SYNTHESIS OF PYROLYSIS CHAR FROM PLASTIC AND MICRO-PLASTIC WASTE MATERIALS AND APPLICATION THEREOF

(M.E. PROJECT)

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DECLARATION OF ORIGINALITY AND COMPLIANCE OF ACADEMIC ETHICS

I hereby declare that this thesis contains literature survey and original research work by the undersigned candidate, as part of his "Master of Engineering in Chemical Engineering" studies. All information in this document have been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to research work.

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CERTIFICATION

This is to certify that Mr. Rajdip Batabyal, final year student in Master of Chemical Engineering examination in the department of Chemical Engineering, Jadavpur University, bearing Registration No: 163438 of 2022-23 has successfully completed the thesis work entitled "Synthesis of Pyrolysis Char from Plastic and Micro-Plastic Waste Materials and Application Thereof" under the guidance of Prof. Papita Das during his master's degree curriculum. This work has not been reported earlier anywhere and can be approved for submission in partial fulfilment of the requirements for the Master of Engineering in Chemical Engineering.

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This thesis is hereby approved as creditable study of an engineering subject carried out and presented in a manner satisfactory to warrant its acceptance as prerequisite to the degree for which it has been submitted. It is understood by this approval that undersigned don't endorse or approve any statement made, opinion expressed or conclusion drawn therein but approve the thesis only for purpose of which it is submitted.

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Abstract

Water scarcity has become a critical global concern exacerbated by population growth, globalization, and industrial expansion, resulting in the production of wastewater containing a wide variety of contaminants. To tackle this challenge, it is necessary to adopt innovative materials and technologies for effective wastewater treatment. This thesis paper provides a comprehensive exploration of the preparation, applications, mechanisms, and economic environmental analysis of plastic char and its various forms in wastewater treatment. The utilization of plastic char in wastewater treatment, particularly in adsorption is thoroughly investigated. The significance of plastic char in adsorption of pollutants such as dye, pharmaceuticals and organics are examined. In this study, the pyrolysis of waste plastic was done in muffle furnace at a temperature of 550◦C for a time period of 3 hours. The paper primarily focuses on the adsorption of dye using two types of plastic char. One is plastic char annealed and other one is plastic char which is treated with NaOH and then annealed. By exploring the latest advancements and insights into various forms of plastic char and also using mixture of corn husk char and plastic char, this paper aims to contribute to the development of more efficient and sustainable wastewater treatment strategies.

1. Introduction

Plastic has been an indispensable tool for raising people's living standards for over fifty years. The medical, construction, transportation, packing, and other sectors all depend on it as a vital component of new product development. Rapid worldwide population expansion has increased the demand for essential plastics. With increase in usage of plastic, there has been an increase of plastic waste. The production of plastic on a global scale has seen a substantial increase over the past seven decades, and it is projected to hit a new record high of 359 million tonnes in 2020 [1]. Plastic waste is a burden to nature. Now the continued rising of plastic demand has led to the growth in waste accumulation every year.

With increase in waste incineration or land filling has proved to be equally hazardous for nature. Mechanical recycling is widely used, and it involves treating plastic waste with a series of methods such as hot washing in detergent solutions, sorting, dry cleaning, and air classification. However, only a small fraction of plastic waste can be mechanically recycled due to the potential for contamination [2].

Now pyrolysis has been found as an effective way to reduce the contamination of plastic waste. Pyrolysis can be defined as the thermal decomposition of materials at a very high temperature in an inert atmosphere, that is, in the absence of oxygen. Excessive vibrations at high temperature results in the breaking of long carbon chain molecules to smaller molecules. The products obtained from the pyrolysis of material (mainly organic material) are a solid char, condensable liquids and non-condensable gasses.

The pyrolysis oil obtained as an end product of pyrolysis, can be used as an effective fuel as it has high calorific value. So it can be used as a potential fuel if significant amount of oil can be extracted. Various researchers are conducting researches, so that it can be used as an alternative fuel. Also coming to another end product, plastic char can be used as adsorbent in the scenario of water pollution.

Now coming to the present scenario, water pollution has resulted in a severe crisis and has led to shortage of natural water resources. With increase in industrialization, the entry of wastewater has increased in the environment thereby endangering microorganisms, plants, animals, aquatic and most importantly human life [3],[4]. The present rapid urbanization and industrialization era presents significant challenges that require attention [5] .

Various studies have reported that approximately 15 % of dyes enter the water bodies after being used in various industries through sewage [6] and contribute to about 20 % of water pollution [7]. The dyes used in various industries are synthetic dyes that have high solubility in water [8]. Due to the resistant and complex structure of dyes, their removal from the environment has always been a concern for researchers [9]. Now it has been seen that the solid char obtained from the pyrolysis of plastic can be used to adsorb dyes from dye solution. Here dye is considered as the pollutant.

On the basis of category of synthetic dye, this paper focuses on adsorption of two major types of dye, one is cationic dye and another is anionic dye, using various forms of plastic char. Now coming to the scenario of cationic dyes, these dyes can be dissociated into positively charged ions in aqueous solution. So a plastic char with a negative group on it can adsorb the dye better. While in the case of anionic dye, the dye molecules

dissociate into negatively charged ions when added to water. So a scenario of positive charges on the adsorbent will help in better removing the dye from the solution. This study comprises of using two types of plastic char, one is plastic char annealed and another is plastic char which is treated with NaOH and then annealed. Methylene blue, a cationic dye called methyl thorium chloride, is a heterocyclic aromatic chemical compound with the formula ($C_{16}H_{18}N_3SCl$). According to reports, cationic dyes were found to be more hazardous than anionic dyes. Although this dye can be used as a disinfectant, in pharmaceutical products, and pesticides, if its concentration increases it can cause several diseases and water bodies can also get contaminated. Now coming to the scenario of dye Eosin Yellow, is a member of the triarylmethane dyes. It is an industrial dye. If the residual dye gets discharged as one of the components of untreated effluent, it can cause water pollution. So reducing the concentration of methylene blue and eosin yellow from wastewater is our utmost concern. Now with the help of two types of plastic char, cation dye methylene blue and anionic dye eosin yellow has been adsorbed.

My project also comprises of adsorbing organic pollutants like ranitidine hydrochloride and anthracene using two types of plastic char. Now giving an insight to ranitidine hydrochloride, it is a non-imidazole compound chemically N{2-[[[5-[(dimethylamino) methyl] - 2-furanyl]methyl]thio]ethyl] -N- methyl -2- nitro-l,lethenediamine, hydrochloride. It acts as a selective hydrogen receptor blockers in therapeutic doses. It is widely used to treat stomach disorders such as peptic ulcer and Zollinger–Ellison syndrome by inhibiting gastric acid secretion [50], [51], [52], [53],[54],[55]. This gastric acid secretion is a result of histamine, food, insulin-induced hypoglycemia, and pentagastrin. So basically it is a medicine used to treat gastric problems in our stomach. It is a known fact that invention of pharmaceuticals was a

major turning point in global, scientific and technological advancement. Life span has increased, various fatal diseases have been cured and living standard has also improved [56]. As the prominence of pharmaceuticals has increased, they are emerging as fast expanding environmental pollutants. In various water bodies, pharmaceutical contaminants has been found over the last three decades [57]. It has been found out that out of 11,926 pharmaceutically active compounds,713 compounds were found out in various sources of wastewater[58]. So herby removing ranitidine hydrochloride from waste water is also our concern. This study also focuses on the removal of ranitidine hydrochloride by using two types of plastic char. Now coming to the scenario of anthracene, it is a low molecular weight polycyclic aromatic hydrocarbons (PAH) compound that has more water solubility [59]. Polycyclic aromatic hydrocarbons(PAHs) are considered as carcinogenic and highly toxic contaminants. So even a low concentration of it getting released in water is very harmful [60]. If little quantity of anthracene gets absorbed also into the water bodies, it is enough to contaminate the water system as the organic colloid of water adsorbs anthracene and thereby increases its concentration in aquatic systems [59]. So herby removing anthracene from waste water is also our concern. This study also focuses on the removal of ranitidine hydrochloride by using two types of plastic char.

The effect of contact time, adsorbent dosage, temperature, and pH on the adsorption behavior of plastic char under batch conditions were studied. PC adsorption kinetics, isotherms, thermodynamics, and regeneration studies were performed to assess the performance of its practical application in the treatment of wastewater.

LITERATURE REVIEW

The study of “pyrolysis of plastic and micro plastic and application thereof” is mainly based on two important factors, one is reducing the negative influence of dumping plastic waste on the environment, and another way is to found out if the waste plastics can be transformed to a material which will be helpful in the process of waste management. Thus various researches have focussed on finding a sustainable and innovative approach on plastic waste management.

The primary goal of this work was to thoroughly review the literature on pyrolysis of plastic waste, focusing on char formation and its potential applications in wastewater treatment. Now coming to the scenario of pyrolysis, in this process an inert, air-free, or regulated atmosphere, thermal treatment converts large plastic polymers into hydrocarbons with different carbon numbers and boiling points [10]. Several categories of plastic waste has been studied which has various compositions. The compositions of plastic wastes have been studied through proximate analysis in various papers. Now the question arises what is proximate analysis. Proximate analysis is a process used to assess the characteristics of plastic used, mainly focussing on four characteristics like moisture content, fixed carbon, volatile matter and ash content. Now it has been found out that higher amount of volatile matter in the plastic on pyrolysis results in higher amount of liquid oil production whereas if the waste plastic has higher amount of ash content, then less amount of liquid oil will be produced as a result of pyrolysis. Thus, if a waste plastic containing high ash content is pyrolysed, the formation of char will increase and the gaseous yield will also increase.

The categorization of plastic waste can serve as an effective initial step in dealing with the waste problem. Table 1 provides an overview of various plastics, including their typical applications and the rate at which they can be recovered. A benefit of pyrolysis is that it can transform thermoplastic and thermoset plastic waste into oils and char of superior grade. Thus, a large amount of hazardous waste can be transformed into useful product while avoiding harmful emissions in the environment. Little amount of carbon monoxide will be emitted. The process of pyrolysis applied to various kinds of waste plastics often results in an average oil production of 45–50 %, gas yield of 35–40 %, and char yield of 10–20 %, with variations depending on the specific pyrolysis technique used in the process [16]. The end product obtained as a result of pyrolysis has lower molecular weight, reduced structural complexity and shorter chain lengths. This reduction in weight and chain lengths in the product of pyrolysis is the result of heat and high pressure throughout the process [17]. The heat and high pressure breaks the bond of the long chain of polymer.

Table 1: Plastic types, uses, recycled products, and recovery rates.

Plastic categories	Communal uses	Product of recycling	At present, recyclable ?	Recovery rate (%)	References
Polyethylene terephthalate (PET)	Food boxes, polyester wool, films, bottles of plastic and furniture are examples of typical	Construction materials, rugs,	Yes	20.5	[11]

	everyday items that are widely used.	beverages in bottles, textiles, apparel, and bedding			
High-density polyethylene (HDPE)	The applications of durable bottles, plastic lumber, toys, automobile components, and shopping bags are diverse and wide-ranging.	Bins for recycling and compostin g	Yes	10.5	[12]
Polyvinyl chloride (PVC)	Flooring, window profiles, toys, non-food bottle caps, and piping	Bin for compostin g	No	0	[13]
Low-density polyethylene (LDPE)	Containers, films, plastic bags, tubes, and sheets of plastic	Sheets for bin covers and pellets	Generally no	6	[14]

Polypropylene (PP)	Food boxes, dishware,furnishings,baggage, and appliances	Sheets of pipelines, containers, pellets, and pegs	Occasionally	1	[15]
Polystyrene (PS)	Plastic cutlery, cafeteria trays, clamshell containers, Styrofoam and packaging pellets are recyclable.	A container for recyclables	Occasionally	1	[12]
Others: polymethyl methacrylate, polycarbonate, etc.	Compact discs (CDs) and digital versatile discs (DVDs), toothbrushes, some types of food containers, and multilayer barrier films	A container for recyclables	No	It varies	[15]

Now coming to the categorization of pyrolysis techniques, it can be classified into three groups namely thermal, microwave assisted and catalytic pyrolysis. In the process of thermal pyrolysis, the waste plastic is heated in a non-oxidative process, i.e., in the absence of oxygen, at a very high temperature in a range between 350 and 900◦C [18]. It is a thermochemical process where liquid, solid product(char) and gases are formed

as products. A temperature of 900◦C is needed to break the bond in the plastic waste and in the intermolecular and intramolecular forces during thermal pyrolysis [19].It has been observed that at a very high temperature the major product is gases while at a lower temperature the major product is char [20].Thermal pyrolysis requires high temperature which results in low product quality.

The process of microwave assisted pyrolysis involves microwave dielectric heating. In this process the heat energy is generated in dielectric material by agitation the molecules. The molecules are agitated by alternating electromagnetic field. In this pyrolysis of plastic waste an adsorbent is used because plastic has a very low dielectric loss factor and cannot adsorb microwave energy which the adsorbents can do. Thus the heat is then absorbed by adsorbent and then heat is transferred to the plastic by the process of conduction [21].The adsorbent will help in heating the waste plastic as the mixture of adsorbent and plastic has a very high dielectric loss factor [22].These materials with extremely high dielectric losses comprise silicon carbide, carbon, and shredded tyre iron mesh. Microwave-assisted pyrolysis has several benefits, including high heating rate, minimized energy loss, and high energy rate of conversion and even heating. The main drawback of this process is that it requires a large initial investment and on-going operating expenses.

Now coming to the third process catalytic pyrolysis, it is the degradation of plastic waste in the presence of catalyst through non oxidative process. The catalysts which have been used in the catalytic pyrolysis of waste plastic include fluid catalytic cracking (FCC), mobile classification materials (MCM-41) silica alumina, and zeolites[23],[24],[25],[26]. Panda and Singh (2011) reported in their work that the catalyst was used to lower the activation energy for the degradation, influencing composition of the product and decreasing process time. There are two ways catalysts

can be used in this process of pyrolysis [27]. The process can take place in in-situ where the plastic and catalyst are first mixed and then heated to the required temperature whereas in the process of ex-situ waste plastic is first heated to give volatile fraction, and then the catalyst is introduced in the pathway of vapour. The method of catalytic pyrolysis is a technique that lowers costs, improves process selectivity, and produces liquid products with a narrower boiling point range.

Now after completing the categorization of pyrolysis techniques, giving an insight in the pyrolytic process of plastic and micro plastic is important. Pyrolysis of waste plastics can be categorized into three different processes namely the conventional pyrolysis, fast pyrolysis and flash pyrolysis. These three processes differ in temperature, residence time, heating rate and products produced as explained in the subsequent sections.

Conventional Pyrolysis - This process involves slow heating in the absence of oxygen at the rate between 0.1◦C/s and 1.0 ◦C/s and temperature between 400 ◦C and 500 ◦C in residence time between 5–30 mins which results in the production of waste plastic char [28] .Slow pyrolysis is carried out at lower temperature, slower heating rate and long residence time. However the quantities of gaseous and liquid product formed will be low. Some of the reactors which can be used for slow pyrolysis are fixed bed reactor, drum, tubular reactor, rotary kilns, and screw/auger. Slow pyrolysis of waste plastic can also be referred to carbonization of waste plastic and it takes place in three phases: Drying phase which occurs at above 100 ◦C for any moisture content in the waste plastic to vaporize as steam, thermal decomposition which occurs at temperature between 350–550 ◦C[29], the components of the waste plastic break down to release volatiles such as carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), tars

and hydrogen (H2) and last is the cooling phase, where the char is cooled in the absence of air.

Fast Pyrolysis – It is a process where waste plastic is heated rapidly to an elevated temperature in the range between 500 ◦C and 700 ◦C [29] at a rate of heating in the range between 10 ◦C and 200 ◦C and in short residence time period between 1 and 10 s [30]. Fast pyrolysis of waste plastic is carried out to convert waste plastic into liquid oil and energy. Thus fast pyrolysis should not be applied for production of waste plastic char, as it favors production of liquid products [31],[32],[33]. The reactors which could be used for fast pyrolysis include circulating fluidized bed reactors, entrained flow reactors, vacuum furnace reactor, rotating reactor, and vortex reactor.

Ultra–fast/Flash Pyrolysis - Flash pyrolysis is the heating of waste plastic at a temperature above 700 ◦C [34] at a heating rate of greater than 1000 ◦C/s. It gives a higher yield of fuel oil than fast pyrolysis and a low water content product with 70 % conversion efficiency[33],[29].Suitable reactors for flash pyrolysis are fluidized bed reactors and entrained flow reactors.

After giving a brief insight on three general categories of pyrolysis, it is also important to give an introduction to plasma pyrolysis. This process of pyrolysis is entirely different from the previous three types of pyrolysis process discussed. In the process of plasma pyrolysis, plasma energy is generated by plasma torches. In the plasma state, the ionized gas conduct electricity, then the electrical energy is converted to heat energy due to its high resistance. The extreme heat provided by the plasma helps in pyrolysing the waste plastics into CO, H2 and hydrocarbons[64]. Gases produced by this pyrolysis process rise to the temperature of about 1200◦C.

Now coming to the synthesis of waste plastic chars, it has been found that the properties, product yield and adsorption capacity of waste plastic char varied with the pyrolysis temperature [35]. Solís et al. (2022) obtained waste plastic char from pyrolysis of different types of waste plastic collected from a municipal solid waste processing plan. The synthesized activated waste plastic char was used to remove lead (Pb) in contaminated water. The plastic char was also characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). The work showed that the produced activated plastic char was effective in removing Pb from the contaminated water. However, the yield of the synthesized plastic char was not determined. Dutta and Gupta (2022) synthesized plastic char by pyrolysing HDPE and PP for the removal of inorganic arsenic and chemical oxygen demand (COD). Now the question is what is COD. COD (Chemical oxygen demand) is a parameter used for determining water quality which represents the degree of organic contamination in water bodies. More the amount of organic contamination, more oxygen will be utilized for its oxidation and more will be the COD of that waste water sample. The produced waste plastic char adsorbed 50 % of COD at a dosage of 4 gm/L for a contact time of 25 min while 60 % arsenic was removed with a dosage of 4 gm/L at a contact time of 30 mins. Moreover, the work of Neelanja and Aniban (2022) revealed that the ultimate and proximate analyses of the synthesized waste plastic char were: carbon (41.3–84.7 %), moisture content (1.2–2.5 %) and volatile matter (46.50–48.0 %).

Martín-Lara et al. (2021) obtained waste plastic char from pyrolysis of mixed waste plastic consumed in the pyrolyser. The characterization of the produced waste plastic char was also carried out. The work indicated that temperature has a great influence on the yield of the waste plastic char. A yield of 14 % at a temperature of 450 ◦C was

recorded. They further recorded that the amount of nitrogen, carbon, and hydrogen content of the synthesized waste plastic char decreased with increase in temperature of pyrolysis. A reduced volatile content and higher ash content were obtained at a higher pyrolysis temperature. It can be stated from the work of Devendra and Shri (2020) that a higher yield of waste plastic char can be obtained at slow heating rate, very low temperature, and long residence time during pyrolysis. The waste plastic char can be used as surfacing material, building material, fuel, and as adsorbent which is the focus of this work.

The amount of hydrogen, oxygen, sulphur, nitrogen, and carbon of the waste plastic can be found out using ultimate analysis. It shows the amount of carbon content in waste plastic char obtained after pyrolysis [36].The proximate analysis shows the amount of volatile matter, moisture content, fixed carbon, and ash content. This composition is very useful for decision making [37],[38],[39],[40].A positive correlation exists between fixed carbon and char yield while a negative correlation exists between volatile and ash content with char yield[41],[42].Hence greater the volatile matter, less is the char production and the gas production from the process increases. Jamradloedluk and Lertsatitthanakor (2014) worked on characterization and utilization of char derived from fast pyrolysis of HDPE plastic wastes. The results of their work revealed the produced waste plastic char had the following result on proximate and ultimate analyses: volatile matter (51.40 %), moisture content (2.41 %), ash (0.61 %) and fixed carbon (46.03 %). The surface area and pore volume of the produced waste plastic char, after activation, increased by 55 % and 44 % respectively whereas the pore size decreased by 5 %. Therefore it comes to the conclusion that activation of waste plastic char increases surface area and pore volume but decreases

pore size which makes waste plastic char suitable for usage as adsorbent for removing pollutants from landfill leachate or wastewater.

Tables 2 and 3 present the proximate and ultimate analysis of various waste plastic from previous research work. It is obvious from the previous works of researchers as shown in Tables 2 – 3 that PET waste plastic have the highest range of percentage of fixed carbon which favours PET waste plastic char most suitable to be used as an adsorbent. In terms of ultimate analysis, previous works of scholars indicated PET waste plastic have the highest percent of carbon when compared with other types of waste plastic. This is revealed that PET waste plastic char is very promising to be used as an adsorbent.

Table 2:-Proximate analysis of various waste plastics

References	Waste plastic type	Volatile matter	Moisture content(%)	Ash(%)	Fixed carbon(%)
Al–Salem et al. (2017)	PS	99.6	0.3		0.2
Zhao et al (2022)	PS	98.54	0.32	0.09	1.05
Janajrehet al. (2020)	PS	99.814	0.09	0.025	0.071
Ahmad et al. (2020)	PS	99.78			0.22

Janajreh et al. (2020)	LDPE	99.816	0.11	0.023	0.051
Al – Salem et al. (2017)	LDPE	99.80			0.3
Wijayanti et al. (2022)	LDPE	95.61	0.3	3.37	0.68
Al–Salem et al. (2017)	PET	91.80	0.5	0.1	7.8
Suriapparaoet al. (2022)	PET	84.80		0.7	14.5
Chattopadhyay et al. (2016)	PET	84.10			13.9
Liu et al. (2020)	PP	99.5			0.5
Chattopadhyay et al. (2016)	PP	96.90			1.0
Bai et al. (2020)	PP	99.28	0.29		0.43
Al–Salem et al. (2017)	PP	99.70	0.2	0.4	1.2
Hakeem et al. (2018)	PP	93.77	0.16	4.45	1.62

Wei et al. (2022)	PVC	97.92	0.65	0.11	1.97
Wang et al. (2018)	PVC	95.89		0.01	4.10
Wu et al. (2022)	PE	99.93			0.07
Duque et al. (2020)	PE	99.4	0.2	0.4	

Table 3:-Ultimate analysis of different kind of waste plastic(Yao et al., 2018).

Waste Plastic Type	Oxygen (%)	Sulphur (%)	Carbon (%)	Nitrogen (%)	Hydrogen (%)
PET	5		77	0.2	13
PP	1	0.06	84		14
HDPE	4	0.08	78	0.06	13
PS	1	0.08	90	0.07	9

Homer et al. (2023) predicted the product yields from pyrolysis of mixed plastic waste using a superposition model. The author reported that the highest composition of PET in the mix of HDPE, PP, PS and LDPE had a positive impact on the yield of waste plastic char. Miskolczi et al. (2004) carried out thermal and thermo–catalytic degradation of HDPE waste for analysing the effects of catalyst (Clinoptilolite, MCM), fluid catalytic cracking (FCC) and HZSM-5 on the yield of pyrolysis product. The work showed that MCM catalyst yielded 19 % char, FCC gave 15 % char and HZSM-5

produced 11 % char. However, the chars produced were not used in the removal of pollutants from landfill leachates or wastewater.

Scott et al. (1999) reported that products obtained from pyrolysis of polypropylene can be influenced with the use of a combination of suitable particle size, catalyst, and temperature. The result of their work indicated that flash pyrolysis was not favorable to plastic char production. Aguado et al. (2007) studied the feedstock recycling of polyethylene in a two-step thermo catalytic reaction. The study revealed that at a temperature of 425 ◦C, 45 % waste plastic char was yield and in the presence of HZSM-5 catalyst, the yield increased to 48 %. This indicates that slow pyrolysis in the presence of a catalyst results in higher yield of waste plastic char. Bagri and Williams (2002) investigated the influence of y -zeolite on the pyrolysis of polyethylene at a temperature of 550 ◦C. The authors found that the y – zeolite increased the concentration of oil produced. However, the authors did not study the influence of the catalyst on the waste plastic char produced.

Previous works of researchers have reported high yield of waste plastic char from pyrolysis of waste plastic using catalyst compared to when catalysts were not used, at the same operating conditions [43],[44],[45],[46],[47]. Chen et al. (2021) examined the application of Co-Ni intercalated vermiculite catalyst in pyrolysis of polystyrene and polypropylene waste plastic in a tube furnace at heating rate of 10 ◦C/min, temperature of 480 ◦C with 10 % pelletized Co/vermiculites and Ni/vermiculites catalyst. The waste plastic char produced were 0.1 and 0.3 % for the Co/vermiculites and Ni/vermiculites respectively. This implied that at the same operating conditions, different catalysts yield different waste plastic char during pyrolysis.

Onwudili et al. (2009) reported that pyrolysis of mixed waste plastic in a fixed bed reactor at a heating rate of 10 ◦C/min at a temperature of 600 ◦C using FCC as a catalyst produced 28 % ware plastic char. Sangpatch et al. (2019) worked on fuel oil generated from Cogon grass derived Al – Si catalysed pyrolysis of waste plastic in a batch glass reactor at a heating rate of 5 ◦C/min, temperature 350 ◦C using 10 % Al – Si catalyst. The work yielded 9.2 % of waste plastic char. Thus it can be found out that the yield of waste plastic char is a function of the prevailing operating conditions. Novarini et al. (2020) studied temperature and the use of zeolite catalysts in the pyrolysis of LDPE waste plastic on the amount of oil produced. The study has stated that 10.80 percent waste plastic char was obtained at a temperature of 200 ◦C in the absence of a catalyst while 5.2 percent waste plastic char was yielded at a temperature of 300 ◦C in the presence of a catalyst for a period of 6 h.

Waste plastic pyrolysis is a way of sustaining a circular economy which is very important in reducing the negative impact of plastic pollution. Moreover, industrial scale and global adoption of pyrolysis process technology in the total conversion of waste plastic is still hampered by lack of adequate knowledge about the kinetic reactions and the mechanism, high energy requirement and inadequate data of real waste plastic pyrolysis experiments. Therefore future studies carried out by researchers should look into how high energy required for total conversion of waste plastic via pyrolysis can be minimized and it will provide a better explanation on the complete conversion of waste plastic through pyrolysis with a view to understand the kinetic reactions and mechanism of the pyrolysis process [48],[49],[46].After giving a brief insight on the importance of pyrolysis for waste plastics, it is important to have an idea of the pyrolysis oil obtained as an end product of pyrolysis. It has already been shown by previous researchers that a high temperature in the process of pyrolysis will

result in less generation of liquid end product and more amount of gaseous products will be formed along with the char. Sudhir B. Desai et al. (2015) produced pyrolysis oil from waste plastic Low Density Polyethylene (LDPE) by pyrolysing it at a temperature of 300-350°C for about 35 minutes. The gases obtained have also being condensed to give low density oil. Operating at this temperature, he obtained 80-90% of the end product is fuel oil. The other end products obtained are producer gas which is about 8-10% and char which is about 2-13%. The sulphur and carbon content is also less in the oil obtained, so the effect of pollution will also be much less. Low carbon oil generally means lower energy will be obtained on ignition of the fuel. The Cetane number will also be less which means the fuel will burn quickly. Pyrolysis oil obtained from LDPE has a content similar to diesel fuel in spite of its calorific value and viscosity being little low.

Now coming to the scenario of High Density Polyethylene (HDPE), it contains long chains of carbon atoms which on pyrolysis will obtain fuel oils whose carbon number is high. More amount of naphtha will be produced resulting in more density of the oil produced. F. Faisal et al. (2023) performed thermal pyrolysis of mixed waste plastic(MWP) and mixed virgin plastics(MVP) containing high density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS) at 1:1:1 ratio. This study also focussed on hydro treating the plastic before pyrolysis. Hydro treatment is known as the refinery process that can improve the quality of the pyrolytic oil by removing heteroatoms and saturating alkenes [62][63]. In the study hydro treatment was carried out to catalyse hydrodesulphurization (HDS), nitrogen removal (HDN), and hydrodeoxygenation (HDO). Hydro treatment helps in the removal of hetero atoms and thus the oil becomes rich in alkanes with low carbon number improving combustion efficiency[62] . Now with the introduction of HDPE, it has been found that

the high heating value of pyrolytic oil is close to the high heating value of standard diesel. Also the cetane index for the distilled and hydro treated products in this study meet the minimum requirement outlined in the Australian, ASTM and EN standards for diesel fuel. However the oil did not satisfy any requirement of the diesel standards.

Now after giving an insight on pyrolysis techniques, types of plastic and various works done on this field, it is important to have an idea on the various types of pyrolysis reactors. Various types of pyrolysis reactors has been designed to convert a diverse variety of polymers into three product categories:- solids, liquids and gases. The reactors are classified on the basis of reactor design and operating parameters. Classifying the reactors, there are batch reactors, semi- batch reactors, fixed bed reactors, fluidized bed reactors, rotary kiln reactors, conical spouted bed reactors.

Batch reactor:-If pyrolysis is performed in this reactor, first the feed has to be entered, and the reactor has to be closed. Here reactants cannot be added during the process of pyrolysis. The reactor is a closed system over here. Different heating rates at which the temperature will increase per minute can be set in the batch reactor at the start of this process. Then the temperature is increased to a set temperature for the pyrolysis to occur. High conversion is observed in this process. However there is a problem in this pyrolysis process. The variety of products from batch to batch cannot be observed in this process. Massive industrial scale of production cannot be obtained from this process.

Semi batch reactor:-Semi batch reactor has certain advantages over batch reactor. Here reactants can be added during the process of pyrolysis as well as the by-products can be separated during the process of pyrolysis. Different heating rates at which the temperature will increase per minute can be set in the semi- batch reactor also at the

start of this process. As heating rate increases, the rate of oil formation increases whereas the rate of char and gas formation decreases. Various literature study has stated that batch and semi batch reactors are the finest reactors in the process of thermal pyrolysis. High conversions can be obtained by these reactors.

Fixed bed reactor: -Fixed bed reactors have certain disadvantages like problems during feeding process. As the particle size and shape of plastic are not same, the feeding will be a problem. The available surface area of catalyst for pyrolysis is also limited. Tekin et al. (2012) stated that the catalyst is palletized and packed in a static bed. As a result, the accessible surface area of the catalyst for the reaction to reach is small. Various researchers have pyrolysed plastics by using fixed bed reactor due to its simpler design. Zanella et al. (2013) chose to use fixed-bed reactor to study co-pyrolysis of coffee and PP wastes into fuels. He thermally cracked the mixture at an operating temperature of 360-420 °C by pyrolysing it at a heating rate of 5°C/min for a residence time of 3 hours. He observed that with a temperature rise from 360 to 380°C, the thermal degradation of plastic has increased.

Fluidized bed reactor: -Numerous studies has recommended use of fluidized bed reactors over use of fixed bed reactors in the process of catalytic pyrolysis of polyolefins (Jung et al., 2010; Lin and Yen, 2005; Luo et al., 2000; Park et al., 2019). The fluidized bed reactor helps in maintain a fixed temperature with high heat and mass transfer rate. Thus, the time of residence decreases. Owing to these advantages, Jung et al., 2010 performed the thermal degradation of polypropylene and polyethylene in fluidized bed reactor. Fluidized bed reactor can be used for large scale operation due to its large operating capacity.

Rotary kiln reactor:-Rotary kiln reactor generally consists of a loading system, rotary kiln, secondary combustion chamber, recovery boiler and a flue gas cleaning system. In the loading system, the plastic waste is loaded and then the plastic waste is pushed into the rotary kiln by horizontal hydraulic cylinder. In rotary kiln there is a 2% slant inclined in the direction of secondary combustion chamber where the incineration of plastic waste takes place. After leaving the reactor(incineration chamber), the flue gas(a product of pyrolysis) at temperature of 1100-1200 °C heats the thermal oil to a temperature of about 280°C. With special pumps, thermal oil is sent to the processing equipment. The flue gases passing through the heat recovery system are cooled to temperatures between 265 C and 280 C. In the cleaning system for flue gas, multisectional bag filters are there to remove the dust. In addition, this system is equipped with metering devices for dosing sorbent and urea. At the screw kiln reactor port, the stable char is restored.

Conical spouted bed reactor:-Conical spouted bed reactor offers effective mixing and can accommodate a wide range of particle sizes. Various researchers have used conical spouted bed reactors for catalytic pyrolysis of plastic. This reactor mainly focuses on the production of oils having high calorific value. Another advantage of this process is it requires short residence time for the pyrolysis to occur.

This paper mainly focuses on using two types of plastic char one is annealed and another is plastic char treated with NaOH and annealed. These two type of chars were used in the process of adsorption for wastewater treatment. The effect of contact time, adsorbent dosage, temperature, and pH on the adsorption behaviour of mixture of corn husk char and plastic char under batch conditions were studied. CHAC-PC adsorption kinetics, isotherms, thermodynamics, and regeneration studies were

performed to assess the performance of its practical application in the treatment of wastewater.

Aims and objective:-

After studying the above literatures, it was found that pyrolysis can be used as an effective method in waste management. Less amount of CO_2 is evolved in the process of pyrolysis. With advancement of technology, waste management has become a serious issue.Land dumping or incinerating the plastic waste has resulted in lot of pollution. So various researches has focussed on pyrolysing the plastic waste and applying the end product of pyrolysis to some use.Some researches focussed on usage of plastic char as adsorbent,while some researches focussed on using the pyrolysis oil and trying to find its characteristics if it can be used as an effective oil.

The main objective of my project is: -

1. To study the pyrolysis process in which plastic is used as raw material
2. To obtain the products from pyrolysis and study its application
3. Char obtained from pyrolysis is used for water purification (removal of dye) from dye solution.It is an important aim of my project to study the amount of dye that a specific amount of char is able to adsorb.
4. A comparative study is done in this aspect varying the amount of dye and the amount of char.

2.1 Materials

2.1.1. Preparation of plastic char

The plastic char used in this study is municipal plastic char. The char has been divided into two parts. One part of the char obtained has been thermally activated to prepare plastic char annealed. Another part of the char is treated with NaOH and then annealed. In the case of thermal activation, about 10 g of plastic char sample was taken in a silica crucible and then the crucible was placed inside a muffle furnace. The muffle furnace was electrically heated up to the desired temperature. The entire process is carried out in the absence of oxygen. The char sample was heated at a temperature of 550 ◦C to make it thermally activated. After heating for about 3 hours, the muffle furnace was turned off and the sample was kept overnight, thereby giving it the perfect time to get cooled.

Now in the second case of plastic char treated with NaOH and then annealed, first 500 mL 5% NaOH solution was prepared and then 10 g of plastic char sample was taken and stirred in the 5% NaOH solution using a stirrer and magnetic bid to prepare plastic char treated with NaOH. Now the char is separated out from the PC-NaOH solution by the process of filtration. Then the char collected in the filter paper is kept in a petri dish and entered in a hot air oven at a temperature of 110◦C and kept for 4 hours, so that moisture gets absorbed and eventually dry char is obtained. This dry char is plastic char treated with NaOH. Now to make this char annealed, this sample was taken in a silica crucible and then thermally activated to make this char annealed. All these chars are stored in ziplock before being used in the batch adsorption experiment.

2.2. Characterization of adsorbent

A detailed morphological analysis of the chars used in my study was conducted using a scanning electron microscope (SEM) under condition of high vaccum and accelerating voltage of 20 kV. Further thermogravimetric analysis of the chars has been performed by thermogravimetric analyser(TGA) (model- TGA 4000, Perkin Elmer) at a heating rate of 10 ◦C/min from 30 to 800◦C under a constant nitrogen purge of 20 ml/min. The thermogravimetric analysis has been performed to study the decomposition pattern of chars with increase in temperature. The transmission spectra were measured on a FTIR spectrometer (Model- Spectrum 2, Perkin Elmer) and recorded within a range of 4000–400 cm^{-1}, with a resolution of 4 cm^{-1}.

2.3. Adsorption Experiments

2.3.1. Batch adsorption experiments

Batch adsorption experiments were conducted at 30◦C in 70 mL glass bottles. To evaluate the adsorption rates, 1g/L,2g/L,3g/l,4g/L of various forms of plastic-chars was first added to 50.0 mL of dye solution of methylene blue and eosin yellow (initial concentration was 10.0 mg/L) and shaken at 110 rpm. At certain time intervals of 30 minutes , 1 mL samples were withdrawn and centrifuged for 10 min at 14,000 rpm in a mini centrifuge (REMI RM-12C). The concentration of dye is then found out by checking the absorbance using a spectrophotometer.

The concentration of each dye was measured in the cubicles using a UV–visible spectrophotometer (THERMO SCIENTIFIC MODEL NUMBER ORION AQUAMATE 8000). Calibration curves for both dyes were established prior to the analyses. Samples were diluted when necessary to fit the calibration range. Measurements on control samples of solutions without any added adsorbent were carried out simultaneously to make sure that the changes in the concentration were not prompted by factors other than interaction with the adsorbents.The dye concentration in each sample was calculated by measuring the absorbance at the maximum absorbance wavelength(664 nm and 517 nm for MB and EY respectively).

To investigate the adsorption capacity of plastic char, experiments were carried out under various conditions like temperature, concentration and pH. In the temperature experiment,the (10 ppm) dye is removed using plastic char at various temperatures of 25◦C,30◦C,35◦C,40◦C.In the concentration experiment,various concentration of dyes like 5ppm,10 ppm,20 ppm, 40 ppm are used.To evaluate the influence of pH,50 ml of 10 ppm solutions are taken and five pH solutions are made, ranging from acidic pH 2 to basic pH 10.After that adsorption experiment is carried out using plastic char.Unlike the dosage experiment, here in the experiment of temperature, concentration and pH, the maximum amount of char that gives the best removal is used.

The dye percentage uptake, amount adsorbed at equilibrium and at different intervals of time, t (mg/g), were calculated using the equations [69],[70],[71],[72],[73].

$$\text{Uptake } (\%) = \left(\frac{C_o - C_e}{C_o}\right) \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)\ V}{W} \quad (2)$$

$$q_t = \frac{(C_0 - C_t)\ V}{W} \quad (3)$$

where qt (mg/g) is the adsorbed quantity after a specific contact time t (min), qe (mg/g) is the adsorbed quantity at equilibrium, k1 (min− 1) and k2 (g/(mg·min)) are rate constants of pseudo-first-order and pseudo second-order model.

2.3.2. Preparation of Methylene blue and Eosin Yellow dye solution

At first 200 mL 100 ppm Methylene blue dye solution is prepared by stirring 20 mg of dye with 200 mL distilled water.Then from 100 ppm solution 20 ml is taken and diluted to make 200 ml 10 ppm solution.Then using various dose of char,the dosage experiment is carried out.Then in the concentration experiment,various concentration of dye solutions are prepared.At first 2.5 mL of 100 ppm Methylene blue dye solution is diluted to 50 mL 5 ppm solution.Then to prepare 50 mL 20 ppm solution,10 ml of 100 ppm dye solution is diluted to 50 mL solution.Then to prepare 50 mL 40 ppm solution,20 ml of 100 ppm dye solution is diluted to 50 mL solution.For the temperature study,50 ml of 10 ppm solution has been prepared for each temperature set in the BOD Incubator Shaker.Finally coming to evaluate the influence of pH in adsorption study,50 ml of 10 ppm solutions are taken and five pH solutions are made, ranging from acidic pH 2 to basic pH 10.The above procedure is same for the experiments where Eosin Yellow dye is used.

2.3.3. Preparation of Anthracene solution and Ranitidine hydrochloride solution

To prepare 100 ppm anthracene solution,20 mg of anthracene is taken and mixed in 20 mL 10% methanol solution(here 35% methanol solution has been diluted to 10% methanol solution) and then 180 ml distilled water is poured in the conical flask and then stirred using magnetic stirrer for 20 minutes.Little heat is provided for methanol to escape thereby preparing 100 ppm anthracene solution.After that the entire process is same that is stated above.

In the preparation of 100 ppm ranitidine hydrochloride solution there is no need to add any methanol.20 mg of ranitidine hydrochloride is mixed with 200 mL distilled water using a magnetic stirrer to prepare 100 ppm solution.

2.4. Adsorption isotherm, kinetic, and thermodynamic study

The four most conventional isotherm Langmeur, Freundlich, Temkin and Dubinin Radushkevich isotherm models were used to study the equilibrium data and study the adsorption procedure on the plastic char and biochar.Kinetic parameters were evaluated through pseudo-first-order, pseudo-second order, and intraparticle diffusion models to find the best adsorption mechanism. Thermodynamic evaluation was carried out to measure the extent of Gibbs free energy changes (ΔG), enthalpy changes (ΔH), and entropy changes (ΔS) at a specified temperature range.

Adsorption kinetics and isotherms:-

1. The adsorption experiment is continued in BOD incubator until equilibrium is reached.

2. Now lagargren pseudo first order model,and Ho & McKay pseudo second order models are tested for representing the adsorption interaction.

Lagergren pseudo-first order equation:-

q_e is equilibrium concentration and q is concentration at any time t .

$$\frac{dq}{dt} = k_{ad}(q_e - q)$$

Integrating between q=0 to q and t=0 to t,

$$\ln(q_e - q) - lnq_e = -k_{ad}t$$

A plot of $\ln(q_e-q)$ against t would give a straight line; slope is rate constant k_{ad} in $time^{-1}$ and intercept would give q_e[74],[75].

Ho & McKay pseudo second order equation:-

$$\frac{dq}{dt} = k_2(q_e - q)^2$$

Here,

Integrating between q=0 to q and t=0 to t and re-arranging,

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

A plot of t/q vs t will give k_2 from its intercept[76],[77].

Where q_t (mg/g) is the adsorbed quantity after a specific contact time t (min), qe (mg/g) is the adsorbed quantity at equilibrium, k_{ad} (min^{-1}) and k_2 (g/(mg·min)) are rate constants of pseudo-first-order and pseudo second-order model.

Now which model fits the data will give us an idea about the adsorption process.

The mechanism of adsorption onto plastic-char can be explored using adsorption isotherms with various initial concentrations.

Langmuir Isotherm:-

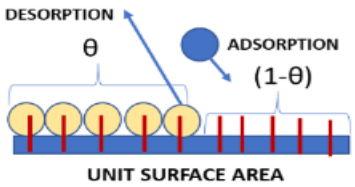


Fig.1: Adsorption and desorption diagram for Langmuir isotherm

All sites are identical, the adsorbent surface is homogenous, and adsorption heat is independent of closure[78].

$$\frac{dq}{dt} = k_a p(1-\theta) - k_d\theta$$

At equilibrium $\frac{dq}{dt} = 0$

$$\theta = \frac{k_a p}{k_a p + k_d} = \frac{K_L p}{1 + K_L p}$$

$$K_L = \frac{k_a}{k_d}$$

$$\theta = \frac{q_e}{q_m} = \frac{K_L p_e}{1 + K_L p_e} \quad \text{that is } q_e = \frac{q_m K_L p_e}{1 + K_L p_e} \quad \text{Or,} \quad q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

Linearized form- $$\frac{1}{q_e} = \frac{1}{q_m K_L}.\frac{1}{C_e} + \frac{1}{q_m}$$

A plot of 1/Ce vs. 1/qe will yield a slope and intercept from which q_m and K_L can be calculated.

Freundlich Isotherm Equation:-

$$q_e = K_F C_e^{\frac{1}{n}}$$

The adsorbent surface is heterogeneous and forms a multilayer with the adsorbate molecule[73].

Linearized as:

$$log\ q_e = logK_F + \frac{1}{n} logC_e$$

A plot of log Ce vs log qe will give a straight line whereby K_F and n can be calculated from intercept and slope respectively.

Now it is important to find out which isotherm fits better.

Thermodynamics study:-

Experiments were carried out at various temperatures (25°C, 30°C, 35°C and 40°C).The results obtained from the tests were used for thermodynamic analysis. The equations used for thermodynamic analysis are as follows[79]:

$$\Delta G_{adsorption} = -RT \ln K_C$$

$$\ln K_C = -\Delta H_{adsorption}/RT$$

$$\Delta G_{adsorption} = \Delta H_{adsorption} - T\Delta S_{adsorption}$$

where, $\Delta G_{adsorption}$ is the adsorption free energy, $\Delta H_{adsorption}$ is the adsorption enthalpy, $\Delta S_{adsorption}$ is the Adsorption entropy, T is the absolute temperature in Kelvin, KC is the thermodynamic equilibrium constant or q_e/C_e and R is the universal gas constant i.e. 8.314 J/molK. The values of $\Delta H_{adsorption}$ and $\Delta S_{adsorption}$ can be estimated from the slopes and intercepts of $\ln K_C$ vs. 1/T plot.

3. Results and discussion

3.1. Char characterization

3.1.1. Thermogravimetry Analysis

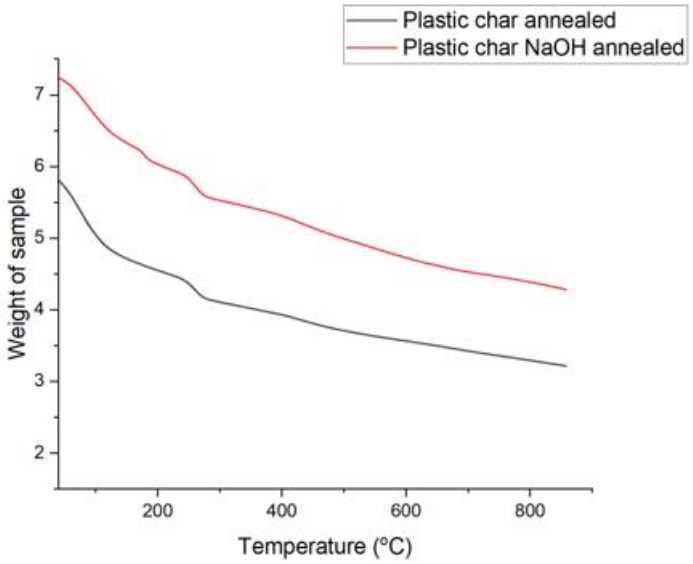


Fig.2:TGA analysis of various forms of char

For the two types of char- plastic char annealed and plastic char treated with NaOH and annealed, there was also significant mass loss in the temperature range of 250-450◦C but the mass loss was much less when a comparative study was done between the three types of chars. The single step mass loss was minimum for plastic char annealed when thermogravimetry analysis was performed. This mass loss is due to the thermal decomposition of major organic components in the chars.Below this temperature range, the material showed relative stability with little mass change. Initially, below 200 ◦C, a mass loss is observed due to the evaporation of residual moisture and the release of volatile compounds present in the char. Between 450 and 600 ◦C, a second significant mass loss occurs due to the rearrangement of carbonaceous structures[88]. As the temperature reaches near 600◦C, third mass loss occurs due to breakdown of carbon backbone structure.

3.1.2.X- ray Diffraction(XRD) Analysis

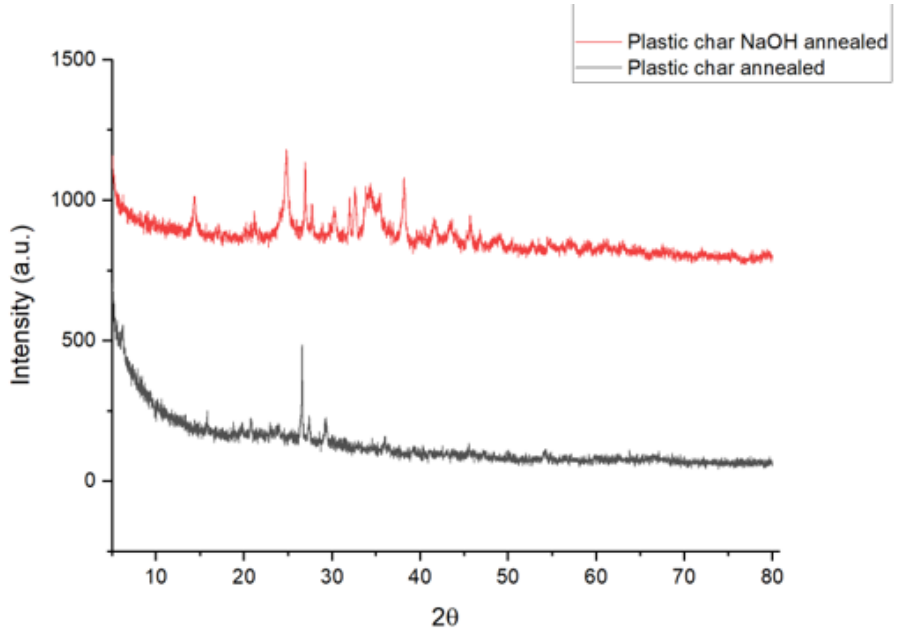


Fig.3:XRD analysis of various forms of char

Figure shows the XRD pattern of two types of char. In the graph of intensity vs 2θ for plastic char treated with NaOH and annealed, the XRD pattern shows a strong reflection at 2θ angle 26.81◦. In the graph of intensity vs 2θ for plastic char annealed, the XRD pattern shows a strong reflection at 2θ angle 28.74◦. Beside this peak, several other peaks also have been observed with lesser intensities.The presence of these peaks indicates that these chars have a crystalline structure[86].

3.1.3.FTIR Analysis

Fourier transform infrared analyses of the char samples were performed to identify the functional groups associated with it. Here infrared light is used to scan test samples and identify the functional groups present in it. Fourier transform infrared spectra of

plastic char annealed and plastic char that is shown in the figure is almost identical. Hence it indicated the presence of the same functional groups in both the type of chars. However, there is a peak in the graph of plastic char at a wavenumber of 3453 cm^{-1}. Different peaks have been obtained in plastic char treated with NaOH and annealed due to presence of OH functional group[86].

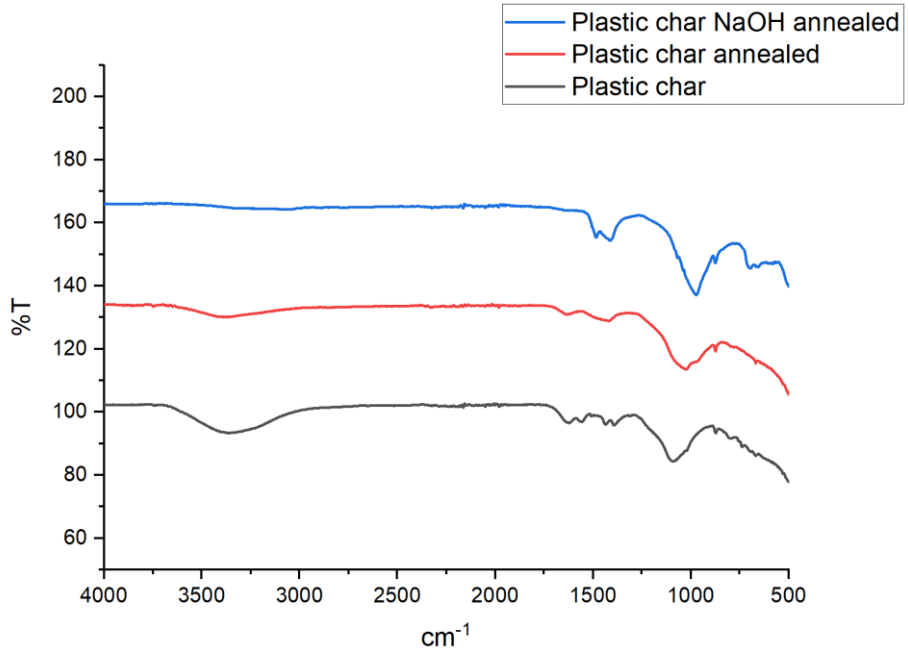


Fig.4:FTIR analysis of various forms of char

3.2. Adsorption experiments

Batch adsorption experiments has been carried out where two types of plastic chars has been used for adsorption of dyes, PAH and organic compound respectively. The adsorption of dye mainly follows pore flling, hydrogen bond, pi–pi interaction, n-pi interaction and ion exchange as the adsorption mechanism [91]. As in the initial stage many free sites were available on both the adsorbent's surface, it contributed to the rapid uptake of pollutant from aqueous solution [92].With time the removal rate

decreases. Now to understand the trend of absorption, various factors like pH, concentration,dose, temperature has been changed in the experiment to understand how the factors affect the adsorption result.The next section in the thesis covers the effect of various factors when each experiments were carried out.

3.2.1. Effects of pH on dye removal as well as removal of PAH and organic compound

The pH of the sample solution can affect the surface electrical charge of the adsorbent. Therefore the influence of pH on the removal percentage of dye solutions was studied in the pH range of 2 to 10.Now after adsorbing the two types of dye-cationic dye and anionic dye, it has been found out that cationic dyes has a basic pH, so plastic char annealed can adsorb it better while in the case of anionic dyes, it has been found out that the pH is acidic, so plastic char treated with NaOH and annealed can remove it better.

3.2.1.1. Graphical representation of various forms of char adsorbing Methylene Blue

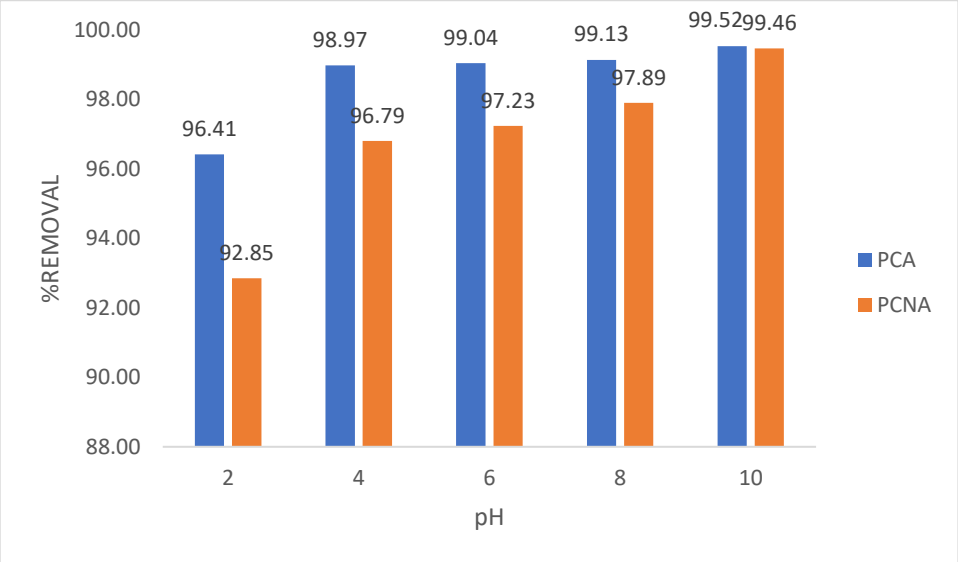


Fig.5:Effect of pH on removal of Methylene Blue using PCA and PCNA, Removal percentage vs pH

The plastic char annealed has been able to remove maximum dye at pH 10. However, as pH decreases, the removal percentage of dye also decreases. In the case of adsorption with plastic char treated with NaOH and annealed, the maximum adsorption is shown in pH 10 but plastic char annealed has shown better removal percentage.With the presence of high pH in the dye solution,presence of OH^- group in the char has hindered the adsorption to some extent. As a result, maximum adsorption has been shown by plastic char annealed. However, the graph where maximum amount of dye methylene blue has been removed by plastic char annealed is attached below.

pH has an effect in influencing the surface charge and ionization of dyes[80] which will further influence the removal efficiency. The study was conducted across a pH range of 2-10. Now in the scenario of methylene blue, it being a cationic dye has more affinity towards negative (OH^-) ions. This contributed to the higher removal of methylene blue at higher pH conditions having more amount of OH^- ions. In the acidic medium, H^+ concentration increases and OH^- concentration decreases.Due to increase in H^+ concentration, the electrostratic repulsion between MB and adsorbent surface increases[81]. As a result, the adsorption efficiency is much less in lower pH conditions. With increase in pH, the concentration of OH^- increases which favours the adsorption process[89].

3.2.1.2. Graphical representation of various forms of char adsorbing Eosin Yellow

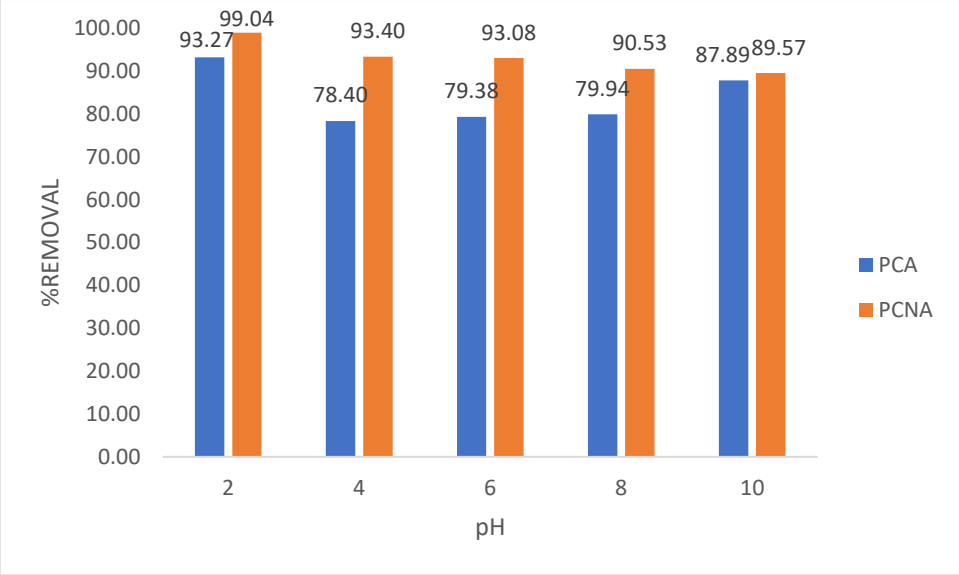


Fig.6:Effect of pH on removal of Eosin Yellow, Removal percentage vs pH

Eosin Yellow being an anioinic dye shows maximum removal percentage at acidic pH that is pH 2. With increase in pH, the removal percentage of dye decreases. However, when plastic char with OH group is used the removal efficiency increases as the basic group helps in adsorbing dye in acidic solution. However I have attached the graph where maximum amount of dye methylene blue has been removed by plastic char annealed.

Eosin Yellow, being an anionic dye has greater affinity towards positive ions. This resulted in the highest adsorption efficiency at lower pH conditions due to highest amount of H^+ concentration present in the dye solution. With increase in pH, the amount of H^+ concentration decreases and OH^- concentration increases[65].As a result there will be a repulsion factor between the dye solution and the adsorbent which will in turn restrict the adsorption process to some extent. So the removal efficiency of eosin yellow decreases with increase in pH of the dye solution[89]. However when PCNA char is used, the OH^- group in the adsorbent surface has

unobstructed interaction with the H^+ ion present in the dye solution. So best result is obtained when PCNA is used.

3.2.1.3. Graphical representation of various forms of Plastic char adsorbing Anthracene

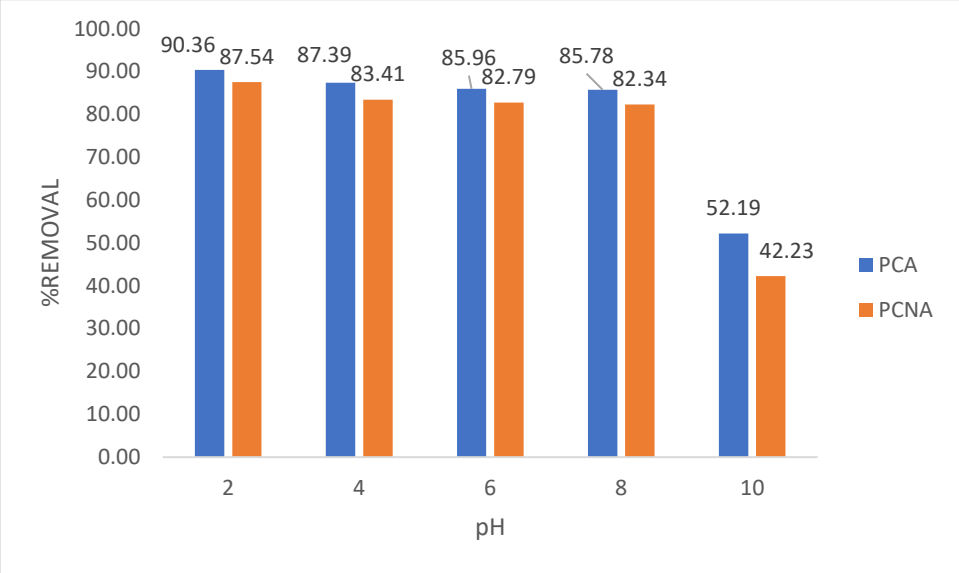


Fig.7:Effect of pH on removal of Anthracene, Removal percentage vs pH

The maximum removal has been shown by plastic char annealed at pH 10. However plastic char annealed char has shown the best removal. However, at pH 10, if plastic char treated with NaOH and annealed is used the presence of OH group hinders the adsorption.

The pH range of 2-10 was selected to study the effect of pH on the adsorption of anthracene using various forms of plastic char. Anthracene has an electron cloud in its structure. The result reveal that at pH 2, the removal efficiency is highest while the removal efficiency decreases with increase in pH. This result is shown by anthracene due to greater interaction between anthracene and positive ions present in the

solution[51]. However, if plastic char treated with NaOH and annealed is used, the adsorption efficiency decreases due to repulsion between the electron cloud of anthracene and negative OH^- group present in the adsorbent surface.

3.2.1.4. Graphical representation of various forms of Plastic char adsorbing Ranitidine hydrochloride

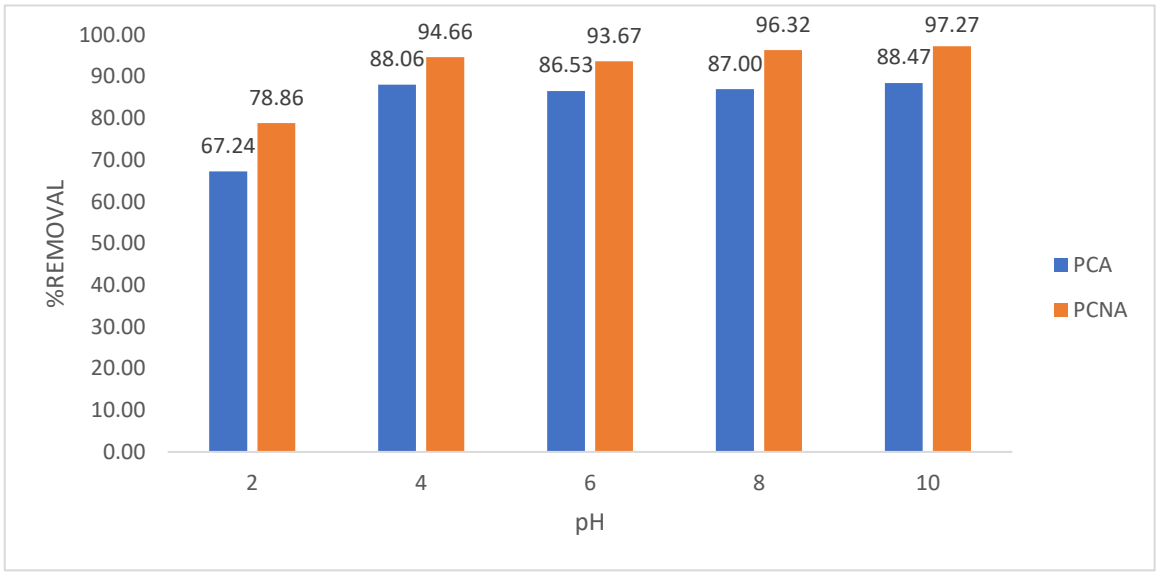


Fig.8:Effect of pH on removal of Ranitidine hydrochloride, Removal percentage vs pH

Maximum amount of ranitidine hydrochloride has been removed at pH 10. However it has been seen that in the case of removal of ranitidine hydrochloride, it has been found that it is slightly acidic,so adsorbing it with plastic char treated with NaOH and annealed yields better result,while in the case of anthracene, the pH is higher. So adsorbing anthracene with plastic char annealed yields better result.

The influence of solution pH onto adsorption of ranitidine hydrochloride is depicted in the figure. However, lowest adsorption occurs at pH 2. With increase in pH the adsorption efficiency increases. The simple reason for this result is due to the positive

charge on nitrogen atoms of rantidine hydrochloride due to protonation. As a result, there will be a repulsion force between rantidine hydrochloride and H^+ ions present in the solution when the pH is low. However, when the pH is high, there will be unobstructed binding between the positive charge of rantidine hydrochloride and the negative OH^- group present in the solution which will help in the process of adsorption thereby improving removal efficiency [51]. If plastic char treated with NaOH and annealed is used, the presence of negative OH^- group in the adsorbent surface farther helps in improving the adsorption efficiency.

3.2.2. Effects of Concentration on dye removal as well as removal of PAH and organic compound

After analysing the effect of pH in the case of adsorption, it is important to have an idea on how the concentration of dye has an effect in the case of removal by the process of adsorption. It has been found out that with the increase in concentration of dye,the removal efficiency has decreased.

3.2.2.1. Graphical representation of various forms of char adsorbing Methylene Blue

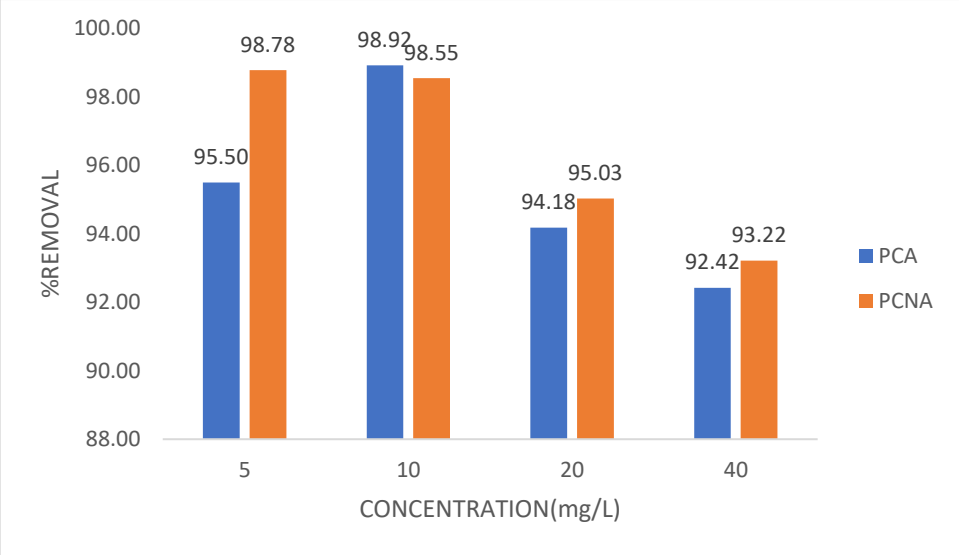


Fig.9:Effect of concentration on removal of Methylene Blue, Removal percentage vs concentration

In the case of plastic char annealed, maximum amount of adsorption occurs when 10 ppm dye solution is used. When the concentration increases, the removal percentage also decreases. In the case of plastic char treated with NaOH and annealed, maximum amount of adsorption when 5 ppm dye solution is used. When the concentration increases, the removal percentage also decreases. However, maximum removal has been shown by plastic char treated with NaOH and annealed.

Methylene blue being a cationic dye has more affinity towards OH^- group. So when plastic char treated with NaOH and annealed is used for adsorption, the removal efficiency improves. So when concentration study was performed used two types of plastic char, thje adsorbent with OH^- group yields better results. Now on giving insight to the removal percentage vs concentration graph, it has been found that with increase in concentration, the adsorption efficiency increses. This is due to the fact, there is limited surface area and pores present in the adsorbent(plastic char) for the process of adsorption.

Now with increase in dose concentration, there will less number of pores available for the dye molecules to get adsorbed. As a result after a significant amount of time, the char will reach its threshold capacity in adsorbing dye. Thus if high amount of dye concentration is used, excess dye will remain in the solution after the threshold capacity of char[66],[67],[68]. Thus the removal efficiency decreases with increase in concentration. In the case of adsorption with PCA the removal efficiency was highest in 10 ppm and not in 5 ppm because of some amount of desorption occurring in the adsorption experiment of 5 ppm dye solution.

3.2.2.2. Graphical representation of various forms of plastic char adsorbing Eosin Yellow

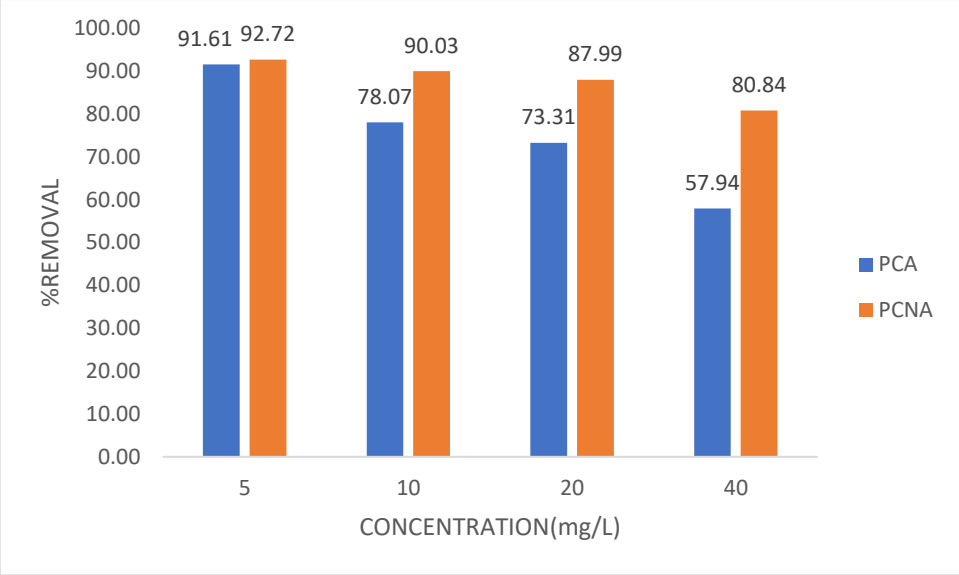


Fig.10:Effect of concentration on removal of Eosin Yellow, Removal percentage vs concentration

In the case of plastic char annealed, maximum amount of adsorption occurs when 5 ppm dye solution is used. When the concentration increases, the removal percentage decreases. In the case of plastic char treated with NaOH and annealed, maximum amount of adsorption when 5 ppm dye solution is used. When the concentration increases, the removal percentage decreases. However, maximum removal has been shown by plastic char annealed.

The maximum amount of adsorption occurs when 5 ppm dye solution is used.When the concentration increases, the removal percentage also decreases. Eosin yellow being an anionic dye has greater affinity towards H^+ ion. So when plastic char treated with NaOH and annealed is used, the presence of OH^- group hinders the adsorption process. Thus the best removal efficiency is shown by plastic char annealed. Now on

giving insight to the removal percentage vs concentration graph, it has been found that with increase in concentration, the adsorption efficiency increses. This is due to the fact, there is limited surface area and pores present in the adsorbent(plastic char) for the process of adsorption. Now with increase in dose concentration, there will less number of pores available for the dye molecules to get adsorbed. As a result after a significant amount of time, the char will reach its threshold capacity in adsorbing dye. Thus if high amount of dye concentration is used, excess dye will remain in the solution after the threshold capacity of char[66],[67],[68]. Thus the removal efficiency decreases with increase in concentration.

3.2.2.3. Graphical representation of various forms of plastic char adsorbing Anthracene

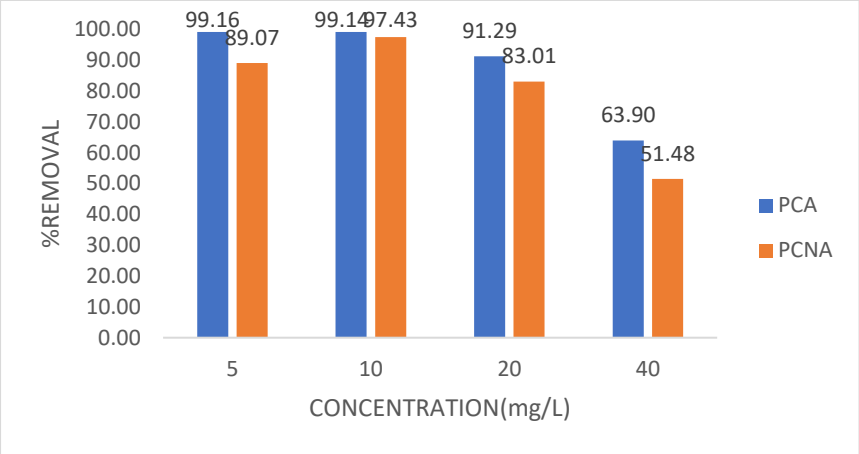


Fig.11:Effect of concentration on removal of Anthracene, Removal percentage vs concentration

The maximum amount of adsorption occurs in the case of plastic char annealed when 5 ppm dye solution is used.When the concentration increases, the removal percentage also decreases. When plastic char treated with NaOH and annealed is used, the removal efficiency decreases.

Anthracene has an electron cloud in its structure. When plastic char treated with NaOH and annealed is used as an adsorbent, there will be a repulsion between anthracene and the adsorbent surface which will reduce the adsorption efficiency. So using plastic char annealed yields best result. Now on giving insight to the removal percentage vs concentration graph, it has been found that with increase in concentration, the adsorption efficiency increses. This is due to the fact, there is limited surface area and pores present in the adsorbent(plastic char) for the process of adsorption. Now with increase in dose concentration, there will less number of pores available for the dye molecules to get adsorbed. As a result after a significant amount of time, the char will reach its threshold capacity in adsorbing dye[66],[67],[68]. Thus if high amount of dye concentration is used, excess dye will remain in the solution after the threshold capacity of char. Thus the removal efficiency decreases with increase in concentration.

3.2.2.4. Graphical representation of various forms of plastic char adsorbing Ranitidine hydrochloride

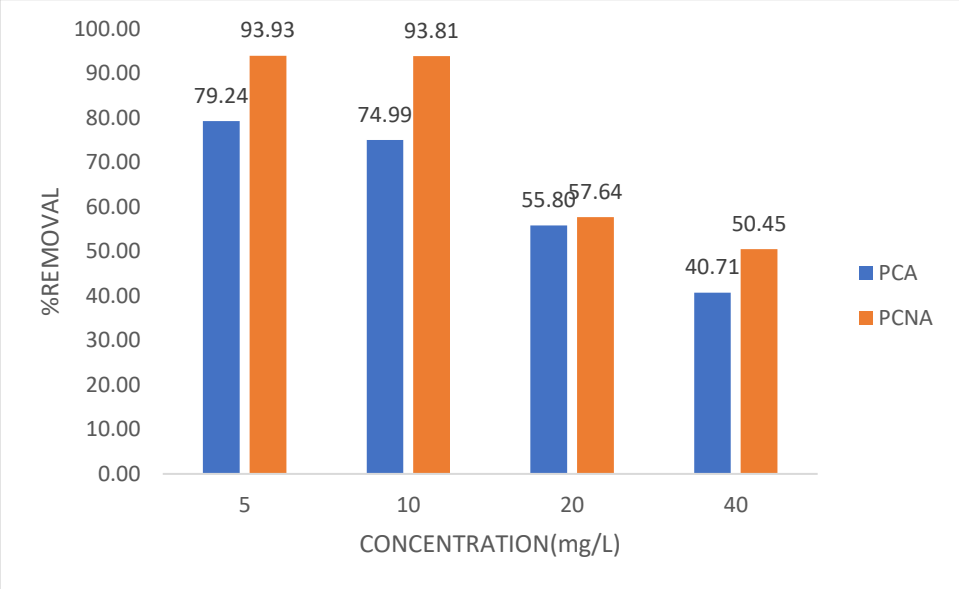


Fig.12:Effect of concentration on removal of Ranitidine hydrochloride, Removal percentage vs concentration

Ranitidine hydrochloride has positive charge on the nitrogen present in the compound. When plastic char treated with NaOH and annealed is used, there will be unobstructed interruption between ranitidine hydrochloride and adsorbent. As a result the removal efficiency will be best. Now on giving insight to the removal percentage vs concentration graph, it has been found that with increase in concentration, the adsorption efficiency increses. This is due to the fact, there is limited surface area and pores present in the adsorbent(plastic char) for the process of adsorption. Now with increase in dose concentration, there will less number of pores available for the dye molecules to get adsorbed. As a result after a significant amount of time, the char will reach its threshold capacity in adsorbing dye[66],[67],[68]. Thus if high amount of dye concentration is used, excess dye will remain in the solution after the threshold capacity of char. Thus the removal efficiency decreases with increase in concentration.

3.2.3. Effects of Dose on dye removal as well as removal of PAH and organic compound

The effect of adsorbent dosage has been studied by performing the adsorption experiment with various dosage of char. With increase in the dosage of char, the efficiency of adsorption has increased. Experimental results have showed maximum removal of dye like methylene blue, eosin yellow in the presence of 200 mg char for 50 ml of stock solution(10 ppm). In the removal of anthracene, 200 mg char has shown

the best removal percentage. However, in the removal of ranitidine hydrochloride, the best removal has been shown by 300 mg char for 50 ml stock solution(10 ppm).

3.2.3.1.Graphical representation of various forms of char adsorbing Methylene Blue

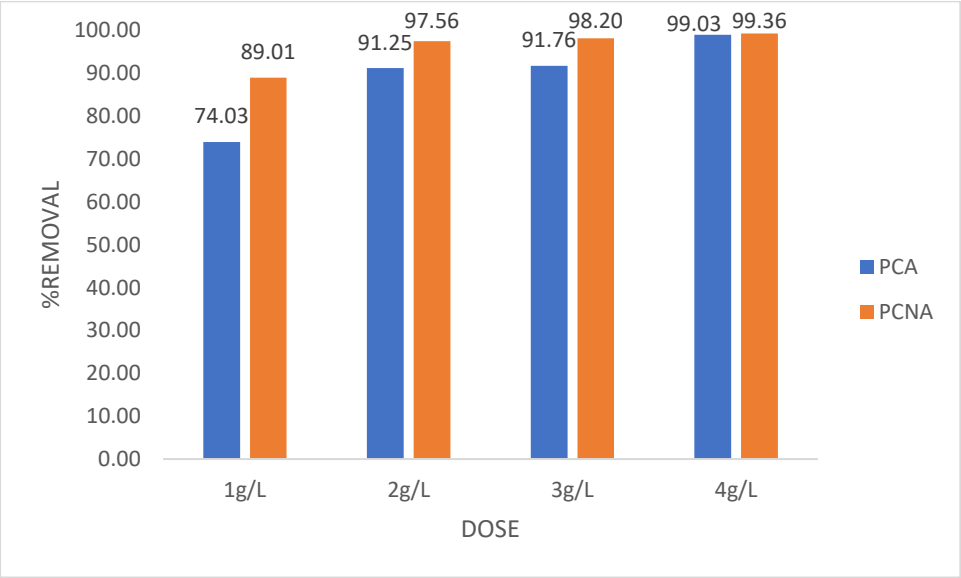


Fig.13:Effect of dose on removal of Methylene Blue, Removal percentage vs dose

When 4g/L dose of plastic char treated with NaOH and annealed is used, maximum adsorption occurs. When other types of char are used, the removal efficiency is less. Methylene blue being a cationic dye has greater affinity for OH^- group. So when plastic char treated with NaOH and annealed is used, best result is obtained. Now on giving importance to the effect of dose in the adsorption process, it has been found that with increase in dose from 1g/L to 4 g/L the removal efficiency increases. This result is due to the fact that with increase in dosage of char there is an increase in surface area and pore size which results is better removal efficiency[83]. However,as the pore size gets filled with pollutant, the removal efficiency does not change much. Towards the end of the experiment, equilibrium is reached in the adsorption process.

3.2.3.2. Graphical representation of various forms of char adsorbing Eosin Yellow

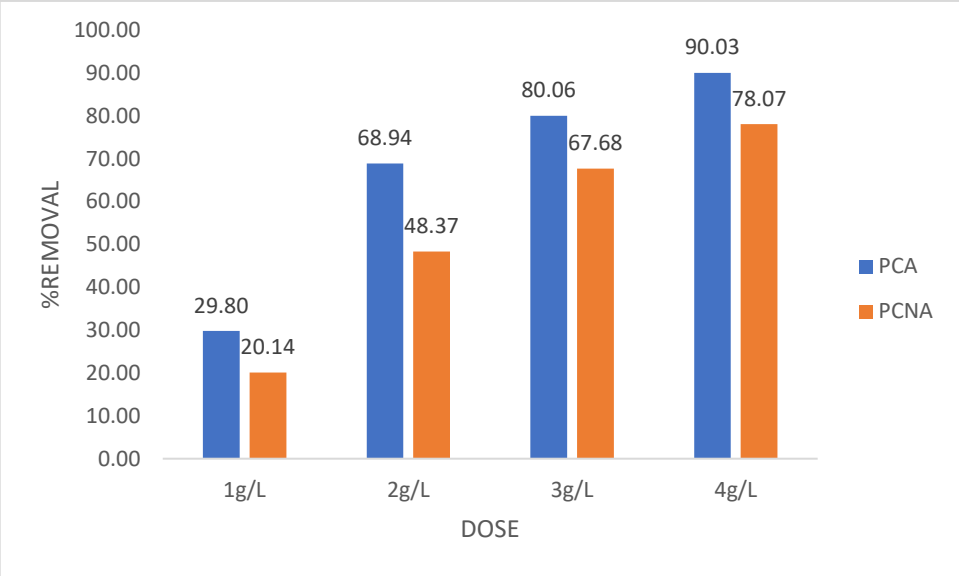


Fig.14:Effect of dose on removal of Eosin Yellow, Removal percentage vs dose

When 4g/L dose of PCA is used, maximum adsorption occurs. When other types of char are used, the removal efficiency is less. Eosin Yellow being an anionic dye has greater affinity towards H^+ ion. So the presence of OH^- group in the adsorbent hinders the adsorption process. So best result is obtained when PCA is used. Now on giving importance to the effect of dose in the adsorption process, it has been found that with increase in dose from 1g/L to 4 g/L the removal efficiency increases. This result is due to the fact that with increase in dosage of char there is an increase in surface area and pore size which results is better removal efficiency[83]. However,as the pore size gets filled with pollutant, the removal efficiency does not change much. Towards the end of the experiment, equilibrium is reached in the adsorption process.

3.2.3.3. Graphical representation of various forms of plastic char adsorbing Anthracene

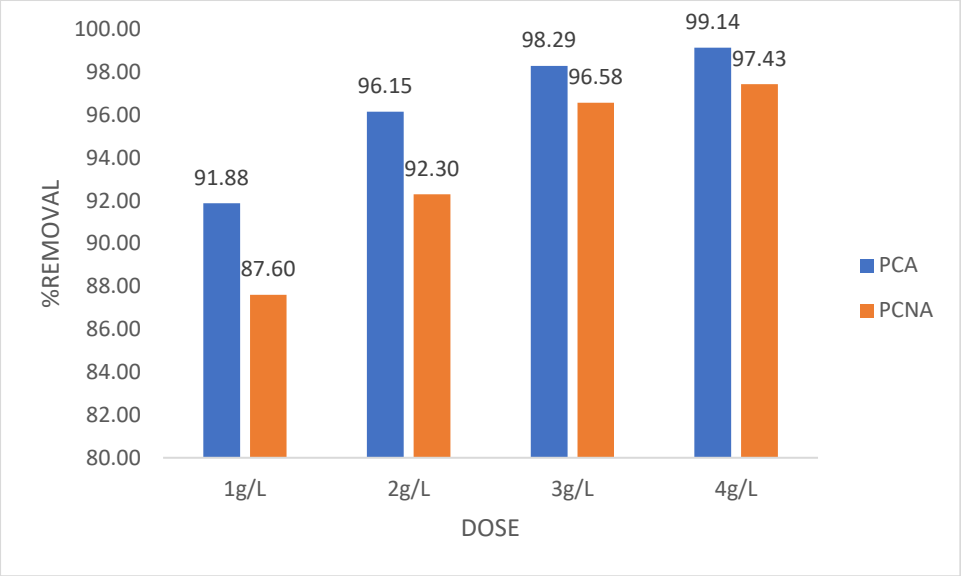


Fig.15:Effect of dose on removal of Anthracene, Removal percentage vs dose

When 4g/L dose of plastic char annealed is used, maximum adsorption occurs. Anthracene has an electron compound in its structure. When PCNA is used as an adsorbent, there is a repulsion factor between OH^- group in the adsorbent and the electron cloud which hinders the process of adsorption. Thus, best removal is shown by PCA. Now on giving importance to the effect of dose in the adsorption process, it has been found that with increase in dose from 1g/L to 4 g/L the removal efficiency increases. This result is due to the fact that with increase in dosage of char there is an increase in surface area and pore size which results is better removal efficiency [83]. However,as the pore size gets filled with pollutant, the removal efficiency does not change much. Towards the end of the experiment, equilibrium is reached in the adsorption process.

3.2.3.4. Graphical representation of various forms of plastic char adsorbing Ranitidine hydrochloride

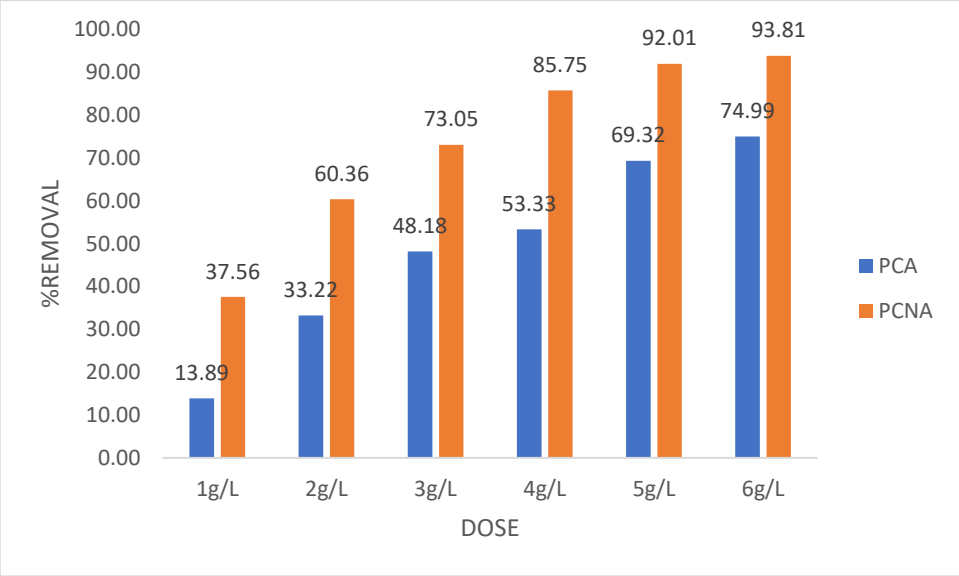


Fig.16: Effect of dose on removal of Ranitidine hydrochloride, Removal percentage vs dose

When 6g/L dose of char is used,maximum adsorption occurs. However, when the char treated with NaOH and annealed is used, the adsorption increases. Ranitidine hydrochloride has positive charge on the nitrogen present in its structure. If PCNA is used there will be unobstructed interaction between the OH^- group in the adsorbent and the positive charge present in Ranitidine hydrochloride which will help in better adsorption. Now on giving importance to the effect of dose in the adsorption process, it has been found that with increase in dose from 1g/L to 6 g/L the removal efficiency increases. This result is due to the fact that with increase in dosage of char there is an increase in surface area and pore size which results is better removal efficiency[83]. However,as the pore size gets filled with pollutant, the removal efficiency does not change much. Towards the end of the experiment, equilibrium is reached in the adsorption process.

3.2.4. Effects of Temperature on dye removal

It is a crucial parameter since it significantly influences the equilibrium capacity in adsorption [82]. With increase in temperature,adsorption increases in the process of chemisorption because heat acts as an activation energy.At first with increase in temperature,first adsorption increases,then decreases. In the case of physisorption, if temperature is increased, the adsorption will decrease.

3.2.4.1. Graphical representation of various forms of char adsorbing Methylene Blue

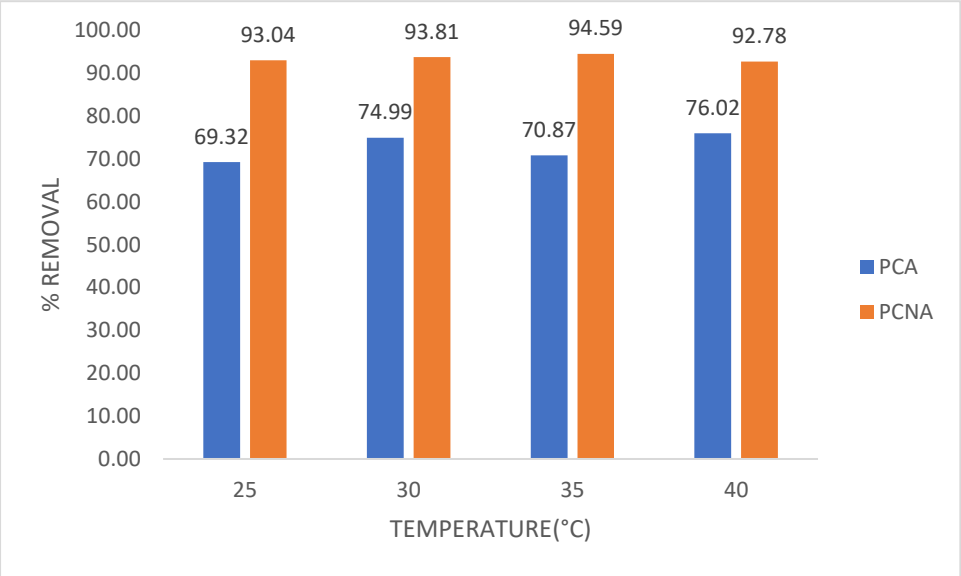


Fig.17:Effect of temperature on removal of Methylene Blue, Removal percentage vs temperature

The experiment was performed along a temperature range of 25°C to 40°C. The maximum adsorption is at 40°C when plastic Char treated with NaOH and annealed is used. The removal percentage increased with increasing temperature which means that adsorption process was endothermic in nature. Temperature rise leads to increased mobility of MB molecules with optimum energy for their interaction with the surface-active sites on the char [84],[87]. Increased porosity and widening of

adsorbent pore sites, due to increasing temperature could also contribute to high removal % of MB [85].

3.2.4.2. Graphical representation of various forms of Char adsorbing Eosin Yellow

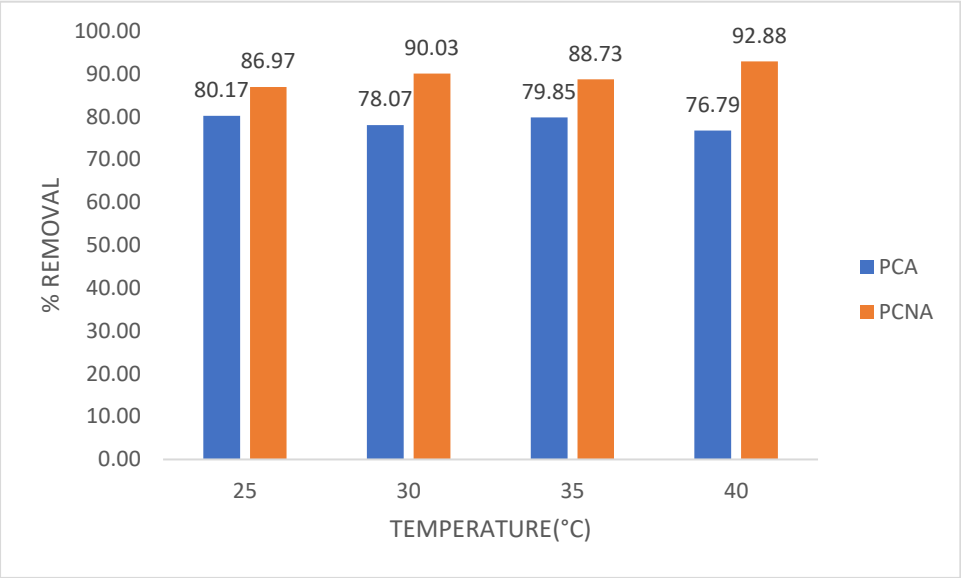


Fig.18: Effect of temperature on removal of Eosin Yellow, Removal percentage vs temperature

The experiment was performed along a temperature range of 25°C to 40°C. The maximum adsorption is at 40°C when plastic Char annealed is used. The removal percentage increased with increasing temperature which means that adsorption process was endothermic in nature. There is slightly less removal at 35°C temperature due to little amount of desorption occurring during the experiment. Temperature rise leads to increased mobility of EY molecules with optimum energy for their interaction with the surface-active sites on the char [84],[87]. Increased porosity and widening of adsorbent pore sites, due to increasing temperature could also contribute to high removal % of EY [85].

3.2.4.3. Graphical representation of various forms of plastic Char adsorbing Anthracene

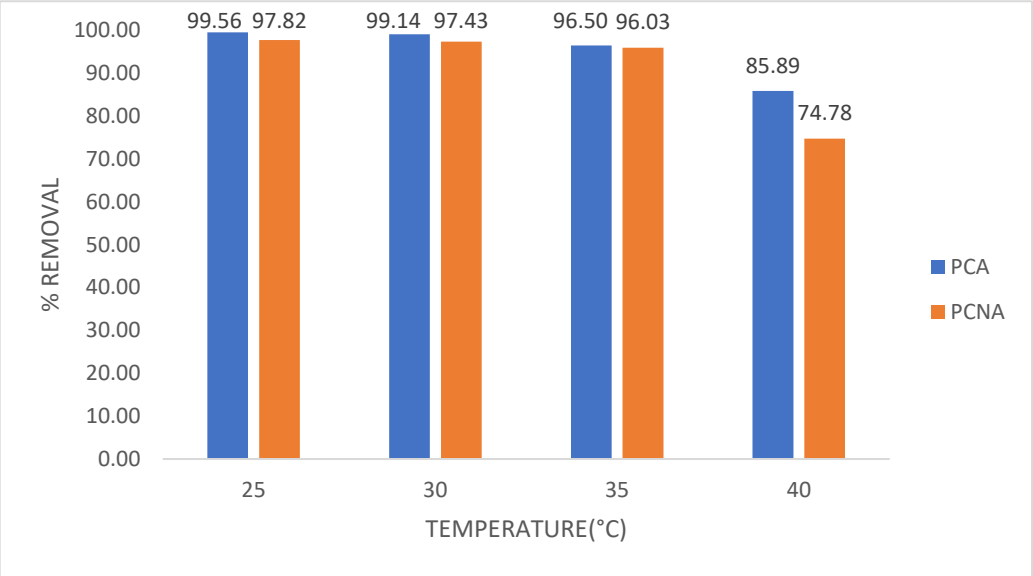


Fig.19: Effect of temperature on removal of Anthracene, Removal percentage vs temperature

The maximum adsorption is at 25°C when plastic char annealed is used. With increase in temperature, removal percentage decreases.Anthracene has an electron cloud in its structure.So when PCNA char is used, there is a repulsion between OH^- group in the adsorbent and the electron cloud which hinders the process of adsorption.So best result is obtained when PCA is used. The removal percentage decreased with increasing temperature which means that adsorption process was exothermic in nature. Temperature rise leads to decreased mobility of anthracene molecules with optimum energy for their interaction with the surface-active sites on the char [84],[87]. Decreased porosity of adsorbent pore sites, due to increasing temperature could also contribute to low removal % of anthracene [85].

3.2.4.4. Graphical representation of various forms of plastic Char adsorbing Ranitidine hydrochloride

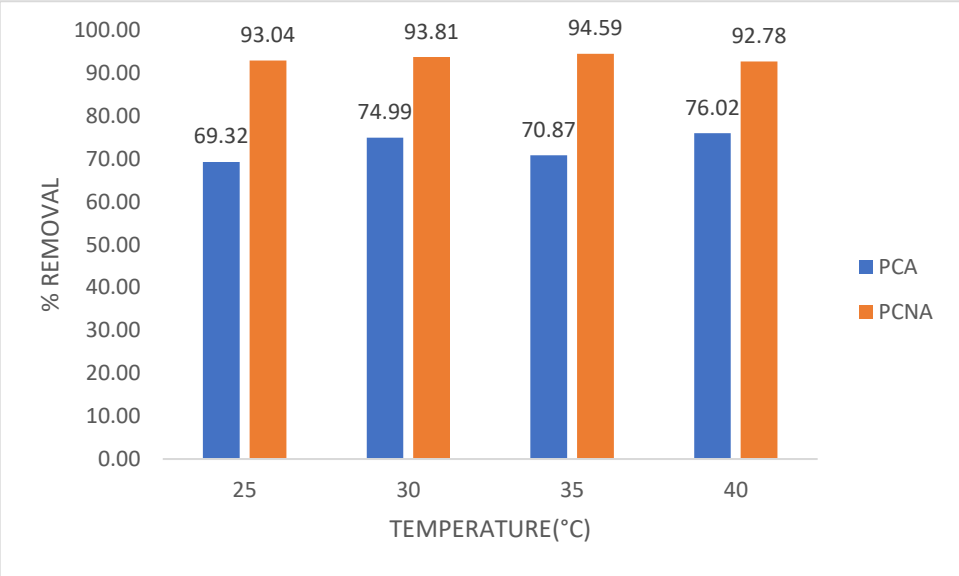


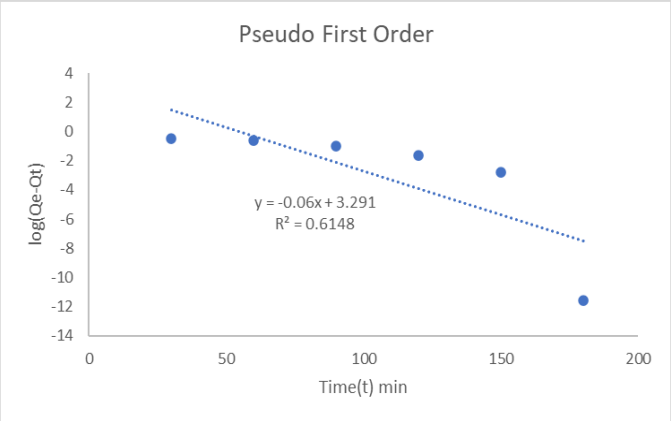
Fig.20: Effect of temperature on removal of Ranitidine hydrochloride, Removal percentage vs temperature

The maximum adsorption is at 35°C. With increase in temperature from 30°C to 35°C the adsorption increases and finally 40°C, the adsorption decreases. The removal percentage increased with increasing temperature which means that adsorption process was endothermic in nature. Temperature rise leads to increased mobility of Ranitidine hydrochloride molecules with optimum energy for their interaction with the surface-active sites on the char [84],[87]. Increased porosity and widening of adsorbent pore sites, due to increasing temperature could also contribute to high removal % of Ranitidine hydrochloride [85]. However, beyond the optimum point, as the temperature increased, weakening of the molecular bonds among the pollutant and the adsorbents was observed, resulting in the decrease of adsorption.

3.2.5. Adsorption kinetics

3.2.5.1. Adsorption kinetics for Methylene Blue

In my thesis, the maximum removal of dye has been observed when PCNA is used to adsorb methylene blue. So the adsorption kinetics data for this scenario is attached.



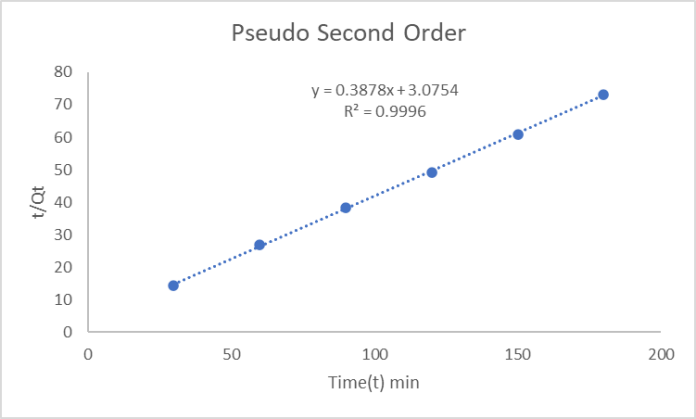


Fig.21:Adsorption kinetics study analysis(Methylene Blue), (a) Pseudo first order, (b) Pseudo second order

Table 4: Adsorption kinetics(Methylene Blue) (a) For pseudo first order (b) pseudo second order

For pseudo first order		
	Slope=(Kf/2.303)	C=log(qe)=3.291
	Kf=slope*2.303	qe=antilog(3.291)
	Kf=0.13818	qe=1954.339456 mg/g
	R^2 = 0.6148	
For pseudo second order		

	Slope=1/Qe	Ks=1/((intercept)Qe*Qe)
	Qe=1/slope	Ks=0.048900578g/ mg-min
	Qe=2.578648788mg/g	
	R^2 = 0.9996	

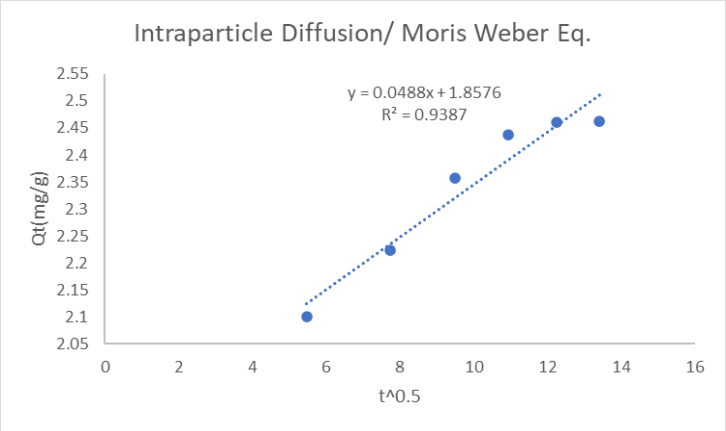


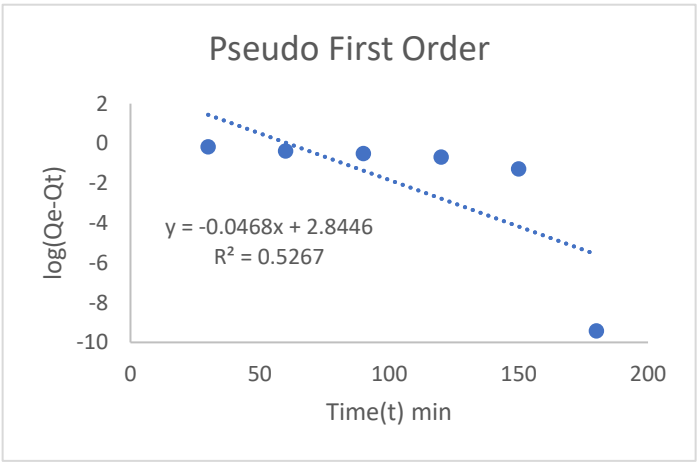
Fig.21:Adsorption kinetics study analysis(Methylene Blue), (c) Intraparticle diffusion/Moris Weber Eq

For kinetic study, “pseudo-first order” and “pseudo-second order” analysis were carried out. “Pseudo-second order” has a greater R^2 compared to that of “pseudo-first order” reaction. This states that the reaction follows “pseudo-second order” reaction mechanism more compared to “pseudo-first order” reaction. Following “pseudo-second order reaction” means there is more chance of the reaction to follow chemisorption process as compared to physisorption[86].In the pseudo second order model, the adsorption capacity at equilibrium is 2.57864 mg/g. From the Moris Weber

equation, the thickness of adsorption layer is 1.8576 and 0.0488 is intraparticle diffusion constant.

3.2.5.2. Adsorption kinetics for Eosin Yellow

In my thesis, the maximum removal of dye has been observed when PCA is used to adsorb eosin yellow. So the adsorption kinetics data for this scenario is attached.



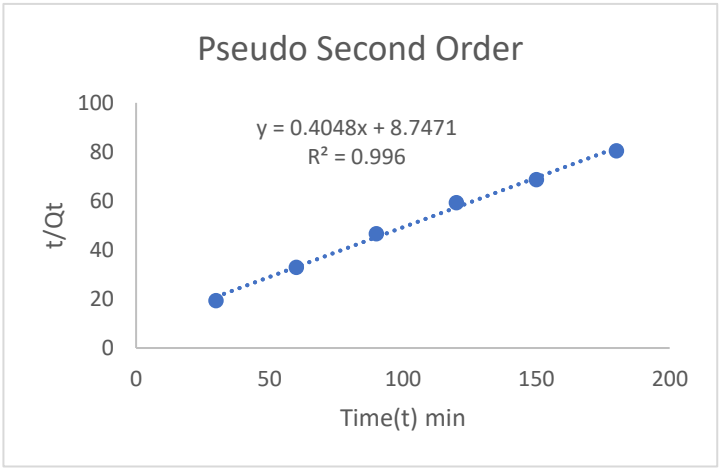


Fig.22:Adsorption kinetics study analysis (Eosin Yellow), (a) Pseudo first order, (b) Pseudo second order

Table 5: Adsorption kinetics(Eosin Yellow) (a) For pseudo first order (b) pseudo second order

For pseudo first order		
	Slope=(Kf/2.303)	C=log(qe)=2.8446

	Kf=slope*2.303	qe=antilog(2.8446)
	Kf=0.1077804	qe=699.1977145 mg/g
	R^2 = 0.5267	
For pseudo second order		
	Slope=1/Qe	Ks=1/((intercept)Qe*Qe)
	Qe=1/slope	Ks=0.018733413g/ mg-min
	Qe=2.470355731mg/g	
	R^2 = 0.996	

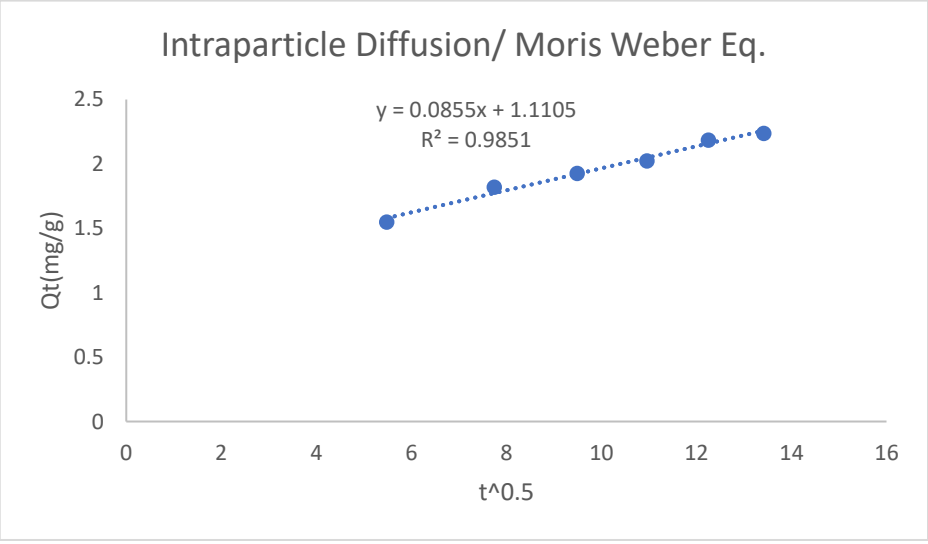


Fig.22:Adsorption kinetics study analysis(Eosin Yellow), (c) Intraparticle diffusion/Moris Weber Eq

For kinetic study, “pseudo-first order” and “pseudo-second order” analysis were carried out. “Pseudo-second order” has a greater R^2 compared to that of “pseudo-first

order" reaction. This states that the reaction follows "pseudo-second order" reaction mechanism more compared to "pseudo-first order" reaction. Following "pseudo-second order reaction" means there is more chance of the reaction to follow the chemisorption process as compared to physisorption[86]. In the pseudo second order model, the adsorption capacity at equilibrium is 2.4703 mg/g. From the Moris Weber equation, the thickness of adsorption layer is 1.1105 and 0.0855 is intraparticle diffusion constant.

3.2.5.3. Adsorption kinetics for Anthracene

In my thesis, the maximum removal of dye has been observed when PCA is used to adsorb Anthracene. So the adsorption kinetics data for this scenario is attached.

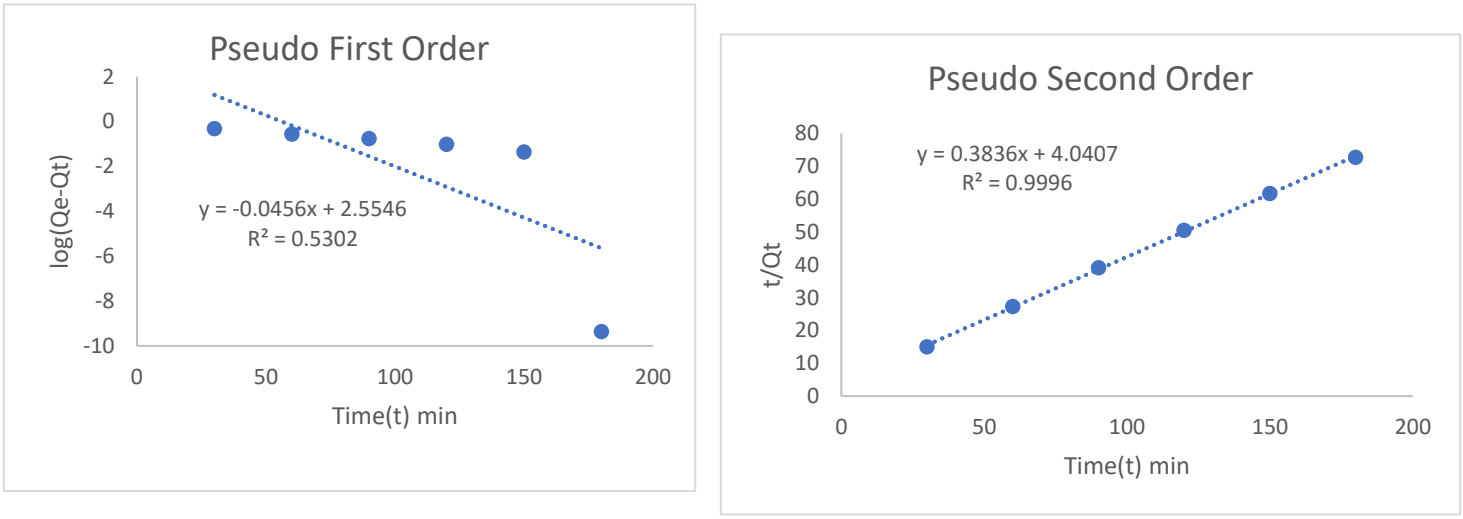


Fig.23:Adsorption kinetics study analysis (Anthracene), (a) Pseudo first order, (b) Pseudo second order

Table 6: Adsorption kinetics(Anthracene) (a) For pseudo first order (b) pseudo second order

For pseudo first order		
	Slope=(Kf/2.303)	C=log(qe)=2.5546
	Kf=slope*2.303	qe=antilog(2.5546)
	Kf=0.1050168	qe=358.5915075 mg/g
	R^2 = 0.5302	
For pseudo second order		
	Slope=1/Qe	Ks=1/((intercept)Qe*Qe)
	Qe=1/slope	Ks=0.0364167g/ mg-min
	Qe=2.606882169mg/g	
	R^2 = 0.9996	

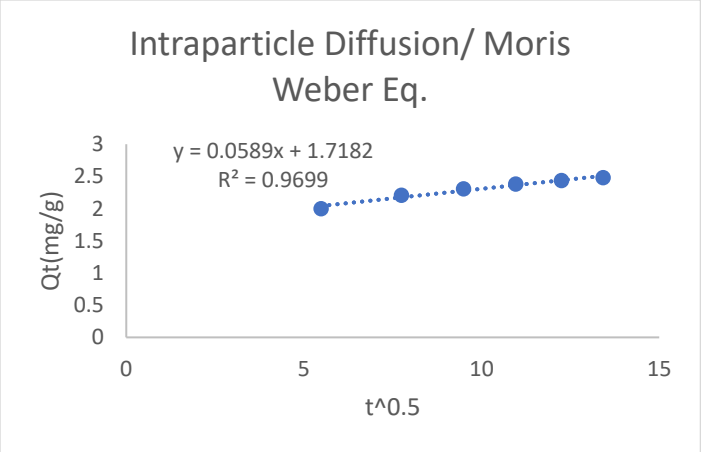


Fig.23:Adsorption kinetics study analysis(Anthracene), (c) Intraparticle diffusion/Moris Weber Eq

For kinetic study, “pseudo-first order” and “pseudo-second order” analysis were carried out. “Pseudo-second order” has a greater R^2 compared to that of “pseudo-first

order" reaction. This states that the reaction follows "pseudo-second order" reaction mechanism more compared to "pseudo-first order" reaction. Following "pseudo-second order reaction" means there is more chance of the reaction to follow the chemisorption process as compared to physisorption[86] .In the pseudo second order model, the adsorption capacity at equilibrium is 2.6068 mg/g. From the Moris Weber equation, the thickness of adsorption layer is 1.7182 and 0.0589 is intraparticle diffusion constant.

3.2.5.4. Adsorption kinetics for Ranitidine hydrochloride

In my thesis, the maximum removal of dye has been observed when PCNA is used to adsorb Ranitidine hydrochloride. So the adsorption kinetics data for this scenario is attached.

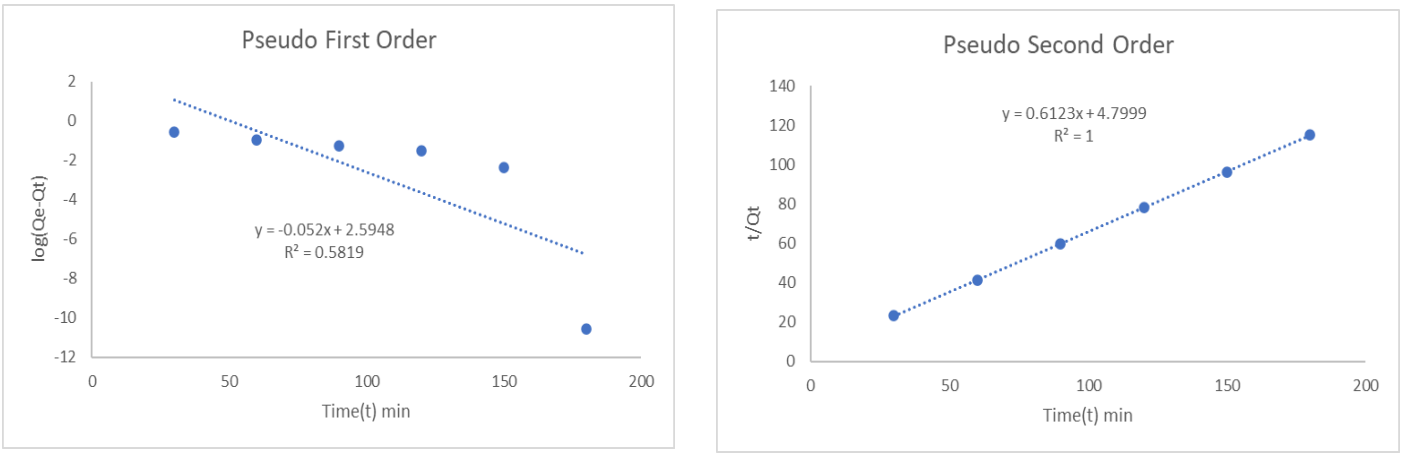


Fig.24:Adsorption kinetics study analysis (Ranitidine hydrochloride), (a) Pseudo first order, (b) Pseudo second order

Table 7: Adsorption kinetics(Ranitidine hydrochloride) (a) For pseudo first order (b) pseudo second order

For pseudo first order		
	Slope=(Kf/2.303)	C=log(qe)=2.5948
	Kf=slope*2.303	qe=antilog(2.5948)
	Kf=0.119756	qe=393.3688807 mg/g
	R^2 = 0.5819	
For pseudo second order		
	Slope=1/Qe	Ks=1/((intercept)Qe*Qe)
	Qe=1/slope	Ks=0.078108146g/ mg-min
	Qe=1.633186347mg/g	
	R^2 = 1	

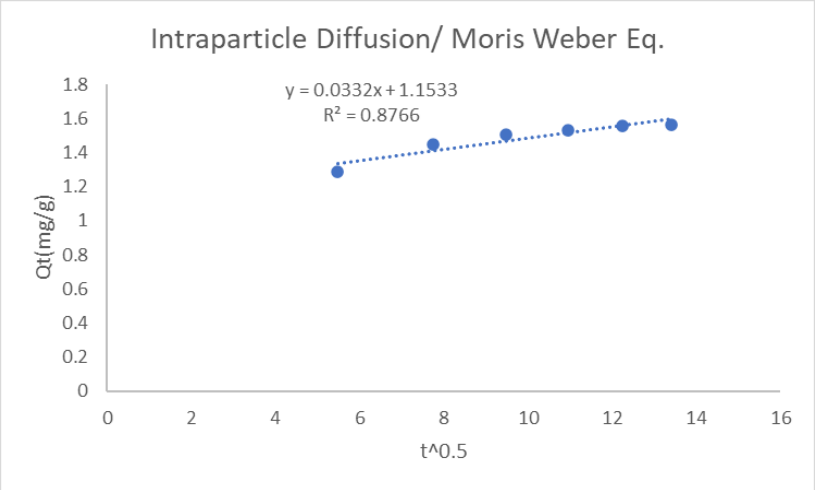


Fig.24:Adsorption kinetics study analysis(Ranitidine hydrochloride), (c) Intraparticle diffusion/Moris Weber Eq

For kinetic study, “pseudo-first order” and “pseudo-second order” analysis were carried out. “Pseudo-second order” has a greater R^2 compared to that of “pseudo-first order” reaction. This states that the reaction follows “pseudo-second order” reaction mechanism more compared to “pseudo-first order” reaction. Following “pseudo-second order reaction” means there is more chance of the reaction to follow the chemisorption process as compared to physisorption[86].In the pseudo second order model, the adsorption capacity at equilibrium is 1.6331 mg/g. From the Moris Weber equation, the thickness of adsorption layer is 1.1533 and 0.0332 is intraparticle diffusion constant.

3.2.6. Adsorption Isotherm

3.2.6.1. Adsorption Isotherm for Methylene Blue

In my thesis, the maximum removal of dye has been observed when PCNA is used to adsorb methylene blue. So the adsorption isotherm data for this scenario is attached below.

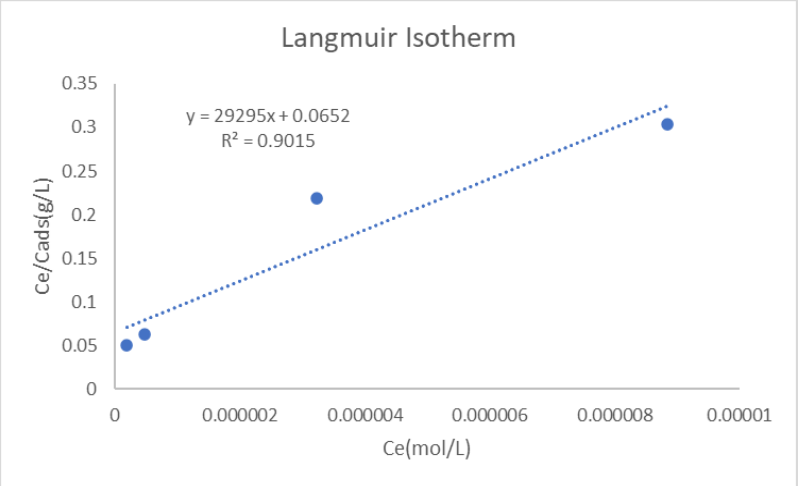


Fig.25:Adsorption isotherm study graphs(Methylene blue) for (a) Langmuir isotherm

Table 8: Adsorption isotherm(Methylene Blue) (a) Langmuir isotherm

m=1/q0 q0=1/m=1/29295=3.41355180064E-5mol/g	1/(q0b)=intercept
q0=0.010918245 g/g	b=1/q0(intercept)
R^2 = 0.9015	b=1/(3. 41355180064E-5*0.0652)
	b=449309.816

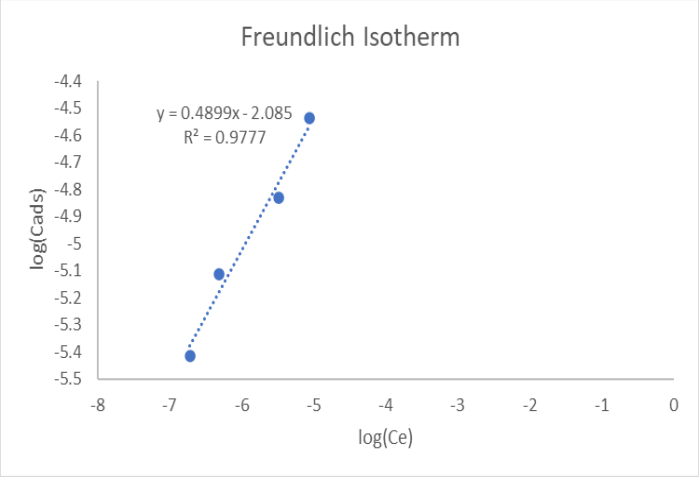


Fig.25:Adsorption isotherm study graphs(Methylene Blue) for(b) Freundlich isotherm

Table 8: Adsorption isotherm(Methylene Blue) (b)Freundlich isotherm

R^2 = 0.9777	
m=(1/n)=0.4899	
n=2.0412329046744	mole to gram conversion
C=log Kf=(-2.085)	Kf=2.629943116g/g
Kf=antilog(C)	g to mg conversion

Kf=8.222426499E-3 mol/g	Kf=2629.943116mg/g

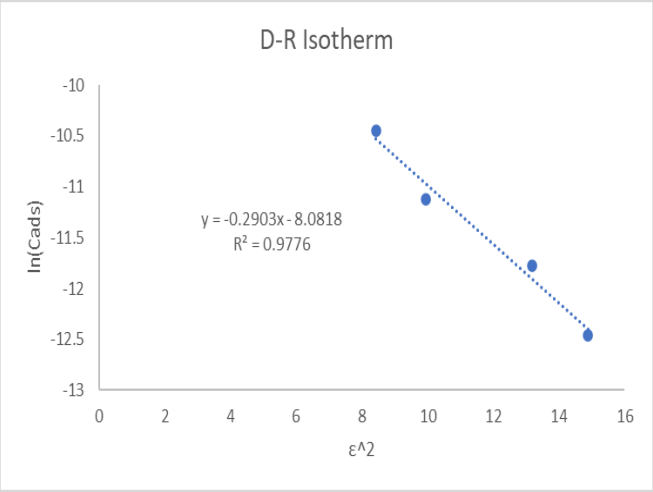


Fig.25:Adsorption isotherm study graphs(Methylene Blue) for (c) D-R isotherm

Table 8: Adsorption isotherm(Methylene Blue) (c)D-R isotherm

β=Slope=0.2903mol^2KJ^-2	R^2 = 0.9776
Es=1/((2β)^0.5)	
Es=1.312385684KJ/mol	

The Langmuir isotherm is applicable for monolayer adsorption on a homogeneous site, whereas Freundlich is valid for multilayer adsorption on heterogeneous sites.From the above graphs, freundlich isotherm suit the model better as it has greater R^2 value. Thus, there is a greater chance of chemisorption taking place in the adsorption[86]. From the D-R isotherm, the energy of adsorption is found to be 1.31238KJ/mole. The parameter β suggests a mean free energy of adsorption which is 0.2903mol^2KJ^-2 [94].

3.2.6.2. Adsorption Isotherm for Eosin Yellow

In my thesis, the maximum removal of dye has been observed when PCA is used to adsorb eosin yellow. So the adsorption isotherm data for this scenario is attached below.

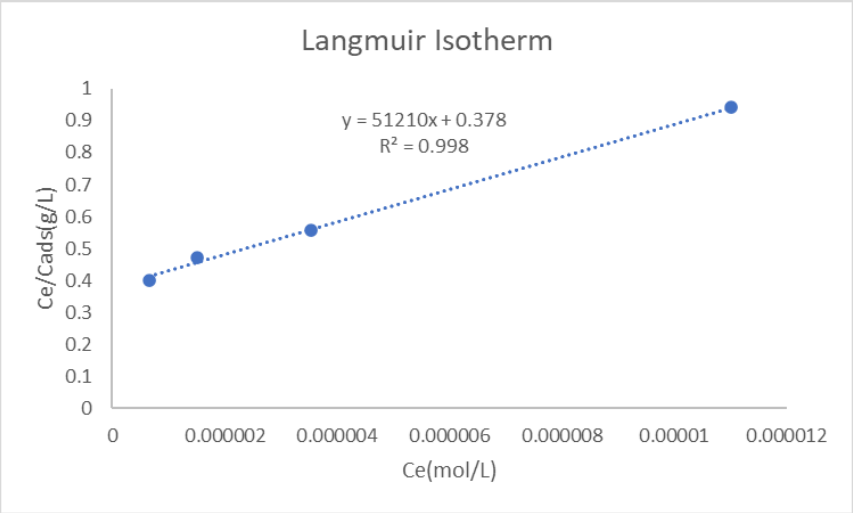


Fig.26:Adsorption isotherm study graphs(Eosin Yellow) for (a) Langmuir isotherm

Table 9: Adsorption isotherm(Eosin Yellow) (a) Langmuir isotherm

m=1/q0 q0=1/m=1/51210=1.952743605E-5mol/g	1/(q0b)=intercept
q0=0.013510642 g/g	b=1/q0(intercept)
R^2 = 0.998	b=1/(1.952743605E-5*0.378)
	b=135476.1905

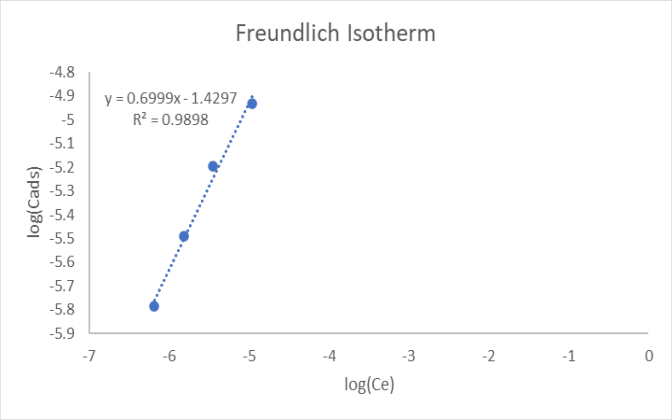


Fig.26:Adsorption isotherm study graphs(Eosin Yellow) for(b) Freundlich isotherm

Table 9: Adsorption isotherm(Eosin Yellow) (b)Freundlich isotherm

R^2 = 0.9898	
m=(1/n)=0.6999	
n=1.428775539	mole to gram conversion
C=log Kf=(-1.4297)	Kf=25.72354249g/g
Kf=antilog(C)	g to mg conversion
Kf=0.037179196 mol/g	Kf=25723.54249mg/g

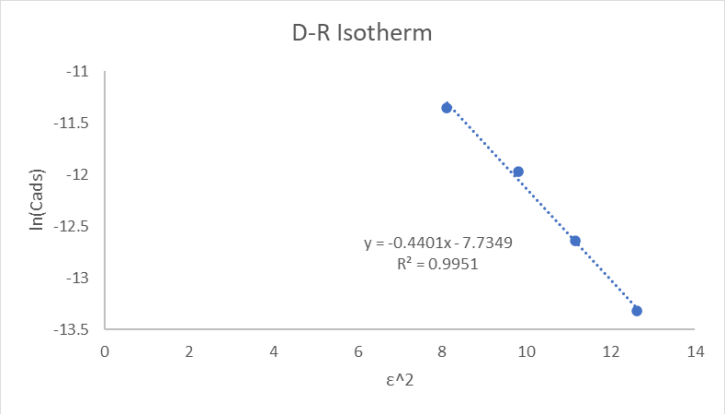


Fig.26:Adsorption isotherm study graphs(Eosin Yellow) for (c) D-R isotherm

Table 9: Adsorption isotherm(Eosin Yellow) (c)D-R isotherm

β=Slope=0.4401mol^2KJ^-2	R^2 = 0.9951
Es=1/((2β)^0.5)	
Es=1.065882466KJ/mol	

The langmuir isotherm is applicable for monolayer adsorption on a homogeneous site, whereas Freundlich is valid for multilayer adsorption on heterogeneous sites.From the above graphs, langmuir isotherm suit the model better as it has greater R^2 value.Thus there is a greater chance of physisorption taking place in the adsorption[86].From the D-R isotherm, the energy of adsorption is found to be 1.06588KJ/mole. The parameter β suggests a mean free energy of adsorption which is 0.4401mol^2KJ^-2 [94].

3.2.6.3. Adsorption Isotherm for Anthracene

In my thesis, the maximum removal of dye has been observed when PCA is used to adsorb Anthracene. So the adsorption isotherm data for this scenario is attached below.

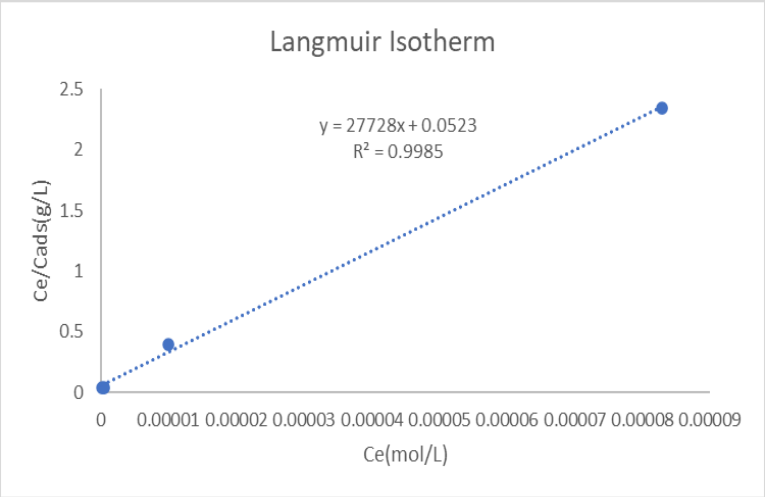


Fig.27:Adsorption isotherm study graphs(Anthracene) for (a) Langmuir isotherm

Table 10: Adsorption isotherm(Anthracene) (a) Langmuir isotherm

m=1/q0 q0=1/m=1/27728=0.0000360646mol/g	1/(q0b)=intercept
q0=0.0064277937 g/g	b=1/q0(intercept)
R^2 = 0.9985	b=1/(0.0000360646*0.0523)
	b=530166.472

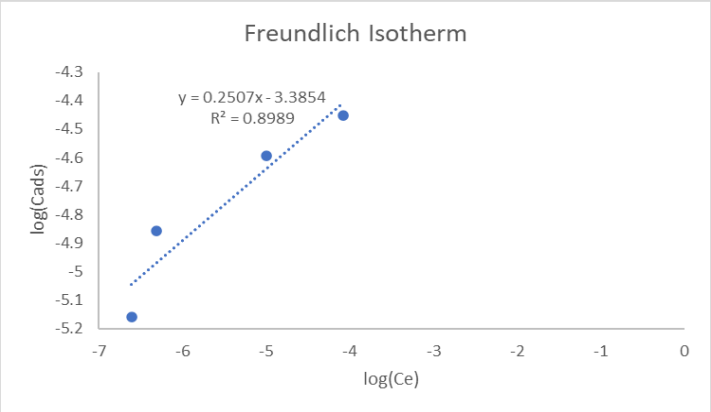


Fig.27:Adsorption isotherm study graphs(Anthracene) for(b) Freundlich isotherm

Table 10: Adsorption isotherm(Anthracene) (b)Freundlich isotherm

R^2 = 0.8989	
m=(1/n)=0.2507	
n=3.988831	mole to gram conversion
C=log Kf=(-3.3854)	Kf=0.07338052373g/g
Kf=antilog(C)	g to mg conversion
Kf=4.11718E-4 mol/g	Kf=73.m38052373g/g

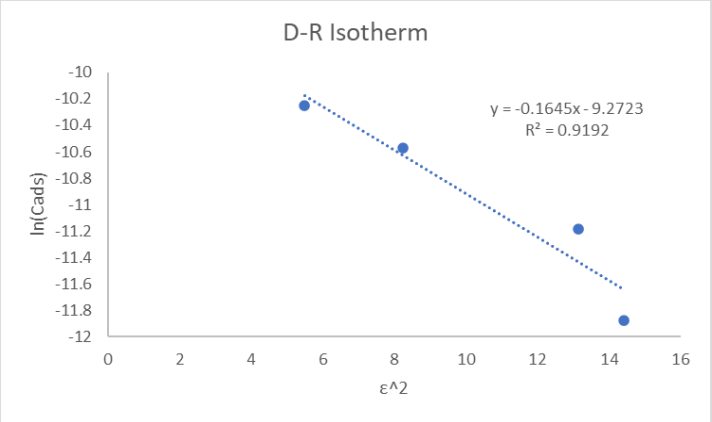


Fig.27:Adsorption isotherm study graphs(Anthracene) for (c) D-R isotherm

Table 10: Adsorption isotherm(Anthracene) (c)D-R isotherm

β=Slope=0.271mol^2KJ^-2	R^2 = 0.7471
Es=1/((2β)^0.5)	
Es=1.358314562KJ/mol	

The langmuir isotherm is applicable for monolayer adsorption on a homogeneous site, whereas Freundlich is valid for multilayer adsorption on heterogeneous sites.From the above graphs, langmuir isotherm suit the model better as it has greater R^2 value.Thus there is a greater chance of physisorption taking place in the adsorption[86].From the D-R isotherm, the energy of adsorption is found to be 1.358314KJ/mole. . The parameter β suggests a mean free energy of adsorption which is 0.271mol^2KJ^-2 [94].

3.2.6.4. Adsorption Isotherm for Ranitidine hydrochloride

In my thesis, the maximum removal of dye has been observed when PCNA is used to adsorb Ranitidine hydrochloride. So the adsorption isotherm data for this scenario is attached below.

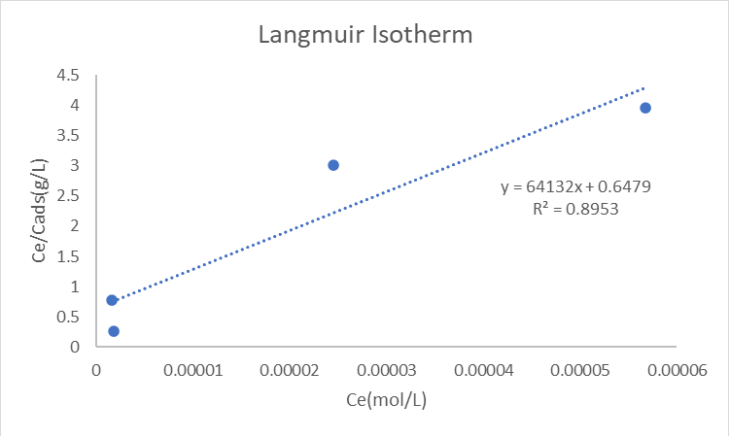


Fig.28:Adsorption isotherm study graphs(Ranitidine hydrochloride) for (a) Langmuir isotherm

Table 11: Adsorption isotherm(Ranitidine hydochloride) (a) Langmuir isotherm

m=1/q0 q0=1/m=1/64132=1.55928E-5mol/g	1/(q0b)=intercept
q0=5.4709E-3 g/g	b=1/q0(intercept)
R^2 = 0.8953	b=1/(1.55928E-5*0.6479)
	b=98984.41117

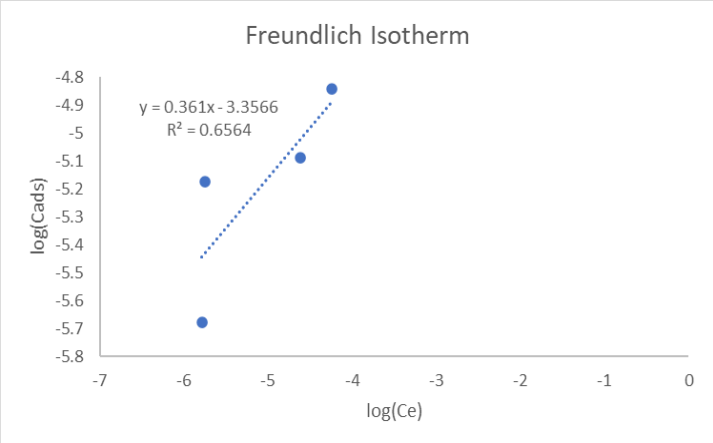


Fig.28:Adsorption isotherm study graphs(Ranitidine hydrochloridee) for(b) Freundlich isotherm

Table 11: Adsorption isotherm(Ranitidine hydrochloride) (b)Freundlich isotherm

R^2 = 0.6564	
m=(1/n)=0.361	
n=2.770083	mole to gram conversion
C=log Kf=(-3.3566)	Kf=0.154359676g/g
Kf=antilog(C)	g to mg conversion
Kf=4.399466E-4 mol/g	Kf=154.359676g/g

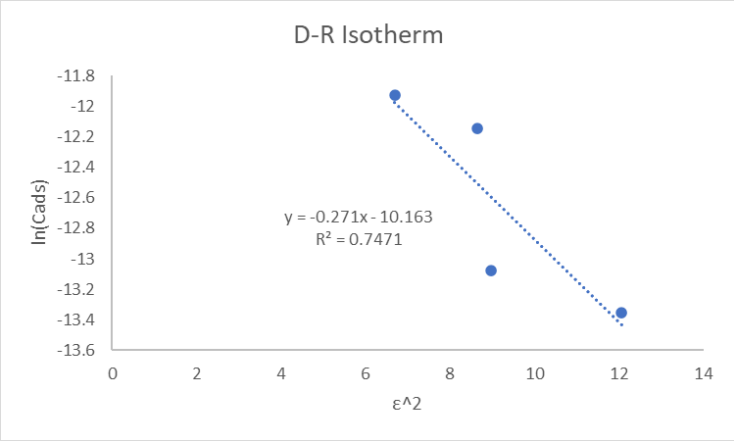


Fig.28:Adsorption isotherm study graphs(Ranitidine hydrochloride) for (c) D-R isotherm

Table 11: Adsorption isotherm(Ranitidine hydrochloride) (c)D-R isotherm

β=Slope=0.2483mol^2KJ^-2	R^2 = 0.9268
Es=1/((2β)^0.5)	
Es=1.419046KJ/mol	

The langmuir isotherm is applicable for monolayer adsorption on a homogeneous site, whereas Freundlich is valid for multilayer adsorption on heterogeneous sites.From the above graphs, langmuir isotherm suit the model better as it has greater R^2 value.Thus there is a greater chance of physisorption taking place in the adsorption[86].From the D-R isotherm, the energy of adsorption is found to be 1.419046KJ/mole. . The parameter β suggests a mean free energy of adsorption which is 0.2483mol^2KJ^-2 [94].

3.2.7. Thermodynamics Study

3.2.7.1. Thermodynamics Study for Methylene Blue

In my thesis, the maximum removal of dye has been observed when PCNA is used to adsorb methylene blue. So the thermodynamics study data for this scenario is attached.

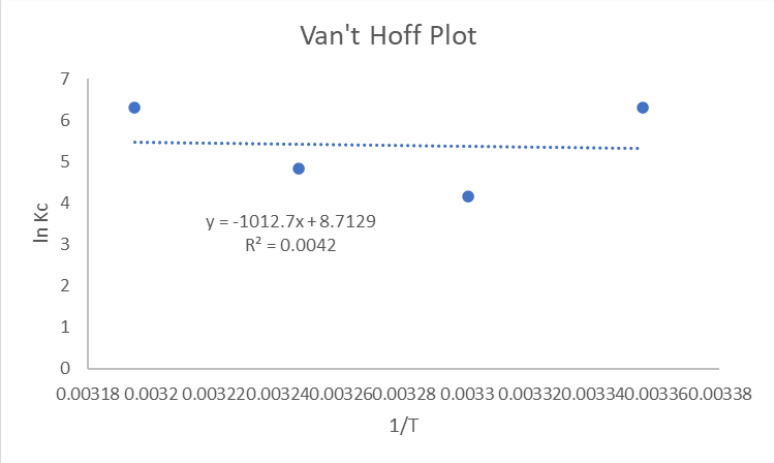


Fig.29: Thermodynamic study (Methylene Blue)

Table 12: Thermodynamic analysis (Methylene Blue)

ΔG=-RTln Kc(KJ/mole)	ΔH(kJ/mole)	ΔS(J/mole.K)
-1.570931043		
-1.038707675	8.4195878	0.07243905
-1.203663299		
-1.570931043		

The intercept and slope of ΔG vs T plot was used to calculate the value of ΔS and ΔH respectively [90].Negative value of $\Delta G_{adsorption}$ shows that the reaction is spontaneous. Positive value of $\Delta H_{adsorption}$ refers towards endothermic reaction. Positive value of ΔS refers towards randomness of MB on the surface of the adsorbents[93].The enthalpy of the adsorption increases with an increase in temperature. This is because, when the temperature is increased, the internal energy of the system increases, which increases the enthalpy[86]. The change in enthalpy in this experiment is 4.80856818KJ/mole and the change in entropy is 0.026669649 J/mole.K.

3.2.7.2. Thermodynamics Study for Eosin Yellow

In my thesis, the maximum removal of dye has been observed when PCA is used to adsorb eosin yellow. So the thermodynamics study data for this scenario is attached.

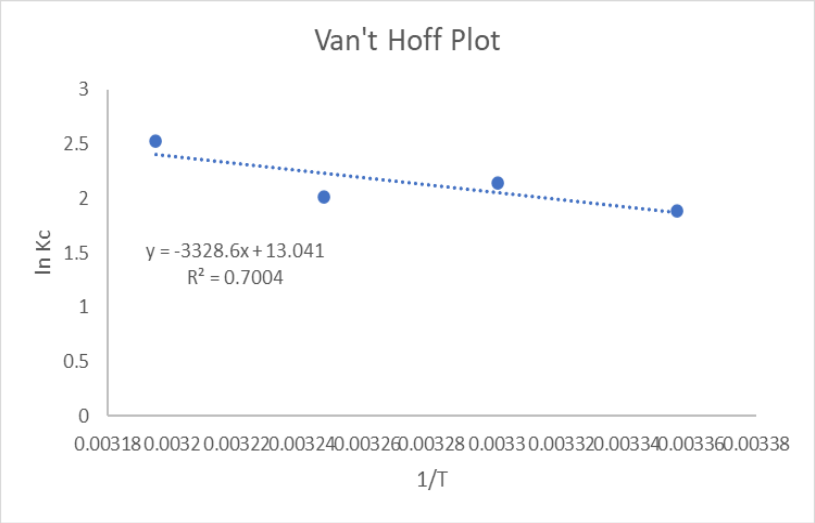


Fig.30: Thermodynamic study (Eosin Yellow)

Table 13: Thermodynamic analysis (Eosin Yellow)

ΔG=-RTln Kc(KJ/mole)	ΔH(kJ/mole)	ΔS(J/mole.K)
-0.470227916		
-0.533929694	27.6739804	0.108422874
-0.503183795		
-0.629520116		

The intercept and slope of ΔG vs T plot was used to calculate the value of ΔS and ΔH respectively [90].Negative value of Δ $G_{adsorption}$ shows that the reaction is spontaneous.Positive value of $\Delta H_{adsorption}$ refers towards endothermic reaction. Positive value of ΔS refers towards randomness of MB on the surface of the adsorbents[93].The enthalpy of the adsorption increases with an increase in temperature. This is because, when the temperature is increased, the internal energy of the system increases, which

increases the enthalpy[86]. The change in enthalpy in this experiment is 27.6739804KJ/mole and the change in entropy is 0.108422874 J/mole.K.

3.2.7.3. Thermodynamics Study for Anthracene

In my thesis, the maximum removal of dye has been observed when PCA is used to adsorb Anthracene. So the thermodynamics study data for this scenario is attached.

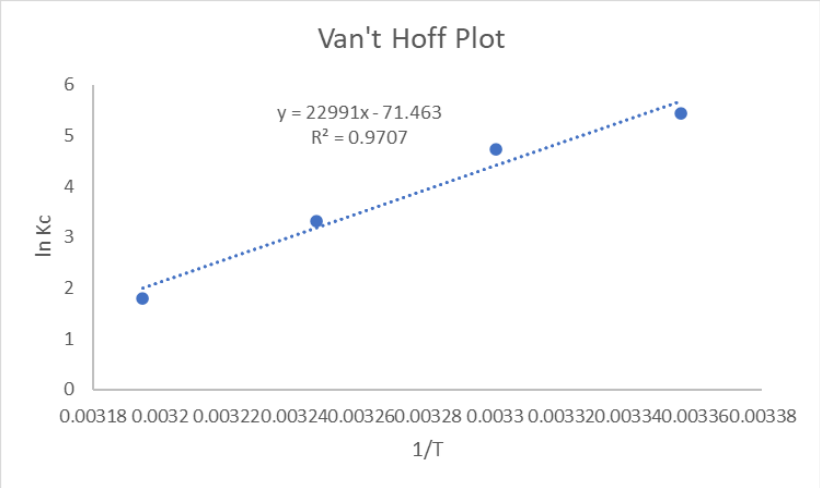


Fig.31: Thermodynamic study (Anthracene)

Table 14: Thermodynamic analysis (Anthracene)

ΔG=-RTln Kc(KJ/mole)	ΔH(kJ/mole)	ΔS(J/mole.K)
-1.35527894		
-1.18130262	191.147174	0.594143382
-0.82888148		
-0.44563776		

The intercept and slope of ΔG vs T plot was used to calculate the value of ΔS and ΔH respectively [90].Negative value of Δ $G_{adsorption}$ shows that the reaction is

spontaneous.Positive value of $\Delta H_{adsorption}$ refers towards endothermic reaction. Positive value of ΔS refers towards randomness of MB on the surface of the adsorbents[93].The enthalpy of the adsorption increases with an increase in temperature. This is because, when the temperature is increased, the internal energy of the system increases, which increases the enthalpy[86]. The change in enthalpy in this experiment is 191.147174KJ/mole and the change in entropy is 0.594143382 J/mole.K.

3.2.7.4. Thermodynamics Study for Ranitidine hydrochloride

In my thesis, the maximum removal of dye has been observed when PCNA is used to adsorb Ranitidine hydrochloride. So the thermodynamics study data for this scenario is attached.

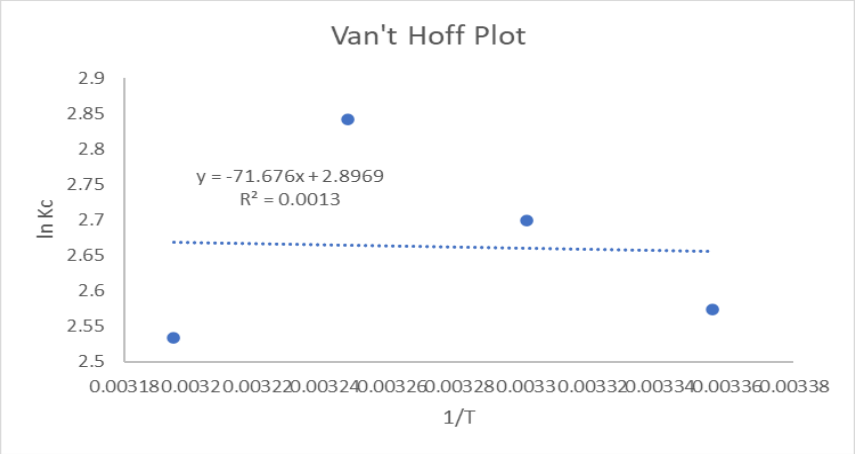


Fig.32: Thermodynamic study (Ranitidine hydrochloride)

Table 15: Thermodynamic analysis (Ranitidine hydrochloride)

ΔG=-RTln Kc(KJ/mole)	ΔH(kJ/mole)	ΔS(J/mole.K)
-0.641872405		

-0.673354672	0.595914264	0.024084826
-0.708747281		
-0.632096014		

The intercept and slope of ΔG vs T plot was used to calculate the value of ΔS and ΔH respectively [90].Negative value of Δ $G_{adsorption}$ shows that the reaction is spontaneous.Positive value of $\Delta H_{adsorption}$ refers towards endothermic reaction. Positive value of ΔS refers towards randomness of MB on the surface of the adsorbents[93].The enthalpy of the adsorption increases with an increase in temperature. This is because, when the temperature is increased, the internal energy of the system increases, which increases the enthalpy[86]. The change in enthalpy in this experiment is 0.595914264KJ/mole and the change in entropy is 0.024084826 J/mole.K.

CONCLUSION

Waste plastic management has become a serious issue owing to the increase in pollution. Pyrolysis has evolved to be a much better technique than land dumping or incinerating.The end products obtained from pyrolysis can be used in the purification of wastewater. The cost and economic implication of converting waste plastic into valuable products is also very rare in the literature which indicates that adequate attention and considerations have not been given to cost and economic implication of conversion of waste plastic to char via pyrolysis. Authorities and policy makers should revisit policies and regulations on waste plastic to focus on most of the plastic value chain. Researchers should carry out further works on the usage of waste plastic char as adsorbent in adsorption process using columns to further evaluate the effectiveness of waste plastic char in the removal of pollutants. This study shows that about 3 hours is needed to adsorb the maximum amount of dye. Research should also be there on how to reduce the time of adsorption and achieve maximum removal.

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