, 350–356.

Kim K.S., Choi H.C., (1998), "Characteristics of adsorption of rice-hull activated carbon", Water Science Technology 38, 95-101.

Koohestanian A., Hosseini M., Abbasian Z., (2008), "The Separation Method for Removing of Colloidal Particles from Raw Water", American-Eurasian J. Agric. & Environ. Sci., 4 (2), 266-273.

Lakshmi U.R., Lataye D.H., Srivastava V.C., Mall I.D., (2009), "Rice husk ash as an effective adsorbent: Evaluation of adsorptive characteristics for Indigo Carmine dye", Journal of Environmental Management 90, 710-720.

Lataye D.H., Mishra I.M., Mall I.D., (2008), "Adsorption of orthophenylene diamine onto bagasse fly ash from aqueous solution", Chemical Engineering Journal 138, 35-46.

Lataye D.H., Mishra I.M., Mall I.D., (2008), "Pyridine sorption from aqueous solution by rice husk ash (RHA) and granular activated carbon (GAC)", Journal of Hazardous Materials 154, 858-870.

Liao P., Yuan S., Zhang W., Tong M., Wang, K., (2012), "Mechanistic aspects of nitrogen-heterocyclic compound adsorption on bamboo charcoal", Journal of Colloid and Interface Science 382, 74-81.

Liu X.M., Zhao Q., Li Y., Song W.C., Li Y.P., Chang Z., Bu X.H., (2013), "Two new indole derivatives as anion receptors for detecting fluoride ion", Chinese Chemical Letters 24, 962–966.

Marquardt D.W., (1963), "An algorithm for least-squares estimation of nonlinear parameters. Journal of the Society for Industrial and Applied Mathematics 11, 431-44.

Mitome T., Uchida Y., Egashira Y., Hayashi K., Nishiura A., Nishiyama N., (2013), "Adsorption of indole on KOH-activated mesoporous carbon", Colloids and Surfaces A: Physicochem. Eng. Aspects 424, 89– 95.

Poulis J.A., Massen C.H., Robens E., (2007), "Saving time when measuring BET isotherms", Journal of Colloid and Interface Science 311, 391–393.

Pryor M.J., Nozaic D., Freese S.D., Rajagopaul R., (1999), "The use of granular activated carbon for the treatment of impounded surface water", Water Science Technology 39, 197-200.

Rafatullaha M., Sulaimana O., Hashima R., Ahmadb A., (2010), "Adsorption of methylene blue on low-cost adsorbents: A review", Journal of Hazardous Materials 177, 70–80.

Ramos R.L., Martinez J., (1995), "Adsorption of chromium (4) from aqueous solutions on activated carbon", Water Science Technology 30, 191-197.

Sekaran G., Muneeswari R., Saranya P., (2010), "Biodegradation of Endocrine disrupting Chemical OrthoPhenylene diamine using intracellular enzymes from Citrobacter freundii and its kinetic studies", Council of Scientific and Industrial Research (CSIR)-Central Leather Research Institute (CLRI) 10, 45-58.

Singh N., (2009), "Adsorption of herbicides on coal fly ash from aqueous solutions", Journal of Hazardous Materials 168, 233–237.

Song X., Zhang Y., Yan C., Jiang W., Chang C., (2013), "The Langmuir monolayer adsorption model of organic matter into effective pores in activated carbon", Journal of Colloid and Interface Science 389, 213–219.

Srivastava V.C., Swamy M.M., Mall I.D., Prasad B., Mishra I.M., (2006), "Adsorptive removal of phenol by bagasse fly ash and activated carbon: equilibrium, kinetics and thermodynamic study", Colloids and Surfaces, A: Physicochemical and Engineering Aspects 272, 89-104.

Srivastava A., Srivastava V.C., (2009), "Adsorptive desulfurization by activated alumina", Journal of Hazardous Material 170(2-3), 1113-1140.

Srivastava V.C., Mall I.D., Mishra I.M., (2007), "Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ions onto bagasse fly ash (BFA) and rice husk ash (RHA)", Chemical Engineering Journal 132(1-3), 267-278.

Srivastava V.C., Mall I.D., Mishra I.M., (2006), "Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash", Chemical Engineering Journal 117, 79-91.

Sun J.C., (1998), "Treatment and utilization of orthophenylene diamine in wastewater", Anhui Huagong 92, 31-33.

Wang S.Q., Zhou D.M., Wang Y.J., Chen H.M., (2003), "Effect of orthophenylene diamine on Cu adsorption and desorption in red soil and its uptake by paddy rice", Chemosphere 51, 77-83.

Wu C.F., Tseng R.L., Huang S.C., Juang R.S., (2009), "Characteristics of pseudo second-order kinetic model for liquid-phase adsorption", Chemical Engineering Journal 151, 1–9.

Yang C.H., (1998), "Statistical Mechanical Study on the Freundlich Isotherm Equation", Journal of Colloid and Interface Science **208,** 379–387.

Yu Z., Peldszus S., Huck P.M., (2008), "Adsorption of selected pharmaceuticals and an endocrine disrupting compound by granular activated carbon", Environmental Science & Technology 43, 1467-1473

Zogorski J.S., Faust S.M., Hass J.H., (1976), "The kinetics adsorption of phenols by granular activated carbon", Journal of Colloid and Interface Science 55(2), 329-341.