COMPETITIVE ADSORPTION OF INDOLE AND ORTHO-PHENYLENEDIAMINE ONTO COMMERCIAL ACTIVATED CARBON

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By

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CERTIFICATE

This is to certify that the dissertation entitled **"Competitive adsorption of indole and ortho-phenylenediamine onto commercial activated carbon"** is an authentic record of my own work carried out as requirement for the award of the degree of Master of Science in Chemistry in the Department of Chemical Engineering, Thapar university, Patiala under the supervision of Dr. J. P. Kushwaha, Assistant professor, Chemical Engineering Department and Dr. Neetu Singh, Assistant professor, Chemical Engineering Department. No part of this project has been submitted for award of any other degree by me.

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It is certified that the above statement made by the student is correct to the best of our knowledge and belief.

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ABSTARCT

Ortho-phenylenediamine and Indole are two of such organic compounds that are highly malignant and have been reported as a threat to human health. Both of these organic compounds are prominent environment pollutants. Indole is a nitrogenous heterocyclic compound has the bicyclic structure and the formula C_8H_7N. It occurs naturally in human feces and has an intense fecal odor. 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.

Various types of methods for their eradication from polluted water bodies have been reported in literature.

In the present study, simultaneous adsorption of OPD (O) and Indole (I) onto low cost adsorbent such as commercial grade activated carbon (ACC) at various temperatures (303 K and 318 K) from O-I binary aqueous solution was performed. Further, the equilibrium adsorption data from the experiments were analyzed using various multicomponent competitive isotherm models isotherm models such as non-modified and extended Langmuir isotherm, extended Freundlich model, Sheindorf–Rebuhn–Sheintuch (SRS) model, and non-modified and modified competitive Redlich-Peterson isotherm model.

In binary solution of O and I, it was observed that increasing the initial concentration of one of the adsorbate affects equilibrium adsorption uptake of another adsorbate from binary mixture. The extended Freundlich isotherm model and SRS models best represented the experimental data from binary adsorption of OPD and Indole at all the temperatures (303 K and 318 K) studied.

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NOMENCLATURE

a_{ij}	competition coefficients of component i by component j, dimensionless
a_R	constant of Redlich-Peterson isotherm, l/mg
$C_{0,i}$	initial concentration of each component in solution, mg/l
K_i	individual extended Langmuir isotherm constant of each component, l/mg
n_m	number of measurements
n_p	number of parameters
N	number of data points
$q_{e,i}$	equilibrium solid phase concentration of each component in binary mixture, mg/g
$q_{e,cal}$	calculated value of solid phase concentration of adsorbate at equilibrium, mg/g
$q_{e,\exp}$	experimental value of solid phase concentration of adsorbate at equilibrium, mg/g
$q_{\max}$	Max adsorption capacity
x_i, y_i, z_i	constants in the extended Freundlich isotherm
β_i	constant in SRS model for each component, dimensionless
$\eta_{L,i}$	multi-component (competitive) Langmuir adsorption constant of each component, dimensionless
$\eta_{R,i}$	multi-component (competitive) R-P adsorption constant of each component, dimensionless
ACC	Activated carbon commercial

CHAPTER 1 INTRODUCTION

1.1 GENERAL

Discharge of various organic pollutants into the environment have severely deteriorated the living conditions of all organisms ranging from micro-organisms in earth or water bodies to the higher species including animals and plants. Most of these pollutants are discarded from industries and laboratories as such without any primary treatments. It is hard to endure life in such adverse conditions. So it became very important to recognize such hazardous pollutants and find appropriate ways to degrade them.

Ortho-phenylenediamine and Indole are two of such organic compounds that are highly malignant and have been reported as a threat to human health. Both of these organic compounds are prominent environment pollutants. Indole and OPD are used as precursors for many organic reactions and released in water bodies as waste or side products. Both are highly toxic and carcinogenic compounds.

1.2 CHARACTERISTICS USES AND TOXICITY OF OPD AND INDOLE

1.2.1 INDOLE

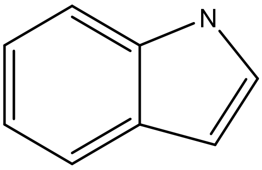


Fig 1.1 Chemical structure of Indole

Indole is a heterocyclic aromatic organic compound with formula C_8H_7N (Fig. 1.1). It is a white solid at room temperature. Indole is present in large amounts in environment and is formed by different bacteria for example, it is a bacterial degradation product of tryptophan, an amino acid present in human body.

Indole is having jasmine flower like smell when present in low concentrations, by virtue of this feature Indole is used in Jasmine Oil industries, and in perfume industries that contain 2.5% of Indole. Its properties are given in Table 1.1.

Toxic Effects of Indole

Indole is genotoxic heterocyclic pollutant and is one of the constituents of petrochemical by-products and is a major waste product found discarded from tar sands, oil shale and also found in effluents from the refinery units of petroleum in large amounts.

Indole is discharged into the environment through industrial waste, coal tar waste, and waste water from coking plants, coal gastification [Fetzner, 1998; Zhang et al.,1998]. Air, tobacco smoke, food, skin contact with vapors, and other products such as perfumes that contain indole are the ways in which human beings are exposed to indole. Indole is very toxic for microorganisms and animals, and is considered as mutagen and carcinogen. According to some experimental evidences indole has been the cause of disorders like glomerular sclerosis hemolysis improper oviduct functioning and chronic arthritis. [Newa et al., 1994; Paradis et al., 1991; Riveles et al., 2005; Forbes and Neale, 1937]. Indole causes the dysfunctioning of anthraxquinone biosynthesis in plants [El-Shagy et al., 1984]

1.2.2 Ortho-phenylenediamine (OPD)

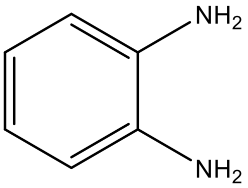


Fig 1.2 Chemical structure of OPD

Ortho-Phenylenediamine also generally referred as OPD. This organic aromatic diamine is having a chemical formula $C_6H_8N_2$. It occurs as a solid at room temperature.

It is used in many drugs as a precursor, in some dye substrates, synthetic polymers. Its properties are given in Table 1.2.

Toxic Effects of OPD

OPD is considered mutagenic and is considered as hazard in case ingestion, inhalation and eye contact. OPD is determined to be a skin irritant and causes asthma like allergy. OPD is a chemical intermediate in the synthesis of fungicides, corrosion inhibitors, and various pharmaceutical products. OPD is also used for the removal of sulfur in the mining ores. It is also used in removal of aldehyde color formers in polymeric products.

TABLE 1.1 PROPERTIES OF INDOLE

PARAMETERS	**INDOLE**
Synonyms	Benzazole, 1-H-Benzo[b]pyrrole
Chemical formula	C_8H_7N
Molar mass	117.15 g/mol
Physical state	Solid
Color	White crystalline
Density	1.17 g/cm^3
Melting point	51°-54°C
Boiling point	253-254°C
Solubility	Soluble in hot water

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

TABLE 1.2 PROPERTIES OF OPD (Orthophenylene diamine)

PARAMETERS	**Ortho-phenylenediamine**
Synonyms	1,2-Diaminobenzene,1,2 Phenylenediamine
Chemical Formula	$C_6H_8N_2$
Molar Mass	108.14 g/mol
Physical state	Solid
Colour	Reddish brown
Density	1.03 g/cm^3
Melting point	102-104°C
Boiling point	252°C
Solubility	Soluble in hot water

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

1.3 VARIOUS METHODS FOR REMOVAL OF INDOLE AND OPD

There are a number of various methods that have been reported in literature to subside the dissolved organic pollutants from the wastewaters. They mainly involve the biological and physico-chemical approaches. Sometimes conversion of these compounds in some other lesser polluting compounds is also done. Such as oxidation of OPD is done which leads to formation of various other derivatives of OPD.

1) Biological methods involve Biodegradation of organic waste. Biodegradation is a process that involves microorganisms, fungi, green plants and their enzymes to remove the organic impurities from wastewaters or transform them into harmless compounds.

Biodegradation is done by two ways, aerobic and anaerobic biodegradation. In aerobic biodegradation, oxygen is needed for degradation at two states of the degradation process, one at the initial attack of substrate and second at the end of respiratory chain.

Anaerobic biodegradation involves breakdown of biodegradable material in absence of oxygen. This one is considered a slower process then the aerobic degradation but it provides renewable energy. The main examples are Upflow Anaerobic Sludge Blanket reactor (UASB) and Anaerobic Biofilter.

2) Chemical oxidation is one of the effective way to treat large amounts of wastewaters where biological cannot withstand due to presence of molecules, refractory to the microorganisms present in water. This technology uses some chemical oxidants (H_2O_2, O_3, ClO_2, K_2MnO_4. Some type of chemical oxidation technologies work at normal pressure and temperature conditions that include Fenton process, use of hydrogen peroxide and ozonation. Whereas some of the technologies work under high pressure and temperature.

3.) Third is the physico-chemical treatments that includes, coagulation, adsorption, membrane separation, electro-chemical treatment. Out of all these, adsorption is most convenient way of subsiding the impurities from wastewaters. Over the last few decades, adsorption has gained an exceptional position among all the other methods of separation technique used in water purification. Adsorption is widely used at industrial level.

1.3.1 The advantages of adsorption over other technologies

1.) Adsorption is a cleaner technology, free from sludge handling problems, which are very general for the chemical and biological processes.

2.) It produces high quality effluents.

3.) Adsorbents are generally of low cost derived from natural products like ACC is obtained from wood or lignin so they are economically efficient.

4.) Handling of experiment is much easier as compared to microbial degradation methods that need complex treatment plant designs.

5.) Adsorption can remove organic waste from wastewater to higher percentages whereas biological methods can remove only upto 30-50% of wastes. [Figaro et al., 2006]

1.3.2 ACC as an adsorbent

Granular Activated Carbon is most commonly used adsorbent. ACC is widely used to remove pollutants from wastewaters due to its higher efficiency of removal and versatility. ACC is made from organic material with high carbon content like wood, lignite and coal.

1.3.3 Composition of ACC

The ACC is composed of carbon matrix that is having irregular and amorphous structure and some parts of graphite called as a graphitic layer that contains some contaminants such as ashes and heteroatoms (nitrogen, oxygen and sulphur) and CO bonds containing compounds. These functional groups are result of activation of carbon and causes hydrolysis over the surface of ACC [El-shagy et. al., 1984]

The rate of adsorption majorly depends on thermodynamic kinetics of interactions between solute-solvent-sorbent and diffusive-convective transport within the ACC (involving porous media). There is great significance of equilibrium stages because the uptake of ions depends on the parameters, like pH, temperature, concentration, ionic strength, and chemical compositions of the solution [Benjamin, 2002]. Adsorption is caused by interactions between the active sites and aqueous solution. ACC surface composition, denoted as COxHy, is described by [Boehm, 2002]. Carbon surface possess different adsorbing sites, distinguished as:

1. Functional groups with acidic properties forms complex with cations [Benjamin, 2002].
2. Basic functional groups directly add up to cations involving some addition reaction.
3. Lewis acid sites are active towards anions and undergo nucleophilic reactions in solution.

[Alfarra et al., 2004]

4. Lewis base sites react with cations or electrophilic substances in solution [Alfarra et al., 2004]

1.3.4 Advantages of using ACC

1. It is highly porous and provides larger surface area for adsorption.
2. There are two main types of activated carbon applied for waste water treatment namely granular activated carbon and powdered activated carbon. The main characteristic that differentiates the two types is their particle size. Advantage of using ACC is its higher uniformity constant that eases the process of backwashing by minimize desorption process and providing a better stratified arrangement and also controls the preterm breakthrough.
3. Moreover, the effectiveness of adsorption treatment with ACC is determined by the type of substance to be removed. Substances with a higher molecular weight and low water solubility are better adsorbed with ACC. Other factors like, presence of other organic compounds, temperature, pH, also effect rate of adsorption.
4. ACC is majorly used as its properties like surface area and pore size distribution can be altered as the experimental needs.

Fig.1.3 Granular Activated Carbon

1.4 OBJECTIVES

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

- To perform the simultaneous adsorption of OPD (O) and Indole (I) onto low cost adsorbent such as commercial grade activated carbon (ACC) at various temperatures (303 K and 318 K) from O-I binary aqueous solution.
- To perform the equilibrium adsorption data analysis using various multicomponent competitive isotherm models isotherm models such as non-modified and extended Langmuir isotherm, extended Freundlich model, Sheindorf–Rebuhn–Sheintuch (SRS) model, and non-modified and modified competitive Redlich-Peterson isotherm model.

CHAPTER 2 ADSORPTION THEORY

2.1 Adsorption

There are many pollution abatement methods that have been reported in literature which includes some physiochemical approaches and microbial degradation methods. Adsorption is one such well-established method of subsiding the harmful chemicals from the solutions. It is a physiochemical method of treating wastewater. Purification of air and water using the adsorption technique has played a major role in pollution control and adsorption of dissolved impurities from water is majorly practiced to clean the waste water. There are various advantages of using adsorption technique including economical, ecological, and technological advantages. Adsorption generally shows high removal efficiency as compared to other techniques for treating domestic and industrial effluents.

Chemical adsorption can be of two types namely Physiosorption and Chemisorption. Adsorption can be a physiosorption (characteristics of van der Waal forces which are weaker type of interactions) or chemisorption (characteristics of stronger covalent forces) depending on nature of bondings between the adsorbent and adsorbate molecules (Table 2.1)

Table 2.1 Comparison between physiosorption and chemisorption

Physiosorption	Chemisorption
Forces operating are weak van der Waals forces of attraction	Ionic or covalent chemical bonds
Heat of adsorption is low (20-40 kJ mol^{-1})	Heat of adsorption is high (80-240kJmol^{-1})
Reversible process	Irreversible process
No need of any activation	Activation energy is needed
Forms multimolecular layer	Forms unimolecular layer
Adsorption takes place at temperature close to condensation temperature of adsorbate	Occurs at wider range of temperatures and at temperature above the condensation temperature.

2.2 MECHANISM INVOLVED IN ADSORPTION

Adsorption can better be given by the following equation:

$$\textbf{Adsorbate + Adsorbent} \xrightleftharpoons[\text{(Desorption)}]{\text{(Adsorption)}} \textbf{Adsorption}$$

Adsorption is the adhesion of molecules from a dissolved solid, liquid or gas to a surface resulting in the formation of thin layer of adsorbate over the adsorbent surface. When a solid surface is exposed to a liquid, molecules from the solution phase accumulates at the surface. This phenomenon of concentration of molecules at a solid surface is adsorption.

- Adsorbate: The substance that concentrates at the surface is called adsorbate.
- Adsorbent: Surface over which the adsorption takes place is termed as adsorbent surface. Higher abrasion resistance, greater thermal stability and smaller pore size to get larger exposed area are features of good adsorbents.

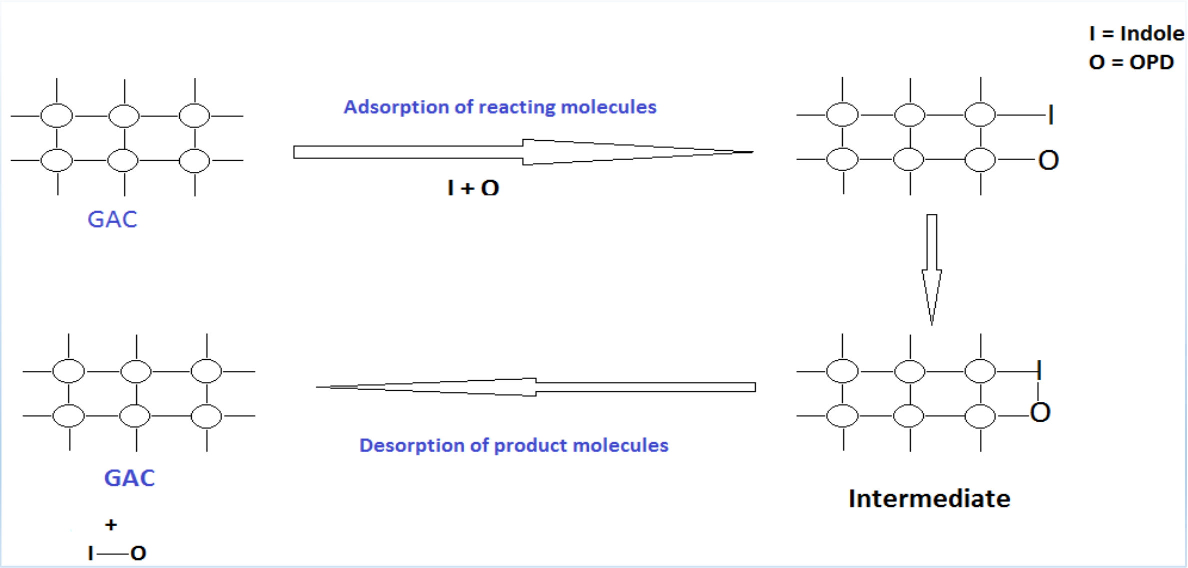


Fig. 2.1 Mechanism of adsorption

2.3 ADSORPTION ISOTHERMS

To study equilibrium characteristics of monocomponent adsorption, isotherms models like Langmuir, Freundlich, and Redlich-Peterson are used extensively. And for the multicomponent adsorption, the extensions of these basic isotherm models are used viz. modified, non-modified and extended Langmuir model; SRS model and extended Freundlich; the modified and non-modified R-P models.

Table 2.2 Various multicomponent isotherm models

Model	Equation	Reference
Non-modified competitive Langmuir Model	$q_{e,i} = \frac{q_{m,i} K_{L,i} C_{e,i}}{1 + \sum_{j=1}^{N} K_{L,j} C_{e,j}}$	(Srivastava et. al., 2006)
Extended Langmuir isotherm model	$q_{e,i} = \frac{q_{\max} K_i C_{e,i}}{1 + \sum_{j=1}^{N} K_j C_{e,j}}$	(Yang, 1987)
Extended Freundlich model	$q_{e,1} = \frac{K_{F,1} C_{e,1}^{n_1 + x_1}}{C_{e,1}^{x_1} + y_1 C_{e,2}^{z_1}}$ $q_{e,2} = \frac{K_{F,2} C_{e,2}^{n_2 + x_2}}{C_{e,2}^{x_{21}} + y_2 C_{e,1}^{z_2}}$	(Srivastava et. al., 2006)
Sheindorf–Rebuhn–Sheintuch (SRS) Model	$q_{e,i} = K_{F,i} C_{e,i} \left(\sum_{j=1}^{N} a_{ij} C_{e,j} \right)^{n_i - 1}$	(Sheindorf et al., 1981)
Non-modified competitive Redlich-Peterson model	$q_{e,i} = \frac{K_{R,i} C_{e,i}}{1 + \sum_{j=1}^{N} a_{R,j} C_{e,j}^{\beta,j}}$	(Srivastava et. al., 2006)
Modified competitive Redlich-Peterson Mode	$q_{e,i} = \frac{K_{R,i} \left(C_{e,i} / \eta_{R,i} \right)}{1 + \sum_{j=1}^{N} a_{R,j} \left(C_{e,j} / \eta_{R,j} \right)^{\beta,j}}$	(Srivastava et. al., 2006)

CHAPTER 3 LITERATURE REVIEW

Many different techniques have been reported in literature to degrade the organic impurities present in wastewaters. In this chapter, various adsorption studies of OPD and Indole on different adsorbents have been reviewed and presented below. Mainly the techniques are classified as physiochemical methods and microbial degradation methods.

3.1 DEGRADATION OF INDOLE BY METHODS OTHER THAN ADSORPTION

Considerable research has been reported in literature regarding the biological ways of Indole degradation and its conversions to lesser harmful compounds.

Fukuoka et al. (2015) have studied the biotransformation of Indole in a soil bacterium Cupriavidus Strain KK10. Various indole bio products were revealed and a number of indole biotransformation pathways were found. Most of these pathways involve oxidation of Indole followed by either carbocyclic ring cleavage or oxidation of Indole ring.

Persolvent fermentation is also applied for biodegradation of Indole [Katapodis et al., 2007]. Thermophilic fungus, was grown in a persolvent fermentation system containing large amount of Indole. The medium is composed of 20% by volume soybean oil (as a second phase) and 2 gram per liters of Indole. Then the Fungus was grown in the system and Indole was completely consumed within 6 days. Fed-batch were performed with 1gL^{-1} Indole supplement and degradation rates of Indole were measured for 4 days. The biodegradation rate was found to 3 g per L.

A similar degradation attempt was made by Chen et al. (2013). They used endophytic Fungus Phomopsis liquidambari to degrade the Indole. Indole was the only source of carbon and nitrogen and hence an optimum concentration of Indole was supplied that was100mg L^{-1}. 41.7% Indole was degraded within 120 hours. Then plant litter was added exogenously that increased the Indole degradation rate to 99.1% within 60 hours. In this degradation, Indole firstly get converted to oxindole and isatin, afterwards the degradation proceeds through C-N bond cleavage in pyridine ring.

Yin B et al. (2005) studied the degradation of Indole using Pseudomonas aeruginosa Gs. The enrichment culture was made in a minimum salts medium with Indole as the only source of carbon and energy. For the immunization of MSM containing 1.0 gL^{-1} yeast, individual colonies of pure culture were selected. Then each set was incubated at 140 rpm and 30°C for

24 hours. Results confirmed Indole degradation in 3-4 days and degradation followed the zero order kinetics.

Wang et al. (2014) studied the degradation of Indole present in soil by fungal strain Phomopsis liquidambari B3. Bio-augmented soil microcosms, were inoculated with 40 g fungus strain inoculum (SA) for 40 days at 28°C in darkness. Results of this experiment confirmed the 93.7% decrease in indole by the end of 40 days, while the biostimulated and control microcosm's values were much lower.

Doukyu and Aono (1997) have studied the indole degradation at higher concentration using the persolvent fermentation method. They used the Pseudomonas sp. Strain ST-200 in this experiment, which grew in a system containing persolvent. For the analysis of results, low resolution electron impact mass spectrometry was applied for the analysis. For this samples were ionized at 230°C at 70eV.^{1}H-NMR spectra and ^{13}C-NMR were recorded at 500 MHz and 50 MHz respectively. Results showed that about 98% of indole was consumed after 48 hrs.

Gu et al. (2002) used some marine sediment to degrade the indole. Indole was degraded under sulphate-reducing and methanogenic conditions. Anaerobic technique named as Serum bottle was used was used. Final identification of intermediates was done using mass spectrometer. Degradation yielded two intermediates identified as oxindole and isatin. Studies confirmed that both conditions use an identical pathway for degradation.

Gai et al. (2010) applied electrochemical oxidation technique to degrade Indole. They employed contact glow discharge electrolysis (CGDE) for the degradation. Indole was largely degraded by this electrolysis method with water. The degradation products after being analysed, were found to inorganic nitrogen and inorganic carbon.

Qu et al., (2015) studied the degradation of Indole using newly isolated bacterial strain named Cupriavidus sp. SHE. Indole was used as the only source of carbon for the experiment. Indole concentrations were determined at 48 hours after inoculation. Strain was found to degrade indole within 24hrs and was found to still harbour the high capacity of indole degradation within pH 4-9 and temperature 25°C and 35°C. To determine the intermediate species of degradation consequence HPLC and mass spectrum analysis were employed. Genome analysis of the bacterium showed the presence of oxidoreductases that was the main reason for efficient degradation of indole.

3.2 ADSORPTIVE REMOVAL OF INDOLE

Mitome et al. (2013) studied the adsorption of Indole on mesoporous carbon which were activated by KOH. For this, firstly mesoporous carbons were synthesized using a soft-templating method and then these carbons were made more efficient for the purpose of adsorption by activating them with KOH. The reason for much better adsorption after KOH treatment were the increased surface area and micropore volume. An artificial intestinal solution containing indole and a buffer solution was made to study the adsorption. The results showed that KOH activated carbon were having higher capacity to adsorb indole. Adsorption equilibrium was established by using Langmuir model of isotherm.

Hiwarkar et al. (2014) investigated the comparative studies for removal of indole using adsorption process with granular activated carbon (ACC) and bagasse fly ash (BFA). They optimized various parameters like pH, contact time, adsorbent dose, and temperature. The adsorbent dose for BFA was 7g/L in equilibrium time of 3 hours whereas for ACC the 20g/L adsorbent dose was given for the equilibrium time of 7 hours. According to the kinetic studies, adsorption followed the pseudo-second order model and equilibrium data was given by Redlich-Peterson isotherm. BFA proved to be a better adsorbent as compared to the ACC as it worked for a wider pH range. Thermal desorption cycles study revealed that ACC can be repeatedly used for more than five cycles whereas BFA cannot be used again as its adsorbing capacity decreases to large extent during repeated desorption-adsorption cycles. Indole removal under the optimum conditions of pH 5.7 were found to be 95% for both ACC and BFA.

Abdullah et al. (2004) studied the adsorption of indole and 2-methylindole on ligand-exchange matrix. They observed that the adsorption equilibrium was well represented by Langmuir & Freundlich isotherm.

Mishra et al. (2008) studied the Indole sorption from aqueous solution on to rice husk ash (RHA) and granular activated carbon (ACC). The thermodynamic calculations indicated that the adsorption process was endothermic in nature, and the Toth and Redlich–Peterson isotherm equations well represented the equilibrium data. The maximum indole adsorption of 90% occurred at the pH 6.2 for RHA, and 91% at pH 6.5 for ACC.

3.3 DEGRADATION OF OPD BY METHODS OTHER THAN ADSORPTION

Ejhieh and Salimi (2011) studied the OPD degradation using the heterogeneous photo catalysis process. They used CuO/X zeolite catalyst that was prepared by doping copper over the zeolite NaX matrix. Before the photo degradation process, characterization of zeolite was done using the atomic absorption spectroscopy, IR spectroscopy, BET, X-ray diffraction, and thermal analysis method. In photo degradation, some factors affected the degradation rates. These include initial concentration of OPD, amount of catalyst, pH etc. Experimentation of the photo catalysis was a simple process. An optimized amount of catalyst was added to OPD wastewater solution. Solution was irradiated under the sun accompanied by continuous stirring. After the desired time solution was taken off from sunlight and so obtained suspension was centrifuged for 10 min. Then to study the degradation process, UV spectrophotometer was used to measure the absorbance. Study of degradation kinetics revealed that OPD degradation followed the Langmuir-Hinshelwood equation.

Mazekiene and Malinauskas (2002) studied degradation of poly (o-phenylenediamine) (POPD) using electrochemical approach. Working electrode was coated with several layers of POPD using potential cycling procedure. Study of POPD degradation was done using the voltamograms (CVs) that were recorded within potential scan limits of -0.2 to 0.9 V. The overall degradation process was found to follow the first- order kinetics and changes as a function electrode potential.

Sekaran et al. (2010) studied the biodegradation of orthophenylene diamine using intracellular enzymes from citrobacter freundii, and showed that the pseudo-second order model with degradation tendency of about 95.87%.

3.4 ADSORPTIVE REMOVAL OF OPD

Yu et al., (2009) studied the adsorption of endocrine disrupting compound present in wastewater. They mainly studied the effects of preloading of organic matter on adsorption capacity and kinetics under different conditions of concentration. They used granular activated carbon (ACC) for adsorbing the pollutants. ACC with wider pore size has shown better capacity for NOM loading. The equilibrium data was well defined according to the Freundlich isotherm model. They were freeze dried for 48 hours. Preloaded (1, 3, 5, 8 and 16 weeks) ACC (30×40 U.S. mesh fraction) was used to get the isotherms using the bottle point method for each. K_f (Frendlich constant) values showed considerable decrease in first 5-8 weeks. Comparison between the structural changes of virgin and preloaded carbon was analysed using SEM (scanning electron microscope). Effects were seen in the different adsorption capacities and mass transfer rates.

Wang et al., (2013) studied the uptake of OPD by paddy rice and its effect on Cu adsorption in red soil. Seeds of paddy rice were rinsed in cold water for about 24 hours , then in warm water for 10min at 52°C and then again at temperature about 40°C for 5 minutes. pH also effected the rates of adsorption, Cu was better adsorbed at higher pH (greater than 6) values in an ion exchangeable form. At pH lower than 5, no Cu complex was formed. The equilibrium isotherm data was given by the Freundlich isotherm equation. As the concentration of Cu increased, wet weight of paddy rice decreased. With 50mg/kg external concentration of Cu, the bio mass of paddy rice was increased by 40.7%, 98%, and 114% in presence 1.0, 2.0, and 4.0 mmol/kg OPD, respectively. Results also showed that Cu was adsorbed mainly in form of Cu-OPD complex in presence of OPD.

Lataye et al. (2008) reported the adsorption of OPD onto bagasse fly ash from aqueous solution. It was reported that the adsorption followed 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.

CHAPTER 4 MATERIALS AND METHODS

4.1 WASTEWATER

The stock aqueous solution of 1 g/l of each of OPD and Indole were prepared by dissolving their appropriate amount in distilled water. Further, working binary aqueous solutions of OPD and Indole (O-I) was prepared by mixing appropriate volumes of each of Q and P from 1 g/l stock solution of each.

4.2 ADSORBENT AND ITS CHARACTERISTICS

Coconut-based commercial grade activated carbon (ACC) was purchased from Pneumatic Engineers Spares & Service, New Delhi, India. It was used as procured. 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). Detailed characteristics has been reported elsewhere (Singh et al., 2014).

4.3 ANALYTICAL METHOD

To determine the concentration of Indole and Orthophenylene diamine (OPD) after the experiments, the solutions were analysed using UV/VIS spectrophotometer (Perkin Elmer, Schimadzu, Japan) and the absorbance at characteristic wavelengths (270 nm and 285 nm for Indole and OPD, respectively).

To determine the calibration curve of the O-I aqueous mixture, a series of mixtures with different standard concentrations of O and I were prepared and the absorbances (A_1 and A_2) at 270 nm and 285nm wavelengths were measured. For the O-I aqueous mixture, the following simultaneous equations, based on the Lambert–Beer's law, were used to solve for each component concentrations:

$$A_1 = k_{1,1}C_B + k_{1,2}C_A$$

$$A_2 = k_{2,1}C_B + k_{2,2}C_A$$

Where, C_A & C_B are the concentration of O and I solutions, respectively.

The coefficients ($k_{1,1}$, $k_{1,2}$, $k_{2,1}$ and $k_{2,2}$) are obtained from fitting the measured absorbances with known A and B concentrations to above equation from the calibration curve, and the final equations were found as follows:

$$A_1 = 0.0264C_A + 0.031C_B$$

$$A_2 = 0.0121C_A + 0.0424C_B$$

Where, A = OPD (absorbs at 285 nm), B = Indole (absorbs at 270 nm)

4.4 EXPERIMENTAL PROGRAMME

In O-I binary aqueous solution-adsorbent (ACC) systems, for each initial concentration (C_0) of O solution: viz., 0, 100, 200, 300 and 400 mg/l, the I concentration was varied in the range of 0, 100, 200, 300 and 400 mg/l.

Isothermal experiments were conducted at 303 K and 318 K. For each experimental run, 100 ml of O-I binary aqueous solution of known C_o each O and I and pH=5.5 with 20 g/l dose of the adsorbent ACC was taken in a 250 ml stoppered conical flask (pH, dose and equilibrium time was taken as 5.5, 20 g/l and 7 h from preliminary experiments, not shown here).

This mixture was agitated in a temperature-controlled orbital shaker at a constant speed of 150 rpm at 303 K and 318 K. Samples were withdrawn after 7 h . Then after, all the samples were filtered and analysed for the residual O and I concentrations using double beam UV/VIS spectrophotometer.

The values of $q_{e,i}$ (mg /g) and the individual adsorption yield Ad_i (%) were calculated using the following relations**:**

$$q_{e,i} = \left(\frac{C_{o,i} - C_{e,i}}{m} \right) \times v \tag{4.1}$$

$$Ad_i = \left(\frac{C_{o,i} - C_{e,i}}{C_{o,i}} \right) \times 100 \tag{4.2}$$

$$Ad_{Tot} = \left(\frac{\sum (C_{o,i} - C_{e,i})}{\sum C_{o,i}} \right) \times 100 \tag{4.3}$$

The calculated equilibrium adsorption data were further fitted to various multicomponent competitive isotherm models such as non-modified and extended Langmuir isotherm, extended Freundlich isotherm, Sheindorf–Rebuhn–Sheintuch (SRS) model, and non-modified and modified competitive Redlich-Peterson isotherm model (Table 2.2) using non-linear regression technique. In order to calculate isotherm parameters for various multi-component models studied, Marquardt's percent standard deviation (MPSD) (Marquardt, 1963).

$$MPSD = 100\sqrt{\frac{1}{n_m - n_p}\sum_{i=1}^{n}\left(\frac{C_{Rt,i,\exp} - C_{Rt,i,cal}}{C_{Rt,i,\exp}}\right)^2} \qquad (4.5)$$

Where, the subscripts ‘exp’ and ‘cal’ represent the experimental and calculated values, n is the number of measurements, and p is the number of parameters in the model**.**

CHAPTER 5 RESULTS AND DISCUSSIONS

5.1 ADSORPTION ISOTHERM

The simultaneous adsorption of OPD (O) and Indole (I) from binary mixtures on ACC was conducted at two different temperatures (303 K and 318 K), and the experimental data are shown in Table 5.1-5.4. Comparison of non-linearized adsorption isotherms of O in the presence of increasing concentration of I, and of I in the presence of increasing concentration of O onto ACC at 303 K and 318 K are shown in Fig. 5.1-5.2, respectively.

It may be observed that an increase in the initial concentration of O up to 400 mg/l, in the absence of I, increases the equilibrium concentration and decreases the adsorption yield. The initial concentration provides the necessary driving force to overcome the resistances to the mass transfer of adsorbate between the aqueous and the solid adsorbent phases. Furthermore, in binary solution of O and I, increasing the initial concentration of one of the adsorbate affects equilibrium adsorption uptake of another adsorbate from binary mixture due to the interaction between the adsorbates and the adsorbents.

The non-linear adsorption isotherms of O in the presence of increasing concentration of I for ACC are shown in Fig. 5.1a and 5.2a, and corresponding isotherms for I in the presence of increasing concentration of O are shown in Fig. 5.1b and 5.2b at 303 K and 318 K respectively. It may be seen that, at any temperature, the equilibrium adsorption uptake of O increases with increase in initial O concentration i.e., up to 400 mg/l at any constant I concentration, whereas the equilibrium adsorption uptake of O decreases continuously with increasing I concentration.

The equilibrium uptake of O on ACC at $C_{o,O}$=100 mg/l in the absence I ($C_{o,I}$) was found to be 4.9 mg/g, whereas at the $C_{o,I}$= 400 mg/l the equilibrium adsorption uptake of O was found to be 4.1 mg/g (Table 5.1). For I, the equilibrium adsorption uptake at same concentration in the absence and presence of O were observed to be 4.8 mg/g and 3.1 mg/g, respectively (Table 5.3). Commonly, it can be concluded that increase in I concentration decreases the adsorption yield of O, and was found true at all the temperature studied (Table 5.1 and 5.2, Fig. 5.1a and 5.2a). Identical approach were observed in the equilibrium uptake of I on with increasing O concentration (Fig. 5.1b and 5.2b).

Table 5.1 Comparison of individual and total adsorption equilibrium uptakes and yields found at different OPD concentrations in the presence of increasing concentrations of Indole onto ACC at 303 K. (Dose=20 g/l, t=7h, pH=5.5)

$C_{0,O}$	$C_{0,I}$	$C_{e,O}$	$Q_{e, exp, O}$	$C_{e,I}$	$Q_{e, exp, I}$	$Ad_O\%$	$Ad_I\%$
0	0	0	0	0	0	0	0
100	0	2.0844	4.89578	0	0	97.9156	0
200	0	17.465	9.12675	0	0	91.2675	0
300	0	72.868	11.3657	0	0	75.71067	0
400	0	140.624	12.9688	0	0	64.844	0
0	100	0	0	4.183	4.79085	0	95.817
100	100	8.80	4.56	19.71	4.0145	91.204	80.29
200	100	53.82	7.31	31.5	3.425	73.0895	68.5
300	100	120.60	8.97	35.21	3.2395	59.79933	64.79
400	100	191.11	10.44	38.62	3.069	52.22375	61.38
0	200	0	0	11.35	9.4325	0	94.325
100	200	11.81	4.41	31.12	8.444	88.19	84.44
200	200	56.74	7.16	43.63	7.8185	71.63	78.185
300	200	122.34	8.88	52.37	7.3815	59.22	73.815
400	200	194.73	10.26	61.37	6.9315	51.3175	69.315
0	300	0	0	24.69	13.7655	0	91.77
100	300	12.89	4.36	55.6	12.22	87.114	81.46667
200	300	59.41	7.03	59.4	12.03	70.2975	80.2
300	300	128.34	8.58	73.61	11.3195	57.22	75.46333
400	300	202.93	9.85	107.18	9.641	49.26775	64.27333
0	400	0	0	64.219	16.78905	0	83.94525
100	400	18.85	4.06	80.13	15.9935	81.148	79.9675
200	400	63.94	6.80	106.65	14.6675	68.0325	73.3375
300	400	139.83	8.01	138.12	13.094	53.39133	65.47
400	400	210.82	9.46	155.94	12.203	47.2945	61.015

Table 5.2 Comparison of individual and total adsorption equilibrium uptakes and yields found at different OPD concentrations in the presence of increasing concentrations of Indole onto ACC at 318 K. (Dose=20 g/l, t=7h, pH=5.5)

$C_{0,O}$	$C_{0,I}$	$C_{e,O}$	$Q_{e,\,exp,\,O}$	$C_{e,I}$	$Q_{e,\,exp,\,I}$	$Ad_O\%$	$Ad_I\%$
0	0	0	0	0	0	0	0
100	0	6.35	4.6825	0	0	93.65	0
200	0	29.5	8.525	0	0	85.25	0
300	0	80.3	10.985	0	0	73.23333	0
400	0	143.67	12.8165	0	0	64.0825	0
0	100	0	0	4.25	4.7875	0	95.75
100	100	8.1428	4.5928	11.968	4.4016	91.8572	88.032
200	100	45.226	7.7387	15.67	4.2165	77.387	84.33
300	100	105.175	9.7412	18.94	4.053	64.94167	81.06
400	100	155.924	12.203	26.72	3.664	61.019	73.28
0	200	0	0	10.13	9.4935	0	94.935
100	200	8.32	4.584	29.32	8.534	91.68	85.34
200	200	47.35	7.6325	33.26	8.337	76.325	83.37
300	200	107.92	9.604	43.73	7.8135	64.02667	78.135
400	200	163.21	11.8395	51.27	7.4365	59.1975	74.365
0	300	0	0	19.41	14.0295	0	93.53
100	300	9.273	4.536	40.88	12.956	90.727	86.37333
200	300	51.2745	7.4363	53.91	12.3045	74.36275	82.03
300	300	113.1177	9.3441	66.89	11.6555	62.2941	77.70333
400	300	167.1945	11.64	78.83	11.0585	58.20138	73.72333
0	400	0	0	35.43	18.2285	0	91.1425
100	400	10.704	4.4648	68.69	16.5655	89.296	82.8275
200	400	73.05	6.3475	95.37	15.2315	63.475	76.1575
300	400	130.868	8.277	121.61	13.9195	56.37733	69.5975
400	400	187.74	10.613	135.83	13.2085	53.065	66.0425

Table 5.3 Comparison of individual and total adsorption equilibrium uptakes and yields found at different Indole concentrations in the presence of increasing concentrations of OPD onto ACC at 303 K. (Dose=20 g/l, t=7h, pH=5.5)

$C_{0, I}$	$C_{0, O}$	$C_{e, I}$	$Q_{e, exp, I}$	$C_{e, O}$	$Q_{e, exp, O}$	Ad_I%	Ad_O%
0	0	0	0	0	0	0	0
100	0	4.183	4.79085	0	0	95.817	0
200	0	11.35	9.4325	0	0	94.325	0
300	0	24.69	13.7655	0	0	91.77	0
400	0	64.219	16.78905	0	0	83.94525	0
0	100	0	0	2.084	4.8958	0	97.916
100	100	19.71	4.0145	8.8	4.56	80.29	91.2
200	100	31.12	8.444	11.81	4.4095	84.44	88.19
300	100	55.60	12.22	12.89	4.3555	81.46667	87.11
400	100	80.13	15.9935	18.85	4.0575	79.9675	81.15
0	200	0	0	17.46	9.127	0	91.27
100	200	31.50	3.425	53.82	7.309	68.5	73.09
200	200	43.63	7.8185	56.74	7.163	78.185	71.63
300	200	59.40	12.03	59.41	7.0295	80.2	70.295
400	200	106.65	14.6675	63.94	6.803	73.3375	68.03
0	300	0	0	72.86	11.357	0	75.71333
100	300	35.21	3.2395	120.6	8.97	64.79	59.8
200	300	52.37	7.3815	122.34	8.883	73.815	59.22
300	300	73.61	11.3195	128.34	8.583	75.46333	57.22
400	300	138.12	13.09425	139.83	8.0085	65.47125	53.39
0	400	0	0	140.62	12.969	0	64.845
100	400	38.62	3.06885	191.11	10.4445	61.377	52.2225
200	400	61.37	6.9315	194.73	10.2635	69.315	51.3175
300	400	107.18	9.6409	202.93	9.8535	64.27267	49.2675
400	400	155.94	12.2028	210.82	9.459	61.014	47.295

Table 5.4 Comparison of individual and total adsorption equilibrium uptakes and yields found at different Indole concentrations in the presence of increasing concentrations of OPD onto ACC at 318 K. (m=20 g/l, t=7h, pH=5.5)

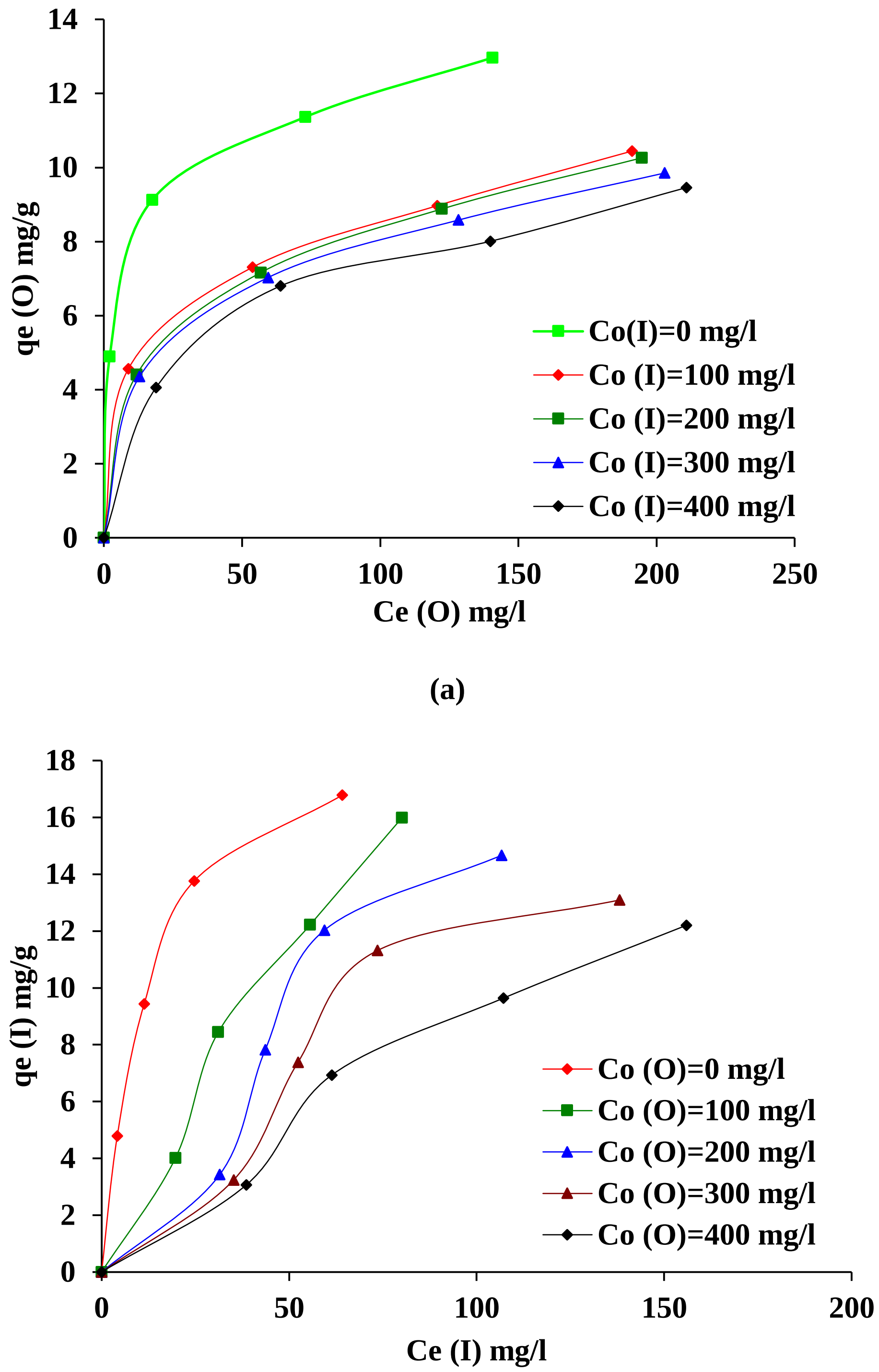
$C_{0,I}$	$C_{0,O}$	$C_{e,I}$	$Q_{e,exp,I}$	$C_{e,O}$	$Q_{e,exp,O}$	$Ad_I\%$	$Ad_O\%$
0	0	0	0	0	0	0	0
100	0	4.25	4.7875	0	0	95.75	0
200	0	10.13	9.4935	0	0	94.935	0
300	0	19.41	14.0295	0	0	93.53	0
400	0	35.43	18.2285	0	0	91.1425	0
0	100	0	0	6.35	4.6825	0	93.65
100	100	11.968	4.4016	8.1428	4.59286	88.032	91.8572
200	100	29.32	8.534	8.32	4.584	85.34	91.68
300	100	40.88	12.956	9.273	4.53635	86.37333	90.727
400	100	68.69	16.5655	10.7	4.465	82.8275	89.3
0	200	0	0	29.5	8.525	0	85.25
100	200	15.67	4.2165	45.226	7.7387	84.33	77.387
200	200	33.26	8.337	47.35	7.6325	83.37	76.325
300	200	53.91	12.3045	51.27	7.4365	82.03	74.365
400	200	95.37	15.2315	73.05	6.3475	76.1575	63.475
0	300	0	0	80.3	10.985	0	73.23333
100	300	18.947	4.05265	105.17	9.7415	81.053	64.94333
200	300	43.73	7.8135	107.92	9.604	78.135	64.02667
300	300	66.893	11.65535	113.117	9.34415	77.70233	62.29433
400	300	121.615	13.91925	130.8	8.46	69.59625	56.4
0	400	0	0	143.67	12.8165	0	64.0825
100	400	26.72	3.664	155.92	12.204	73.28	61.02
200	400	51.27	7.4365	163.21	11.8395	74.365	59.1975
300	400	78.83	11.0585	167.19	11.6405	73.72333	58.2025
400	400	135.83	13.2085	187.74	10.613	66.0425	53.065

Generally, the multicomponent adsorption behavior can be explained in three ways; synergism (the effect of the mixture is greater than that single components in the mixture), antagonism (the effect of the mixture is less than that of each of the components in the mixture) and non-interaction (the mixture has no effect on the adsorption of each of the adsorbates in the mixture) (Srivastava et al., 2006). The combined effect of the binary mixture of O and I seems to be antagonistic (Table 5.1-5.4) at all the temperatures. These antagonistic effects can be analyzed by comparing the adsorption of two components in single and binary components system. As an example, from Table 5.2, it was expected that the total adsorption yield was found to be 77.61 % for the initial concentration of 400 mg/l of each component, containing total concentration of 800 mg/l of O and I in the mixture [Ad_T %=77.61%= 100×[(64.08% of O +91.14% of I]/800 mg/l of initial concentration]. However, the experimental total adsorption yield was found to be only 59.55% [Ad_{Tot}%=59.55%= 100×[(53.06% of O)+(66.047% of I)]/800 mg/l of initial concentration]. Thus, it can be concluded that the binary mixture of O and I exhibits antagonistic effect on adsorption resulting in lower sorption yield.

Furthermore, it can also be observed that the equilibrium uptake of binary adsorption on ACC is quite high for I as compared to O at all the temperature studied. This is due to the fact that there is little competitive adsorption indicating either the adsorption potential is dominated by solute-solvent interactions.

5.2 Adsorption Isotherm Modelling

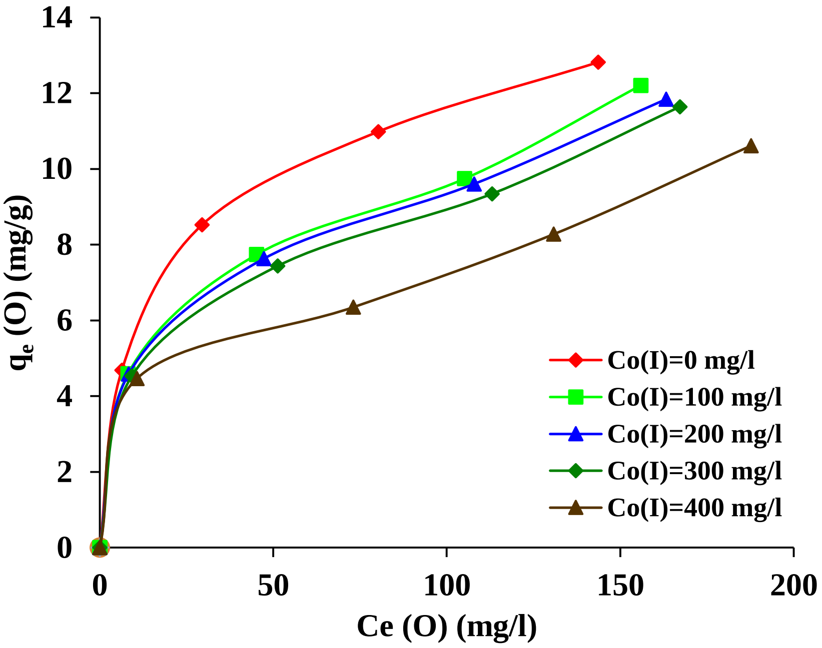
In order to design an adsorption system, it is required to correlate the equilibrium adsorption data with the multicomponent adsorption isotherm models. In the present study, equilibrium adsorption data for simultaneous adsorption of Q and P at various temperatures (303 K and 318 K) were fitted to various multicomponent competitive isotherm models (non-modified and extended Langmuir isotherm, extended Freundlich isotherm, Sheindorf–Rebuhn–Sheintuch (SRS) model and non-modified and modified competitive Redlich-Peterson isotherm model). The parametric values for all the isotherm models and MPSD values between the experimental and calculated q_e values are shown in Table 5.5.



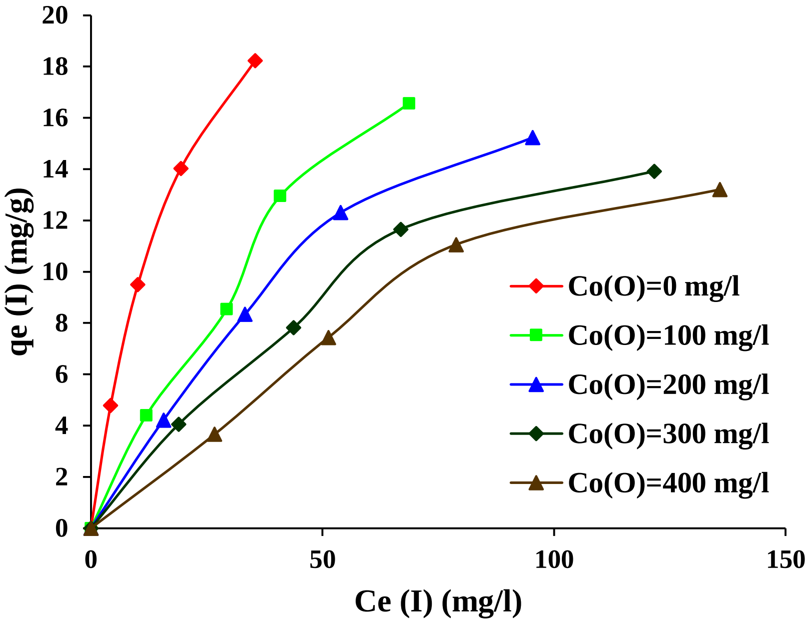
(a)

(b)

Fig. 5.1 Comparison of non-linearized adsorption isotherms of (a) OPD in the presence of increasing concentration of I, and (b) Indole in the presence of increasing concentration of OPD onto ACC at 303 K (pH=5.5, t=7h, ACC dosage=20 g/l)



(a)



(b)

Fig. 5.2 Comparison of non-linearized adsorption isotherms of (a) OPD in the presence of increasing concentration of I, and (b) Indole in the presence of increasing concentration of OPD onto ACC at 318 K (pH=5.5, t=7h, ACC dosage=20 g/l)

5.2.1 Isotherm models for adsorption of OPD and Indole onto ACC

From the comparisons of experimental and calculated values of q_e using MPSD error function, the extended Freundlich isotherm model and SRS models best fit the experimental data from binary adsorption of O and I onto ACC at all the temperatures (303 K and 318 K) studied (Table 5.5). The MPSD for extended Freundlich model and SRS model were found to be 16.06 and 16.46, and 12.68 and 13.12 at 303 K and 318 K, respectively, for the adsorption O and I on ACC (Table 5.5).

This is expected that ACC have heterogeneous surface, and the single component adsorption of O onto ACC have also been reported to follow the Freundlich adsorption isotherm (Yu et al., 2009). Therefore, the binary adsorption of O and I on ACC can be represented satisfactorily and adequately by the extended Freundlich isotherm model. Whereas, the SRS model, which is also based on Freundlich isotherm model, fitted next to extended Freundlich model with MPSD values of 16.46 and 13.12 for at 303 K and 318 K, respectively.

Furthermore, the competition coefficient, $a_{ij,}$ describes the adsorption reticence on component *i* due to presence of component *j*. In the present study, the competition coefficient at T=318 K, the a_{IO} and a_{OI} values were found to be 1.53 and 0.063 (Table 5.5), respectively, indicating that the inhibition in adsorption of I in the presence of O is higher as compared to the inhibition in adsorption of O in the presence of I. This was followed at all the temperatures studied.

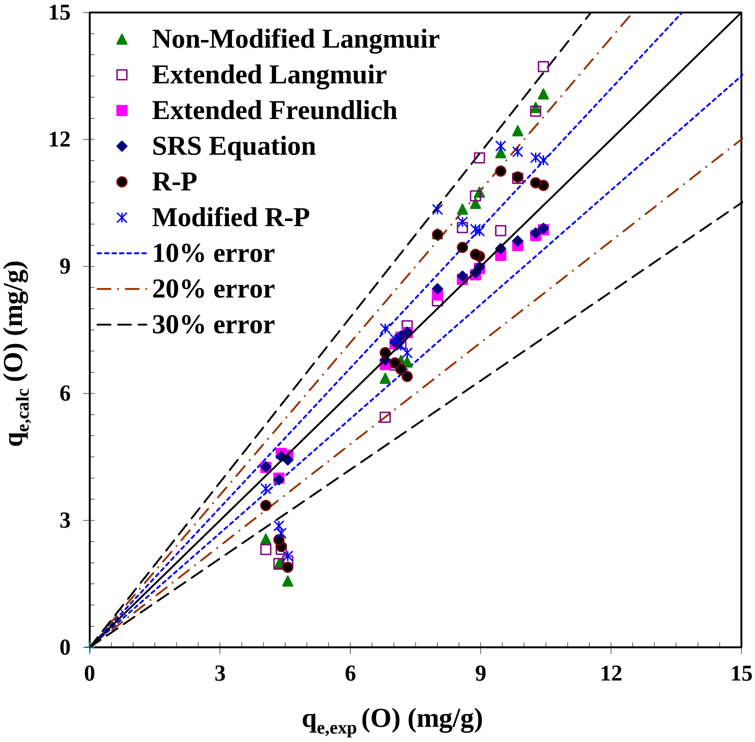
The K_L value, which is non-modified Langmuir isotherm model parameters, increased from 0.009 to 0.011for O, and 0.004 to 0.015 for I for 303 K and 318 K, respectively, showing increasing temperature favours the adsorption. Also, q_{max} value is increased from 21.3 to 25.18 at increased temperature from 303 K and 318 K, respectively.

The comparisons of experimental and calculated q_e values of O and I onto ACC have also been represented in parity graph (Fig. 5.3 and 5.4). The best fitment of experimental binary adsorption data of O and I onto ACC at 303 K and 318 K on extended Freundlich isotherm model can also be seen, where all of the data points are distributed around 45^o and 10% error line. The Langmuir model which shows a poor fit to the experimental data when compared to Freundlich model with the MPSD values of 31.79 and 29.38 at 303 K and 318 K, respectively (Table 5.5).

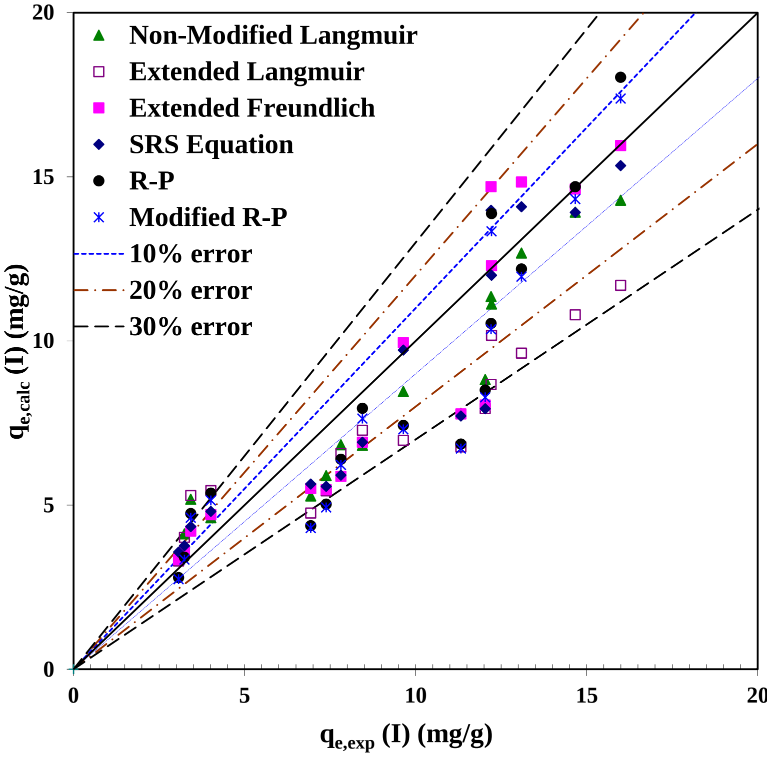
The non-modified and modified R-P models showed high and nearly same MPSD vales; 27.9 and 27.1, and 27.28 and 26.83, at 303 K and 318 K, respectively. The fits of these models are comparable to the fits of the Langmuir based models (Table 5.5 and Fig 5.3 and 5.4).

Table 5.5 Multicomponent isotherm parameters for the simultaneous adsorption of OPD (O) and Indole (I) by ACC

At 303 K					**At 318 K**				
Non-modified Langmuir Model									
Adsorbate	q_m	K_L			Adsorbate	q_m	K_L		
O	21.17	0.009			O	27.29	0.011		
I	61.83	0.004			I	33.91	0.015		
MPSD	31.79				MPSD	29.38			
Extended Langmuir Model									
Adsorbate	K_i	$q_{\max}$			Adsorbate	K_i	$q_{\max}$		
O	0.016	21.3			O	0.016	25.18		
I	0.02				I	0.026			
MPSD	34.61				MPSD	29.54			
Extended Freundlich Model									
Adsorbate	x_i	y_i	z_i		Adsorbate	x_i	y_i	z_i	
O	0.922	0.091	1.03		O	0.725	0.0005	1.91	
I	0.451	7.02	0.398		I	1.18	0.773	0.868	
MPSD	16.06				MPSD	12.68			
SRS Model									
Adsorbate	a_{ij}	a_{ji}	n	K_F	Adsorbate	a_{ij}	a_{ji}	n	K_F
O	1	0.067	0.186	3.83	O	1	0.063	0.242	3.06
I	432.5	1	0.685	3.28	I	1.53	1	0.425	2.308
MPSD	16.46				MPSD	13.12			
Non-modified competitive R-P Model									
Adsorbate	K_R	a_R	β		Adsorbate	K_R	a_R	β	
O	1.05	1.77	0.839		O	0.623	0.107	0.777	
I	1.32	2.7	0.01		I	0.951	0.065	0.774	
MPSD	27.9				MPSD	27.104			
Modified R-P Model									
Adsorbate	$\eta_{R,i}$				Adsorbate	$\eta_{R,i}$			
O	0.848				O	0.907			
I	1.05				I	1.07			
MPSD	27.28				MPSD	26.83			

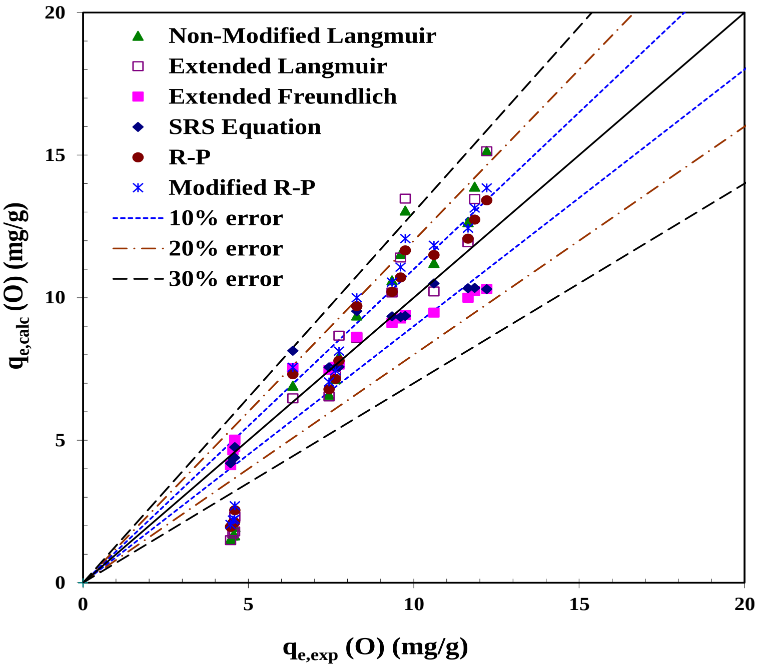


(a)

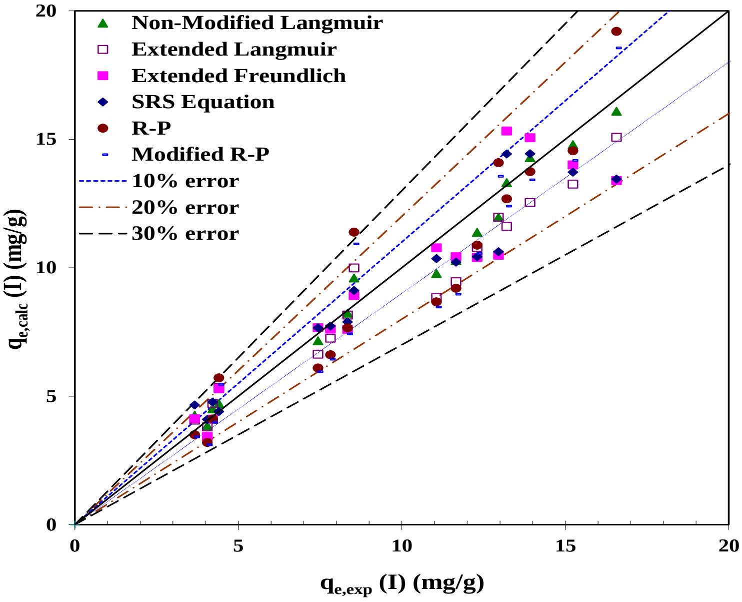


(b)

Fig. 5.3 Comparison of the experimental and calculated q_e values of (a) OPD (O) (b) Indole (I) in a binary mixture of O and I by ACC 303 K.



(a)



(b)

Fig. 5.4 Comparison of the experimental and calculated q_e values of (a) OPD (O) (b) Indole (I) in a binary mixture of O and I by ACC 318 K

CHAPTER 6 CONCLUSIONS

The following conclusions are drawn from the present study:

1. In binary solution of O and I, increasing the initial concentration of one of the adsorbate affects equilibrium adsorption uptake of another adsorbate from binary mixture.
2. At any temperature, the equilibrium adsorption uptake of O increases with increase in initial concentration of O at any constant I concentration, whereas the equilibrium adsorption uptake of O decreases continuously with increasing I concentration.
3. It was be observed that the equilibrium uptake of binary adsorption on ACC is quite high for I as compared to O at all the temperature studied
4. At the equilibrium OPD and Indole removal decreased with increasing concentration of the other adsorbate, and the combined action of OPD and Indole adsorption was found to be antagonistic.
5. The extended Freundlich isotherm model and SRS models best represented the experimental data from binary adsorption of OPD and Indole at all the temperatures (303 K and 318 K) studied.
6. Inhibition in adsorption of Indole in the presence of OPD is higher as compared to the inhibition in adsorption of OPD in the presence of Indole.
7. The adsorption capacity of ACC in the binary mixtures were found to be quite high for Indole as compared to OPD at all the temperature studied.

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