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PROTEIN ABSORPTIVE ON NANO-PATTERNED HYDROGENATED AMORPHOUS CARBON MODEL SURFACES

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ABSTRACT

During the industrial revolution era, fundamental developments occurred in agriculture, industries, transportation, economic policies and social structure. Industrial development is very important for economic growth and human welfare of any country particularly, developing countries. However, there is a growing concern that the continued expansion of the industries will cause irreparable damage to the biosphere[1]. Industrial growth leads to pollution thereby affecting the environment. Pollution is extensively described because the alternate in bodily, chemical and organic characteristics of air, land and water. Industrial pollution has adversely affected biodiversity during the last two centuries and keeps to growth at an alarming rate. In general, industrial pollution generally contaminates almost all the sources of drinking water, releases toxic substances into the environment and affects the overall quality of all the compartments of environment[2].Among all these, aquatic environments are mostly polluted and this directly affects the human health. Inappropriate handling and disposal of wastes into water

bodies often causes water pollution. For example, it has been reported that, every day 2 million tons of sewage, industrial and agricultural wastes are liquidated into water bodies worldwide[3]. The United Nations approximations that the amount of wastewater produced yearly is about 1,500 km^3 which accounts for six times more than the water that occurs in all the rivers of the world[3]. This created an impact than one in eight people worldwide are deprived of safe and clean drinking water. Water pollution is found to be the major cause of deaths and diseases worldwide. It accounts for the deaths of 14,000 people per day globally and in India alone, it has been estimated that approximately 580 people die due to water pollution related illness every day[4]. Major contaminants found in wastewater include but not limited to dyes and pigments, heavy metals, phenolic compounds, pharmaceuticals, agrochemicals and endocrine disruptors. Comprehensive descriptions of the priority pollutants are discussed below.

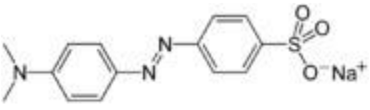
INTRODUCTION

Pigments and dyes are extensively used in the leather-based and textile dyeing, paper, printing, pharmaceutical and cosmetic industries. They are also utilized in high-tech packages like medical, electronics, images, natural photoconductor and thermal transfer printing.

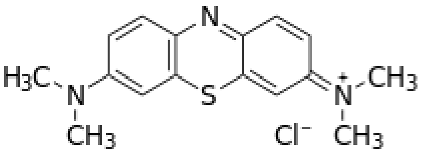
Basic dyes are water soluble dyes completed to paper, polyacrylonitrile, modified nylons and changed polyesters. Traditionally primary dyes have been used for coloring silk, wool and cotton. Basic (cationic) dyes are desired at the same time as brightness of color is more critical than fastness to moderate and washing. The principal chemical lessons of primary dyes are diazahemicyanine, triarylmethane, cyanine, trimethylamine, hemicyanine, thiazine, oxazine and acridine. These sort of dyes show off organic hobby and are often used in medicinal drug as antiseptics. Cationic capability is decided in numerous forms of dyes along with cationic azo dyes, methine dyes, anthraquinone, di- and triarylcarbenium, phthalocyanine and in lots of other polycarbocyclic and solvent dyes. These cationic dyes with delocalized rate are grouped as methine dyes. These institution of dyes can be considered as vinylogous amidinium salts and are characterized by excessive shade strength. Diphenylmethane and triphenylmethane dyes are monomethine dyes which consist of two or three terminal aryl organizations out of which atleast one institution is substituted with the aid of a donor group para to the methine carbon atom. Generally or 3 groups are substituted and the most vital donor is the amino organization. This group consists of the maximum well-known dyes together with malachite green and crystal violet that are some of the oldest synthetic cationic dyes5.

Synthetic organic dyes

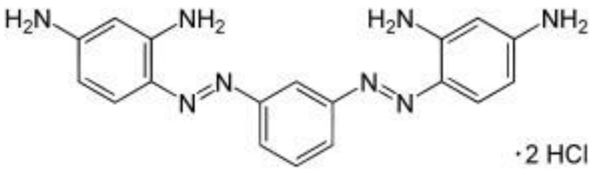
Acid dyes are water soluble anionic dyes and are implemented to paper, leather-based, nylon, wool, silk, changed acrylics. They are also used to a point for ink-jet printing, meals and cosmetic. These kinds of dyes encompass azo, anthraquinone, triphenylmethane, azine, xanthene, nitro and nitroso dyes. The azo dyes are the maximum significant dyes secretarial for over 50% of all business dyes. They include atleast one azo organization (-N=N-). Azo dyes are confidential as mono azo, di-azo and tri-azo dyes contingent at the quantity of azo businesses contained by means of the dye. Tetra-azo and poly-azo corporations of dyes are of very rare kind. The azo collection is devoted to two groups, of which as a minimum one is an fragrant group5. Few examples of chemical shape of the dyes are given beneath:



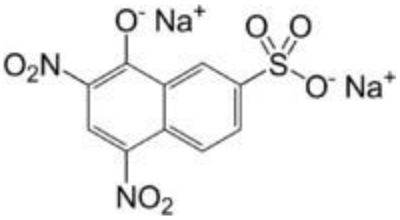
Methyl Orange



Methylene Blue



Bismarck Brown Y



Naphthol Yellow S

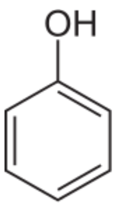
Fig.1.1. Chemical structure of dyes

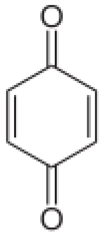
Dyes are widely used in several industries. During dyeing operation, unreacted dyes are released as effluents and discharged into aquatic streams by the industries [6]. For example, the total dye consumption of leather industry alone is more than 3.2x10^{6} kg/year and approximately 0.5 to 1.3x10^{6} kg/year of dyes are satisfied into the aquatic torrents by the leather industries[7].

Human eye can detect dye at assemblage as low as 0.005 mg/L in clear water[8]. Moreover, many of these dyes have been recognized as toxic or even mutagenic and carcinogenic. Many dyes are even produced by known carcinogenic substances like benzidine. Hepatocarcinomas and nuclear anomalies in experimental animals and chromosomal aberration in mammalian cells[9]. Hence, stringent environmental regulations are enforced in several countries for the control of leather and textile effluents.

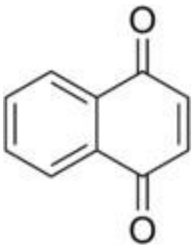
Phenolic compounds

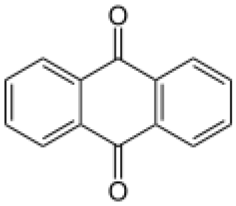
Phenolic compounds are shaped in very large amounts for use as solvent and also as preliminary materials for many chemical syntheses. They are mostly used in industries which include refineries, pharmaceuticals, resins, pesticides, dyes, plastics, herbicides and explosives[10]. Although, they are categorized as important industrial chemicals, the effluents from these industries are rich in phenolic compounds and pose serious threat to the environment. For example, oil refinery effluents contain phenol assemblage in the range of 500 to 1500 mg/L and coking plant effluents have assemblage between 200 and 1200 mg/L[11]. The US-Environmental Protection Agency (EPA) has motionless standard permissible limit of phenol in any form in potable water as 0.5 ppb whereas the limit for wastewater release are 0.5 ppm for surface waters and 1 ppm for sewerage systems[12]. The toxicity of phenolic compounds mostly be contingent on the number, nature and position of the substituted functional groups on the aromatic ring. Generally, exposures to phenolic compounds may cause liver damage and haemolytic anemia. Some phenolic compounds such as bisphenol A and alkylphenols indulge in endocrine disrupting activities even at very low assemblages. Simple phenols such as pyrogallol proved to exhibit mutagenicity.. Hence the release of these phenolic compound in rivers and other water bodies without proper pretreatment will result in serious environmental damage. Examples of phenolic compounds with chemical structure are given below:





Phenol 1,4-Benzoquinone



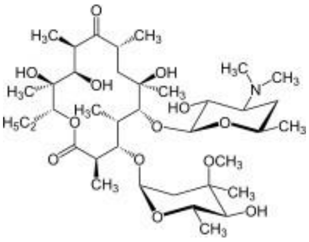


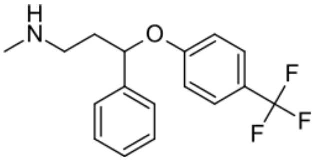
1,4-Naphthoquinone 9,10-Anthraquinone

Fig.1.2. Chemical structure of phenolic compounds

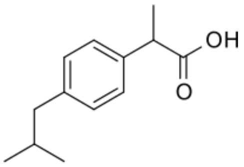
Pharmaceuticals

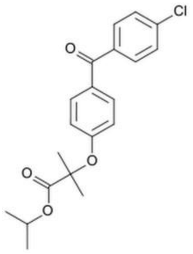
Pharmaceutical compounds are ubiquitous, persistent and biologically active compounds. Yet, these compounds are frequently detected in public water bodies since there are no legal requirements have been set for their discharge. The consumption of these pharmaceutical compounds has been predicted to increase in the coming years owing to improving quality of the life worldwide[14]. They are metabolized in human body and excreted and may undergo further modifications due to the physical, chemical and biological processes both in sewage treatment processes and water bodies. Generally, raw wastewater contains pharmaceutical compounds in the range of 10^{-3} to 10^{-6} mg/L and the chemical, physical and biological properties of all these compounds vary greatly[15]. Some of the frequently detected pharmaceuticals in the water bodies are antibiotics. Even though pharmaceutical compounds are detected in water bodies worldwide, the complete toxicological studies of these compounds and their metabolites are yet to be investigated. However, the absence of such data cannot rule out the adverse outcome as a outcome of chronic contact to these chemicals. Chemical structures of few pharmaceuticals are given below:





Erythromycin Fluoxetine



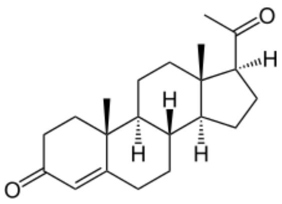


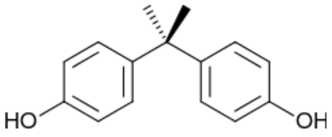
Ibuprofen Fenofibrate

Fig.1.3. Chemical structure of pharmaceuticals

Endocrine disruptors

Endocrine disruptors are synthetic chemical compounds and evidently occurring plant compounds which may also have an effect on the endocrine machine of the mammals. Many of these disruptors are related to developmental, reproductive and other health troubles that have an effect on the verbal exchange gadget of glands, hormones and cellular receptors that manipulate the organic inner features. They have an effect on the hormonal capabilities by means of (1) mimicking the intercourse hormones estrogen and androgen by means of binding to hormone receptors or by influencing pathways, (2) blocking, preventing, and altering hormonal binding to hormone receptors, (three) changing production and breakdown of herbal hormones and (four) modifying the function of hormone receptors17. Endocrine disruptors can grow to be in wastewater through pharmaceutical merchandise like birth manipulate capsules and from sure chemical present in soaps, detergents, plastics, meals and personal care products18. They are especially grouped as xenoestrogens, alkylphenols and bisohenol A. They are notably carcinogenic and can reason delivery defects and other developmental problems like getting to know disabilities, interest deficit disorder and brain developmental troubles. They are also frequently related to prostate most cancers, breast cancer, thyroid cancer, feminizing of men and masculine consequences on female19. Hence the elimination of those chemical compounds from municipal and industrial wastewater is of important situation. Examples of endocrine disruptors with their chemical structures are as follows:





Progesterone Bisphenol A (BPA)

Testosterone Estriol

Fig.1.4. Chemical structure of endocrine disruptors

Absorptive

Although certain phenomena related to absorptive had been familiar in ancient instances, the term absorptive changed into proposed via Bois-Reymond and brought into the literature with the aid of Kayser51. Absorptive is the surface-based technique wherein ions, atoms or molecules from one phase adhere to the floor of other segment. The adsorbing segment is called as chemisorptive and the fabric focused or adsorbed at the floor of the chemisorptive is termed as adsorbate. Absorptive is a result of surface electricity. In a bulk material, all of the bonding requirements of constituent atoms are frequently stuffed and there will now not be any bond deficiency. On opposite to this, there can be bond deficiency within the atoms of smooth surfaces for the reason that they're no longer wholly surrounded by means of other atoms. Thus it's far energetically favorable for the atoms of the smooth surfaces to bond with different atoms which happens to be to be had from bulk substances. The genuine wildlife of bonding (ionic, covalent or metal) be contingent on the nature of the classes concerned. But the absorptive of adsorbate molecules over the chemisorptive surface is usually through physisorption or chemisorption.

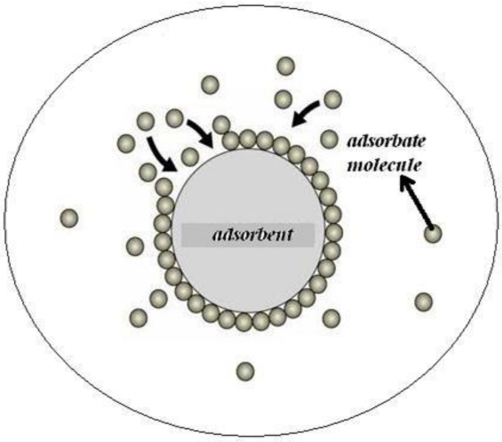


Table.1.1. Differences between physisorption and chemisorption

Physisorption	**Chemisorption**
Can occur only at temperatures underneath the boiling point of the adsorbate molecules	Can occur at all the temperatures
Heat of absorptive is lesser than 40 KJ/mol	Heat of absorptive can even be more than 200 KJ/mol
The amount of absorptive mainly depends on the nature of adsorbate than the chemisorptive	The amount of absorptive depends on both the nature of adsorbate and the chemisorptive
Does not require appreciable activation energy	Requires appreciable amount of activation energy

AIM AND SCOPE OF THE PRESENT INVESTIGATION

The wastewater treatment is of great concern in any of the industrial operations as the industrial processes involve large volume of organic and inorganic compounds for their products manufacturing. Due to stringent environmental conditions and public concerns, the industrial effluents need to be properly preserved before liquidating into the environment. Among several physico-chemical and biological wastewater treatment methods, absorptive ispreferable since it is simple, effective and economical without the production of any secondary pollutants. The competence of the absorptive procedure be contingent on the chemisorptive properties. Conventional chemosorptive have lot of demerits, hence the present investigation is focused on the development of some new hybrid chemosorptive from the renewable sources like lignocellulosic biomass, liquid biomass, biopolymer (chitosan) and graphene based materials. The prepared chemosorptive were characterized and their adsorptive properties have also been exploited in detail for the elimination of selected organics and inorganics from simulated wastewater.

Preparation of hybrid chemosorptive

Magnetized Corn Cob Activated Carbon (MCCAC)

In tropical countries like India, disposal of the lignocellulosic waste biomasses produced from agricultural residues and food industries result in the production of secondary wastes. Hence the preparation of triggered carbon from lignocellulosic waste materials are considered to be both economical and as a solution for the waste disposal problems.

In industries, absorptive process is carried out by vairous operational procedures. They are as follows: simple batch-type contact tanks, agitated batch contact tanks, fixed-beds, pulsed beds, steady-state moving beds, agitated beds, fluidized beds and moving mat filters. the chemisorptive particles need to be separated from the effluent stream for regeneration and reuse. Conventionally, the chemisorptive particles are separted using settling or filtration. However, settling is a time consuming process whereas filtration is energy consuming process. In the case of continuous column processes, the column has to be taken out of the train after exhaustion and the chemosorptive will be agitated with the regenerating agents to remove the residual adsorbates attached to the chemosorptive. There may be a considerable loss of chemisorptiveparticles during the elimination and regeneration operations[1,2]. Recently chemosorptive coated with magnetite nanoparticles and its applications considered very promising in environmental remediation process. Recently, few research works on the development of magnetized activated carbon and their applications were reported elsewhere[4,5].

However, most of these prepared magnetized activated carbon particles have the drawback of lesser surface area when compared to the unmagnetized chemosorptive. Moreover the preparation of these magnetic activated carbon particles involves several steps withsequential addition of chemicals. Hence an attempt has been made to prepare novel magnetized activated carbon particles from corn cob waste biomass using a simple single- step sol-gel magnetization procedure.

Chitosan Coated Bentonite (CCB)

Biopolymers are eco-friendly materials which are easily biodegradable, non-toxic and economical. These biopolymers possess chemically active surface functional groups whichare considered vital for an chemisorptive. Chitosan is the N-deacetylated derivative of chitin which is the second most abundant biopolymer. It has both an amine group ($-NH_2$) and a hydroxyl group (-OH) in its polymeric chain and hence it can interact and adsorb bothcationic and anionic molecules. Nevertheless, chitosan has its own limitations such as weak mechanical property, low bulk density and tendency to swell and float when immersed in water. Hence coating and immobilizing chitosan over a low cost material with high mechanical stability would be a wise idea for utilizing the absorptive properties of chitosan effectively. Hence, the present study is aimed to improve the properties of chitosan bycoating it on bentonite clay.

Continuous column absorptive studies

The column parameters were evaluated to predict the breakthrough parameters and column efficiency of all the hybrid chemisorptive-adsorbate systems. When the unmganetized chemosorptive such as CCB and PLBAC were used, it was difficult to recover the spent chemisorptive particles from the column. However, when magnetized chemosorptive such as MCCAC and GO-Fe_3O_4 nanocomposites were used in the continuous column, simple magnetic procedure was employed for the elimination of the spent chemosorptive from the micro column.

Preparation of chemosorptive

Magnetized Corn Cob Activated Carbon (MCCAC)

Preparation of biomass

Corn cobs gathered from neighborhood agricultural area, have been reduce into small portions with knife and washed with distilled water to take away sand and dust. Then the material turned into dehydrated under sunshine for forty eight hours to get rid of dampness.

Preparation and characterization of activated carbon

Corn cobs had been dried at 105°C for two h. The fabric became then animated in a muffle furnace at the fee of 20°C min-1 from room temperature to 500°C for two h below inert atmospheric conditions using N2 fuel. The acquired carbonized biomass was then floor using mortar and pestle and sieved. The carbon particles of length underneath 125 µm were accrued and used for further studies. The carbon powder became then loaded in alumina boats and kept right into a tubular furnace underneath N2 glide of one hundred cm3 min-1 and heated at a charge of 20°C min-1 to the final temperature of seven hundred°C. After accomplishing the very last temperature, nitrogen waft changed into reduce off and it turned into set below carbon dioxide flow of 100cm3 min-1 for 1.5 h. Then CO2 deliver turned into stopped and the prepared activated carbon became cooled to room temperature underneath inert atmosphere1. The schematic illustration of the coaching of MCCAC turned into shown in fig.3.1.

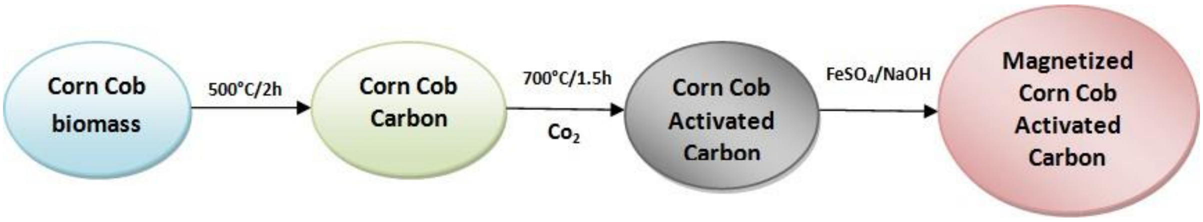


Fig.3.1. Schematic representation of the preparation of MCCAC

Chitosan Coated Bentonite (CCB)

Bentonite was pre-treated with hydro fluoric acid (HF) to improve its surface properties as follows: Bentonite was soaked in HF acid stirred well. The mixture was left for settling and the supernatant solution was decanted from bentonite. HF treated bentonite was then washed with acetone followed by distilled water and dried at 120°C in a hot air oven. The chemisorptive was finally ground and stored in an air tight container. The preparation of CCB was shown schematically in fig.3.2.

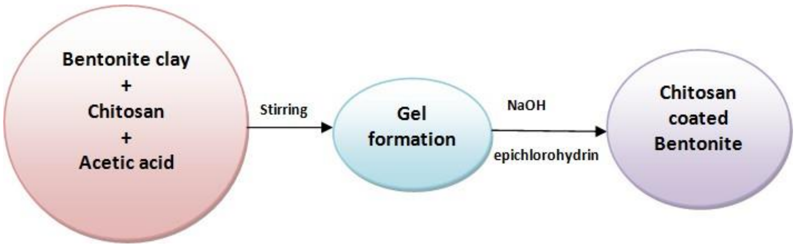


Fig.3.2. Schematic representation of preparation of CCB

Phenolic rich Liquid Biomass based Activated Carbon (PLBAC)

Preparation of phenolic resin by hydrothermal method

Cashew nut oil which is rich in phenol content was used for the preparation of phenolic resin by hydrothermal method. A typical procedure is given below: A mixture of 5mL of cashew nut oil, 4.54 g of hexamethylenetetramine (HMTA) and 5.45g of $ZnCl_2$ was heated at160°C for 5 h in a muffle furnace. HMTA was used as a curing agent and $ZnCl_2$ was added to the mixture as a templating agent. The prepared polymeric resin was washed in distilled water and dried at 100°C[6]. The pictorial representation of the obtained polymeric resin is shown in fig. 3.4

Preparation of activated carbon from polymeric resin

The polymeric resin was carbonized at 800°C for 5 h under nitrogen atmosphere in a tubular furnace. During polymerization and carbonization processes, $ZnCl_2$ plays a major role. As a well known chemical activator, $ZnCl_2$ acts as a dehydration agent up to 500°C during carbonization process. It work as a sacrificial scaffold for the polymer meeting during the polymerization process. During thermal treatment, it again prevents the contraction of pores. The procedure forthe preparation of PLBAC was demonstrated in fig.3.4

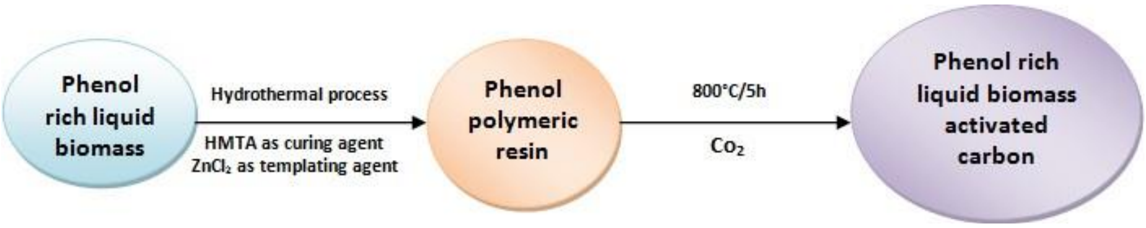


Fig.3.4. Schematic representation of preparation of PLBAC

Characterization of the prepared chemosorptive

MCCAC and GO-Fe_3O_4 chemosorptive were characterized by Vibrating Sample Magnetometer (VSM) to evaluate their magnetic properties. GO-Fe_3O_4 nanocomposites were characterized by Raman spectroscopy for its structural properties. Differential Scanning.

Magnetized corn cob activated carbon (MCCAC) based absorptive systems

Magnetized corn cob activated carbon

Several low cost and renewable resources have been explored for the provision of triggered carbon from recent past[1]. Abundant quantities of lignocellulosic waste biomasses were produced from agricultural activites and food industries. Disposal of these waste biomasses result in the production of secondary wastes. Hence the preparation of activated carbon from lignocellulosic waste biomasses would solve two problems: (1) the disposal of large volume of solid wastes and (2) by utilizing these waste biomasses for the manufacture of triggered carbon, wealth can be generated from the waste. Therefore, activated carbon particles were prepared from several lignocellulosic waste biomasses such as palm flower[2,3], walnut shell[4,5] and lotus seed[6] by different methods. The annual production of corn was estimated to be 1,016,431,783 tonnes in the year 2013 globally. India alone accounted for the production of 23,290,000 tonnes of corn in 2013. When these corns are mainly used in food industries, the corn cobs are often regarded as waste. The disposal problem of these corn cobs could be overcome by preparing activated carbon particles from these waste biomasses. Hence corn cob waste biomass was chosen as the precursor for the preparation of activated carbon particles. These activated carbon particles were used for the absorptive of several organics and inorganics in aqueous phase. However, the used activated carbon has to be separated for the regeneration and reusability. Conventionally, the separation of chemosorptive is time-consuming which results in the considerable loss of chemisorptive[7]. To overcome these demerits, nano-sized magnetite particles were coated onto the surface of corn cob waste biomass based activated carbon using a simple single-step magnetization procedure. Hence an attempt has been made to prepare and exploit for its absorptive properties for the elimination of different types of model pollutants from simulated wastewater by batch and continuous reactor systems. The detailed procedure for the preparation of MCCAC is given in section 3.1.1 of chapter 3.

Characterization of MCCAC chemisorptive

FT-IR spectrum of MCCAC grow to be shown in fig.5.1. The peaks at 583 and 888 cm-1 corresponds to the stretching correspondingly. The much less severe top at 1058 cm-1 is the illustration of C-O vibration and the height at 1602 cm-1 is because of C=O stretching vibration. The occurrence of OH organizations inside the chemisorptive is discovered at 3417 cm^{-1}.

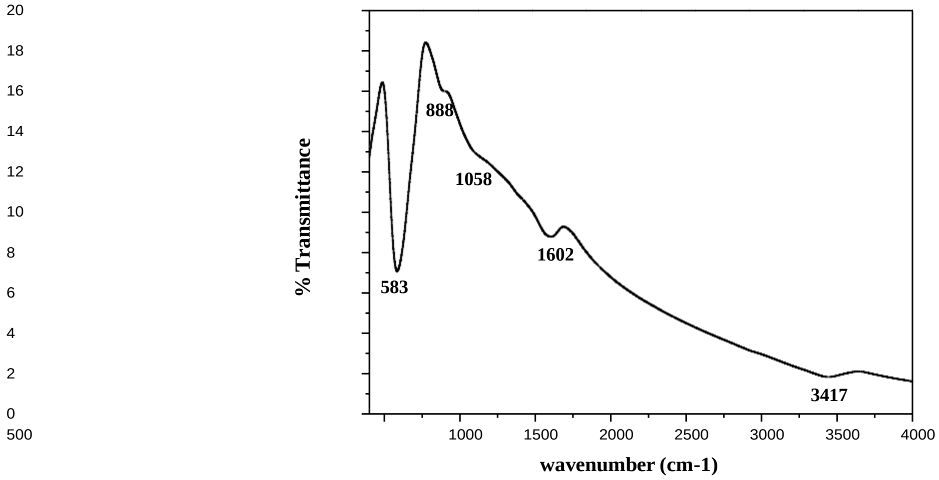
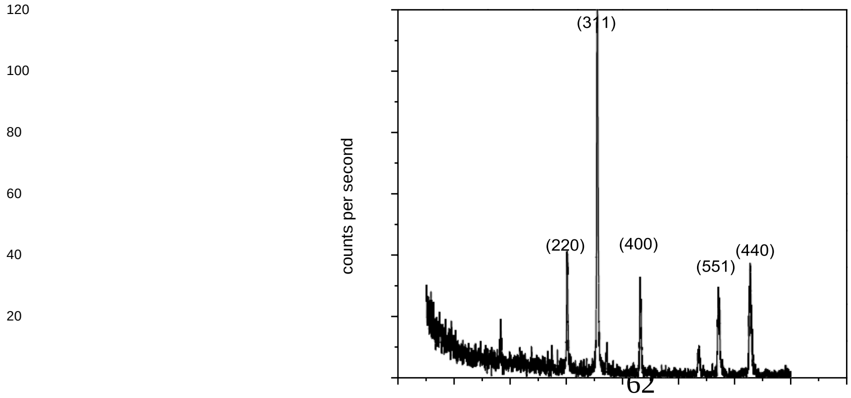


Fig. 5.1. FT-IR analysis of MCCAC chemisorptive

XRD analysis of MCCAC chemisorptive

The XRD pattern of MCCAC was given in fig.5.2.The peak positions of the plane (22 0), (3 1 1), (4 0 0), (5 1 1) and (4 4 0) of MCCAC coordinated exactly with the regular data of magnetite (JCPDS 19-629)[8].



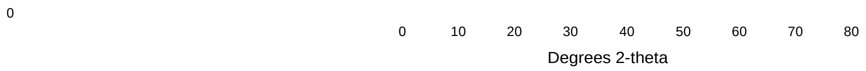


Fig. 5.2. XRD pattern of MCCAC chemisorptive

VSM analysis of MCCAC chemisorptive

Fig.5.3 Shows the VSM curve of MCCAC at room temperature. MCCAC unveiled excellent paramagnetic behaviour, considered via robust magnetic vulnerability. Fullness magnetization price of the prepared MCCAC end up found to be forty eight.Forty three emu/g which is greater than enough for conservative magnetic parting whilst as associated to the lesser magnetization fee of four.Four emu/g noted some place else thru Gorria et al. (2007)9. The coercivity and retentivity of MCCAC resolute from VSM records were found to be 298.07 oersted and 0.425 emu correspondingly.

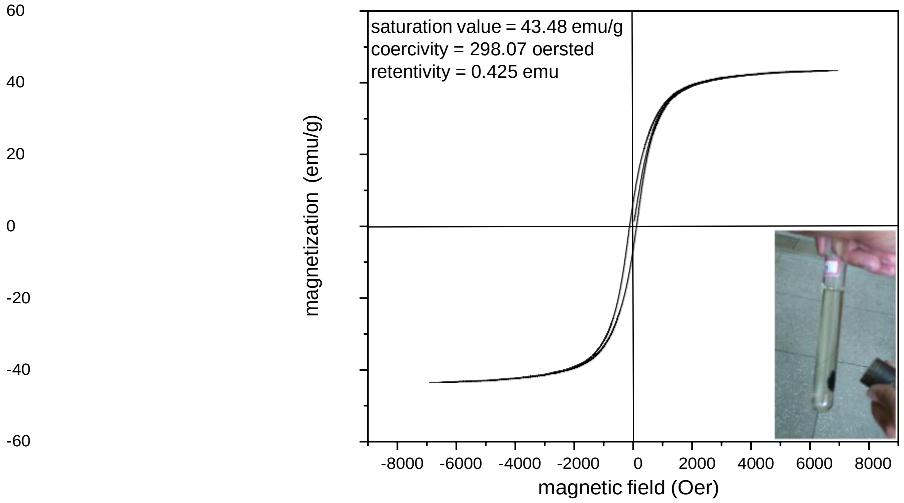


Fig. 5.3. VSM curve of MCCAC chemisorptive

Surface area and porosity analyses of MCCAC chemisorptive

The floor vicinity and porosity of MCCAC become calculated from absorptive/desorption isotherm plot, BET and BJT plots as illustrated in fig. 5.4. Surface place became determined to be 143 m2/g and 282 m2/g for unmagnetized corn cob activated carbon and MCCAC correspondingly.

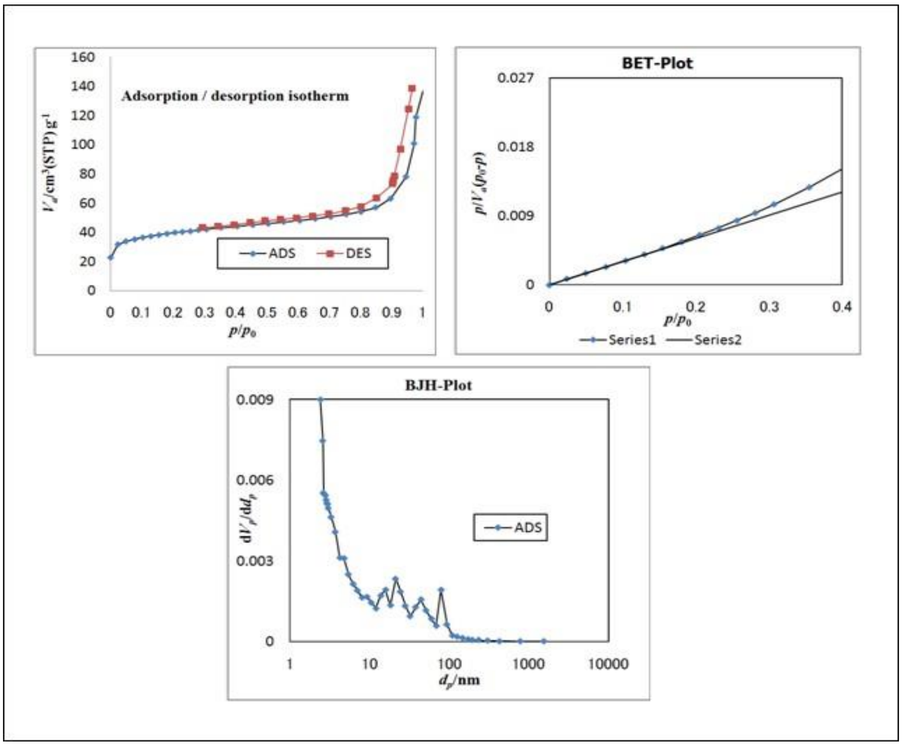


Fig. 5.4. Surface area and porosity analyses of MCCAC chemisorptive

Absorptive of dyes onto MCCAC chemisorptive

Due to inefficient dyeing process, 10-15% of the dyestuffs enter into the wastestreams. Most of these dyes have been identified as toxic, mutagenic and carcinogenic[12]. Hence the elimination of these dyes from industrial effluents is mandatory before they are discharged into the environment. Therefore, the dye elimination efficiency of the prepared chemisorptive is evaluated for three model dyes namely Malachite Green (MG), Orange G (OrG) and Amido Black 10B (AB) from the synthetic effluents.

Table 5.1. Isotherm models parameters for the absorptive of dyes onto MCCAC chemisorptive

Isotherm model parameters	MG dye	OrG dye	AB dye
Langmuir isotherm			
q_m(mg/g)	59.732	53.055	46.098

K_L	0.8725	0.1474	0.1248
R_L	0.0015	0.0089	0.0105
χ^2	21.403	12.334	9.7544
Freundlich isotherm			
K_f(L/g)	16.668	10.119	8.7304
n	3.925	3.304	3.347
χ^2	0.0573	0.4328	0.2655
Temkin isotherm			
B_1	7.1399	7.6171	6.8215
K_T (L/mg)	26.959	3.5793	2.7308
χ^2	5.8353	4.3825	3.1810

Absorptive equilibrium data were examined using Langmuir, Freundlich and Temkin isotherm model reckonings. The plots for Langmuir, Freundlich and Temkin isotherms were shown in figures 4.3, 4.4 and 4.5 for MG, OrG and AB dye molecules correspondingly. Table 5.1 shows the calculated isotherm parameters and chi-squared values obtained from the isotherm plots. The chi-squared values of Freundlich isotherm were minimum when compared to Langmuir and Temkin isotherms. Hence, by the assumptions of Freundlich isotherms, it was confirmed that the absorptive of all the three dyes (MG, OrG and AB) onto MCCAC was through multilayer absorptive and the surface of MCCAC was heterogeneous in nature.

The absorptive capacity of MCCAC was compared for the absorptive of MG, OrG and AB dye molecules in terms of „q_m‟. It was noted that the absorptive capacity of MCCAC for MG dye was better when compared to OrG and AB dye molecules. Hence, it can be concluded that non-azo dye was better adsorbed than mono-azo and di-azo dye molecules. Also, the absorptive capacities were 59.73, 53.05 and 46.098 mg/g for MG, OrG and AB dye molecules correspondingly. The R_L values for the absorptive of all the three dye molecules onto MCCAC were given in table 5.1. The R_L values of all the studied absorptive systems were between 0 and 1 indicating the favorability of the absorptive processes. In addition, it could be noted that when the initial assemblage of dye molecules were less, the R_L values tend to approach closer to 0 making the process irreversible.

Chitosan Coated Bentonite (CCB) based absorptive systems

Chitosan coated bentonite

Chitosan is the N-deacetylated derivative of chitin biopolymer. It has both amine (-NH_2) and hydroxyl groups (-OH) in its polymeric chain and hence it can adsorb both cationic and anionic molecules[43]. However, it has limitations such as weak mechanical property, low bulk density and also tendency to swell when it was dissolved in water[43]. Hence, the present study is aimed to prepare hybrid material based on chitosan and clay minerals like bentonite. Coating of chitosan on bentonite may improve its mechanical stability and adsorptive properties of chitosan. To achieve this, chitosan was cross-linked and coated on the bentonite clay and named as Chitosan Coated Bentonite (CCB). The detailed experimental procedure for the preparation of CCB was given in section 3.1.2 of chapter 3

Characterization of CCB chemisorptive

FT-IR analysis of CCB chemisorptive

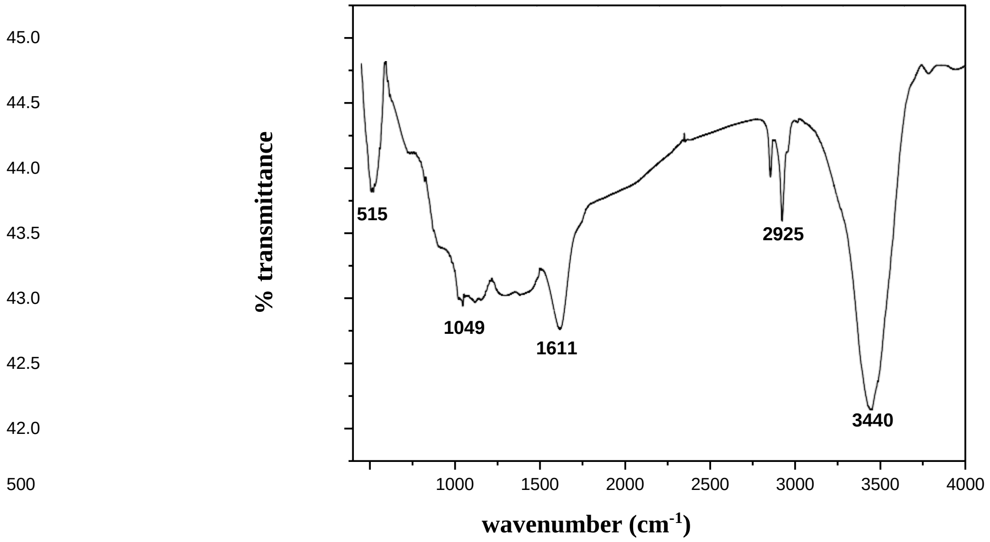


Fig. 6.1. FT-IR analysis of CCB chemisorptive

Fig. 6.1 represents the FT-IR analysis of CCB. The peak at 515 cm^{-1} resembles to Al-O-Si bending vibration. The peaks at 1049 cm^{-1} and 1611 cm^{-1}are due to N−H bending vibration and C-O-C groups of chitosan. 2925 cm^{-1} is allocated to C−H stretching vibration of −CH2 and

−CH3 groups. The peak at 3440 cm^{-1} in CCB beads can be assigned to widening vibration of hydroxyl group.

Graphene oxide-iron oxide (GO-Fe_3O_4) nanocomposites based absorptive systems

Graphene oxide-iron oxide nanocomposites

Graphene is composed of single layers of carbon atoms densely packed which attracted tremendous attraction from late 2004[46]. It has unique property of good chemical stability. But, the graphene sheets generally suffer from agglomeration problems. Also, the graphene based materials are very difficult to separate from aqueous solution owing to their smaller particle size[47]. To overcome the above mentioned limitations, magnetite nanoparticles could be incorporated with graphene oxide. Hence the fabrication of graphene oxide-iron oxide nanocomposites coalescing the belongings of graphene and magnetite nanoparticles mayprove to be a better approach to overcome the agglomeration and separation problems. The detailed procedure for the preparation of GO-Fe_3O_4 nanocomposites was provided in section 3.1.3 of chapter 3.

Characterization of GO-Fe_3O_4 nanocomposites

FT-IR analysis of GO-Fe_3O_4 nanocomposites

FT-IR spectrum of GO-Fe3O4 nanocomposites was proven in fig. 7.1. The shoulder height at 618cm-1 is outstanding to the lattice absorption of Fe3O4. The peak at 1024cm-1 is because of C-O widening vibration.

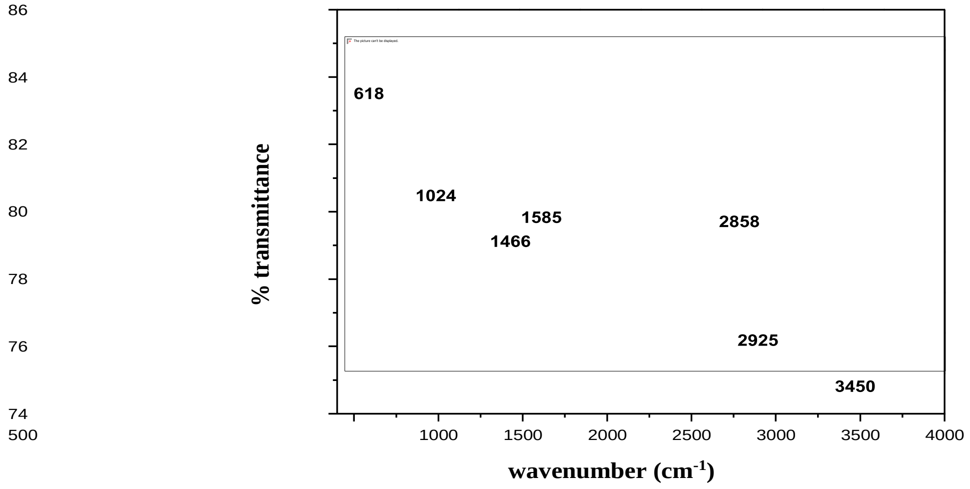


Fig. 7.1. FT-IR spectrum of GO-Fe_3O_4 nanocomposites

XRD analysis of GO-Fe_3O_4 nanocomposites

In the XRD pattern of GO-Fe_3O_4 nanocomposites as exposed in fig. 7.2, the peak in (220), (311), (400), (511) and (440) seaplanes corresponds to the crystal structures of Fe_3O_4 (JCPDS card no. 19-0629) whereas (001) is the distinctive peaks of GO[48].

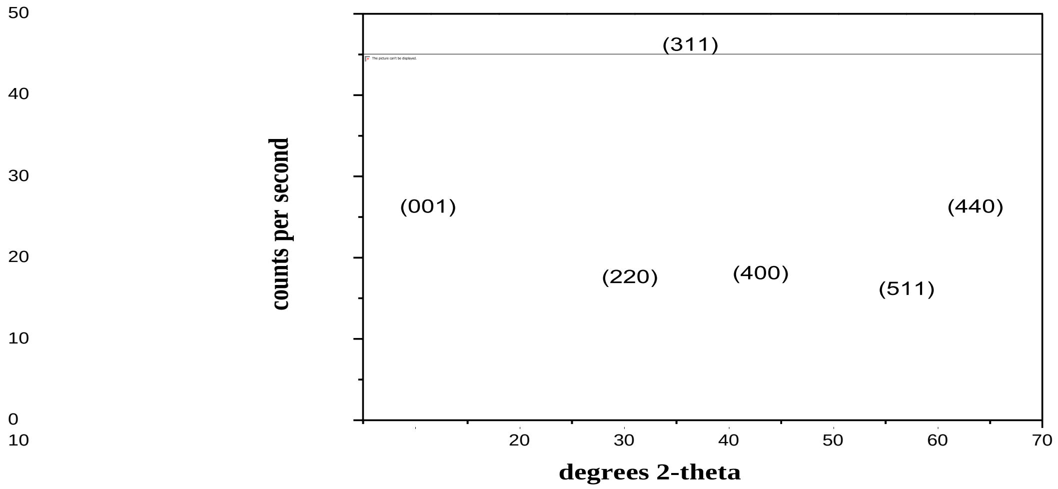


Fig. 7.2. XRD patterns of GO-Fe_3O_4 nanocomposites

Raman analysis of GO-Fe_3O_4 nanocomposites

Raman spectroscopy changed into used to signify the crystal shape, faults and problems in GO-Fe3O4 Nano composites. As proven in fig. 7.Three, the Raman spectrum exhibited severe peaks particularly G-top (1598 cm-1) and D-top (1365 cm-1). D-top is due G-height was zero.995 which proved that the synthesized GO-Fe3O4 Nano composites had less flaws while in comparison with the current literature values[49].

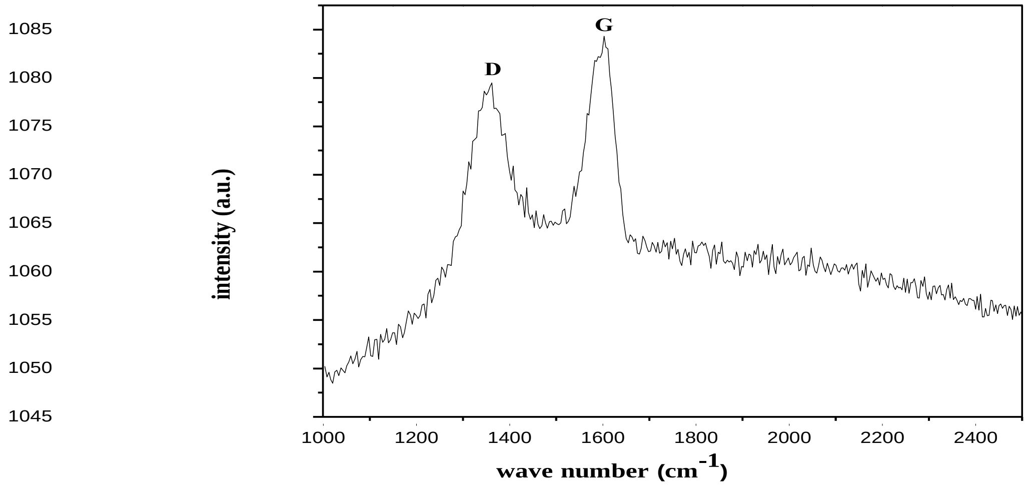


Fig. 7.3. Raman spectrum of GO-Fe_3O_4 nanocomposites

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SUMMARY & CONCLUSIONS

The emergence of industrial revolution had adversely affected the aquatic environment. Industrial wastewater mostly contains organic and inorganic pollutants. Among many other physico-chemical techniques, absorptive is mostly preferred to treat industrial effluents. Overthe past, many conventional and non-conventional chemosorptive developed for the absorptive of several inorganic and organic pollutant. However, most of prepared chemosorptive had their own merits and demerits. In the present study, four new chemosorptive have been developed from several raw materials by using different techniques. These chemosorptive were well-characterized and utilized for the absorptive of several several organic and inorganic impurities from simulated and composite industrial wastewater. The summary of the work done and the important conclusions drawn from this thesis are as follows:

- Four new chemosorptive namely Magnetite coated Corn Cob Activated Carbon (MCCAC), Chitosan Coated Carbon (CCB), Graphene Oxide-iron oxide (GO-Fe_3O_4) nanocomposites and Phenolic rich Liquid Biomass based Activated Carbon (PLBAC) were prepared.
- Activated carbon was prepared by pyrolysis of corn cob waste biomass followed by magnetization by simple single-step sol-gel process. MCCAC was categorized FT-IR, XRD, VSM, surface area, porosity, SEM, TEM, zero point charge and surface functionality. The prepared MCCAC was superparamagnetic with a magnetization value of 48.43 emu/g. The magnetite nanoparticles were of cubic to spheroidical shape in the size range of around 50 nm.
- CCB was prepared by coating chitosan biopolymer onto bentonite clay with epichlorohydrin as cross-linking agent. CCB was characterized using FT-IR, XRD, DSC, TGA, surface area, porosity, FE-SEM, HR-TEM, surface area, porosity, zero point charge and surface functionality. CCB exhibited a good thermal stability and around 42% of the chemisorptive remained as residue even at 800°C.
- Phenolic resin was prepared from phenol rich liquid waste biomass namely cashewnut shell liquid waste by hydrothermal process. The prepared phenolic resin was then carbonized and activated by physical pyrolysis method. The prepared PLBAC was characterized by FT-IR, XRD, surface area, porosity, FE-SEM, HR-TEM, zero point charge and surface functionality. The zero point charge of PLBAC was found to occurat pH 6.
- Maximum absorptive occurred at around pH 7 for MG, pH 2 for OrG, AB and Cr(VI) and pH 3

for 2,4-D for all the prepared chemosorptive.

- The % of absorptive increased with the increase in the initial chemisorptive dosage for the absorptive of all the studied adsorbates onto the prepared chemosorptive.
- Increase in the initial assemblage of all the studied adsorbates resulted in thedecrease in the % of absorptive of adsorbates onto the prepared chemosorptive.
- The equilibrium data for the absorptive of all the studied adsorbates onto the prepared chemosorptive followed Freundlich isotherm. This suggested that the absorptive of all the studied organic and inorganic molecules onto the surface of all the prepared chemosorptive were heterogeneous in nature.
- The thermodynamic parameters for all the studied absorptive processes evaluated using ITC suggested that the absorptive processes were spontaneous, favourable and exothermic in nature.
- The kinetic data for the absorptive of all the studied organic and inorganic model pollutants best fitted with the pseudo second-order model equation suggesting that the absorptive of all the adsorbates onto the chemosorptive was by chemisorption.
- The absorptive of all the studied adsorbates onto the prepared chemosorptive was both by film diffusion and intraparticle diffusion mechanisms.
- Film or boundary layer diffusion was found to be rate controlling step for the absorptive of all the model pollutants onto the prepared chemosorptive.
- Unceasing column studie were performed and the breakthrough parameter were assessed for each absorptive system.
- Reusability studies were carried out representatively for MCCAC chemisorptive and GO- Fe_3O_4 nanocomposites and it was observed that around 80% of the adsorptive efficiency was retained even after three or four cycles of operation.

While comparing the absorptive efficiency of each of the prepared chemisorptive absorptive individual adsorbates Langmuir monolayer volume (q_m, mg/g), the following trend was observed.

For MG dye molecules:

GO-Fe_3O_4 (94.04) > PLBAC (71.32) > MCCAC (59.73) > CCB (52.94)

For OrG dye molecules:

GO-Fe_3O_4 (79.11) > MCCAC (53.05) > CCB (51.39) > PLBAC (49.08)

For AB dye molecules:

$GO\text{-}Fe_3O_4$ (66.40) > MCCAC (46.09) > CCB (45.04) > PLBAC (43.50)For

Cr(VI):

$GO\text{-}Fe_3O_4$ (75.80) > CCB (48.90) > PLBAC (36.19) > MCCAC (29.88)

For 2,4-D:

$GO\text{-}Fe_3O_4$ (67.26) > PLBAC (55.62) > CCB (38.34) > MCCAC (3.76)

It was experimental that all the prepared chemosorptive were actual in eliminating all the selected organic and inorganic pollutants from the aqueous phase. However, $GO\text{-}Fe_3O_4$ nanocomposites were concluded as the best of all the four chemosorptive based on the performed absorptive studies. When comparing the other three chemosorptive, MCCAC chemisorptive was effective in removing the azo dyes. CCB was found to a better chemisorptive for adsorbing Cr(VI). PLBAC was capable of treating the aqueous solution containing 2,4-D and MG dye molecules effectively.

The prepared chemosorptive were also tested for treating composite tannery wastewater collected from pilot tannery, Central Leather Research Institute, Chennai. $GO\text{-}Fe_3O_4$ nanocomposites showed better absorptive property for the elimination of contaminants from tannery wastewater when compared to other prepared chemosorptive. The absorptive efficiency of the chemosorptive for the elimination of pollutants from tannery wastewater decreased in the following pattern:

$GO\text{-}Fe_3O_4$ > MCCAC > PLBAC > CCB

Overall, the prepared chemosorptive were efficient in removing several pollutants from simulated aqueous solutions and real wastewater from leather tannery. These chemosorptive may be exploited for the elimination of numerous other pollutants from aqueous and gas effluent streams in future.

References

1. Zhang, T., Walawender, W.P., Fan, L.T., Fan, M., Daugaard, D., Brown, R.C., Chem.Eng. J. **105(1-2)**, 53-59 (2004)
2. Oliveira, L.C.A., Rios, R.V.R.A., Fabris, J.D., Garg, V., Sapag, K., Lago, R.M.,Carbon

40(12), 2177–2183 (2002)

3. Ngah, W.S.W., Md Ariff, N.F., Hanafiah, M.A.K.M., Water Air Soil Pollut. **206(1)**,225-236 (2010)
4. Hummers, W.S., Offeman, R.E., J. Am. Chem. Soc. **80(6)**, 1339-1339 (1958)
5. Wu, J.L., Shen, X.P., Jiang, L., Wang, K., Chen, K.M., Appl. Surf. Sci. **256(9)**, 2826–2830 (2010)
6. Xu, Z., Guo, Q., Carbon **52**, 464-467 (2013)
7. Cesano, F., Rahman, M.M., Bertarione, S., Vitillo, J.G., Scarano, D., Zecchina, A., Carbon **50**, 2045-2060 (2012)
8. Brunauer, S., Emmett, P.H., Teller, E.J., J. Am. Chem. Soc. **60**, 309-319 (1938)
9. Barret, E.P., Joyner, L.G., Halenda, P.P., J. Am. Chem. Soc. **73(1)**, 373-380 (1951)
10. Boehm, H.P., Carbon **32**, 759–769 (1994)
11. Kosmulski, M., J. Colloid Interf. Sci. **337(2)**, 439-448 (2009)
12. Reymond, J.P., Kolenda, F., Powder Technol. **103(1)**, 30-36 (1999)
13. Zalac, S., Kallay, N., J. Colloid Interf. Sci. **149(1)**, 233-240 (1992)
14. Al-Degs, Y.S., El-Barghouthi, M.I., Issa, A.A., Khraisheh, M.A., Walker, G.M., Water Res. **40(14)**, 2645–2658 (2006)
15. Oller, I., Malaot, S., Sanchez-Perez, J.A., Sci. Total Environ. **409(20)**, 4141-4166(2011)
16. Weber, E.J., Wolfe, N.L., Environ. Toxicol. Chem. **6(12)**, 911-920 (1987)
17. Anjaneyulu, Y., Chari, N.S., Raj, D.S.S., Rev. Environ. Sci. Biotechnol. **4(4)**, 245-273(2005)
18. Bansal, M., Singh, D., Garg, V.K., J. Hazard. Mater. **171(1-3)**, 83-92 (2009)
19. Ramesh, K., Thirumangai, V., Intl. J. Eng. Res. Appl. **4(1)**, 63-70 (2014)
20. Konradsen, F., van der Hoek, W., Cole, D.C., Hutchinson, G., Daisley, H., Singh, S., Eddleston, M., Toxicology **192(2-3)**, 249–261(2003)
21. Ongley, E.D., “Control of water pollution from agriculture. Irrigation and Drainage Paper 55”, Food and Agriculture Organization of the United Nations, Rome (1996)
22. Srivastava, S., Sinha, R., Roy, D., Aquat. Toxicol. **66(3)**, 319-329 (2004)

23. Sun, S.P., Li, C.J., Sun, J.H., Shi, S.H., Fan, M.H., Zhou, Q., J. Hazard. Mater. **161(2-3)**, 1052-1057 (2009)

24. Mittal, A., Thakur, V., Gajbe, V., Environ. Sci. Pollut. Res. **20(1)**, 260-269 (2013) 25. Mohan, D., Singh, K.P., Singh, V.K., Ind. Eng. Chem. Res. **44(4)**, 1027-1042 (2005)26. Richard, F.C., Bourg, A.C.M., Water. Res. **25(7)**, 807-816 (1991)

27. Pellerin, C., Booker, S.M., Environ Health Perspect. **108(9)**, A402-A407 (2000)

28. Bukowska, B., Comp. Biochem. Physiol. C Toxicol. Pharmacol. **135(4)**, 435-441 (2003)

29. Mohan, D., Pittman Jr., C.U., J. Hazard. Mater. **137(2)**, 762-811 (2006)

30. Bansal, R.P., Goyal, M., “Activated carbon absorptive”, CRC Press, Florida (2005)

31. Rojas, G., Silva, J., Flores, J.A., Rodriguez, A., Ly, M., Maldonado, H., Separ. Purif. Technol. **44(1)**, 31-36 (2005)

32. Yue, Z., Bender, S.E., Wang, J., Economy, J., J. Hazard. Mater. **166(1)**, 74–78 (2009)

33. Karagoz, S., Tay, T., Ucar, S., Bioresour. Technol. **99(14)**, 6214–6222 (2008)

34. Prado, A.G.S., Moura, A.O., Andrade, R.D.A., Pescara, I.C., Ferreira, V.S., Faria, E.A., de Oliveira, A.H.A., Okino, E.Y.A., Zara, L.F., J. Therm. Anal. Calorim. **99(2)**, 681-687 (2010)