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Synthesis of Agro- based Copolymers for Treatment of Waste

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ABSTRACT: Environment is confronted with a variety of natural and synthetic organic compounds in its compartments, following rapid industrialization and urbanization. These continuously growing challenges elevate the need for implementing the clean and cost effective technologies. The plan of the present investigation is the copolymerization of natural and synthetic materials for the development of adsorbents followed by its application for the removal of environmental pollutants. Starch is selected as natural biopolymer and cyclodextrin represents the synthetic polymer. Both materials are copolymerized and further modified with the Cabbage fibres and epichlorohydrin as cross linker.

FTIR analysis reveals the presence of cyclodextrin in the synthesized copolymer through stretching vibration of $-CH_2$, $-C-O-C$ at 2931cm^{-1} and 1016cm^{-1}, respectively. On the other hand, starch based copolymer cross linked with epichlorohydrin is identified by the absorption band of epoxy group at 931cm-1. The presence of terminal and internal epoxy group at 763cm^{-1} and 669cm^{-1} also supports the synthesis. The SEM illustrated wider cavities that are expected to enhance the uptake capacity of modified copolymers for organic moieties. The inclusion complex of β-Cyclodextrin depicts rectangular features with milky white surface. The samples were scanned 10-71 of 2θ by steps of 0.015 with Cu K α radiation (λ = 1.54059) operating at 40 kv and 100 mA.

The synthesized Copolymers were applied as adsorbents in a batch experiment to determine efficiency for the removal of a wide range of environmental pollutants. The results of UV-Vis disclosed that crystal violet and congo red is removed to a comparable extent. Atomic absorption analysed the Lead (85-95%) is more efficiently removed than Chromium (60-70%). It might be related to higher molecular weight of the former than the later. Similarly, the fused aromatic rings demonstrated less removal for pyrene (202.25g/mol) than anthracene (178.23g/mol). The synthesized copolymers were also applied for the adsorption of PCBs from transformer oil to present model of in-situ remediation.

KEYWORDS:β-Cyclodextrin; Starch; Transformer oil, Epichlorohydrin, Cabbage leaf powder

1 INTRODUCTION

Environment is confronted with variety of synthetic organic compounds (Nagy [14] et al., 2008). The ultimate effects on the survival of human beings elevate the need for implementing the clean and cost effective technologies Persistent organic pollutants are such as PCB's manufactured in 1929 and were banned in 1979 but it is still used in electric transformers, capacitors, lubricating oils, printing inks, adhesives, sealants and additives in plastics and paints from where it enters into environment (Pentyala[25] et al., 2011).

Polyaromatic hydrocarbons (PAHs) are highly mobile organic toxicant enter into environment from both natural and anthropogenic sources. Extensive applications of azo dyes in food, leather tanning, paper and textile industry is growing interest in finding adequate and cost effective adsorbent for its exclusion from environment because it can transform carcinogenic aromatic amines in the environment through formation of covalent and physical bonds (Julinova [23] et al., 2012).

Elevated industrial hazards lead towards the lethal release of chromium into environment which is matter of concern. According to ministry of environment and forest the permissible limit for chromium in industrial effluents is 0.05mg/L whereas maximum recommended limit of chromium for drinking water is 0.05mg/L by World Health Organization (WHO) (Khatoon [17] et al., 2013).1n 1909 concept of adsorption was first originated by McBain (Browski et [6] al., 2001). Natural as well as synthetic adsorbents such as fly ash zeolites are used for the removal of pollutants from wastewater due to the availability of exchangeable adsorption sites on the surface of sorbent. In polymer science literature reported about various Starch based naturally existing biopolymer made up of two components amylose (linear linkage of glucose units by 1-4 bonds) and amylopectin (branched, dense structure with 1- linkage) contain polymer chain of glucose units which gain much acceptance due to its high biodegradable properties (Barikani [5] et al., 2007).Modification of starch with acrylonitrile and acrylic acid to forms copolymers as effective adsorbents for the removal of basic dyes such as methylene blue and rhodamine blue (Dhodapkar [9] et al., 2009).

β-Cyclodextrin is considered as an efficient adsorbent due inimitable property of forming inclusion complexes with solid, liquid and gaseous moieties through host guest interactions which are responsible for the complexation of guest molecule to cyclodextrin cavity. It can remove organic moieties from water as low as part per trillion level (Sambasevam [30] et al., 2013).Mechanism is shown by following equation:

$$CD \quad + \quad G \quad \rightleftharpoons \quad CD - G; \qquad = \qquad K = kR / kD$$

(Cyclodextrin) (Guest) (Inclusion complex) (Recombinant disassociation constants)

2 MATERIAL AND METHODS

The plan of the present investigation is the copolymerization of natural and synthetic materials as adsorbents for the removal of environmental pollutants. They were synthesized from two different sources, Starch and β-Cyclodextrin. Cabbage fibre and linker (epichlorhydrin) was added to each co-polymer (Rima [27] et al., 2013).

β-Cyclodextrin (60 mg) was dissolved in 75 ml of pyridine and heated at 70 ^{0}C. To this solution, cabbage fibres (28mg) and acetic acid (25 ml) were added and stirred brown to yellow solids started to appear after 30 minutes. (Rima [27] et al., 2013) while Starch based co-polymer was synthesized by dissolving Starch (60mg) in pyridine carboxaldehyde (75 ml). Yellow solid product was obtained in 20 minutes which was washed repeatedly with distilled water and ethanol to remove unreacted pyridine carboxaldehyde. Both synthesized co-polymers (CCD1 and CST1) were modified with cross-linker epichlorohydrin (10 ml) (Yu [38] et al., 2003), stirred, filtered, washed and the residue was dried. The products were coded as CCDE and CSTE.

The significance of present research is an attempt to greener synthesis (than reported by Rima[27] et al., 2013) in selecting acetic acid as a solvent than highly toxic toluene diisocyanate (Arnold [2] et al., 2012).Furthermore, usage of cabbage fibres and starch are reported for the first time in the present research. The modified copolymers were subjected to standardized characterization techniques to study the surface and bulk properties of the materials. Functional groups identification was made on FTIR, SEM and XRD.

2.1 BATCH ADSORPTION EXPERIMENTS

The sorption capacities of synthesized copolymers were investigated by applying as adsorbents for the removal of dyes, heavy metals, polyaromatic hydrocarbon and polychlorinated biphenyls. A close batch approach was carried out by taking known mass of copolymer as adsorbent was added an aliquot was taken after known contact time between adsorbate and adsorbent till equilibrium is attained.

Adsorption of dyes (Methyl orange, Crystal violet, Congo red) and PAHs (Pyrene and Anthracene) on synthesized copolymer was recorded on UV-Visible spectrophotometer (UV-1601, Schimadzu Japan) at a wavelength of maximum absorbance (λ max) 590 nm and 497 nm for dyes and maximum absorbance (λ max) for Pyrene (412 nm) and Anthracene (471 nm). Each batch experiment was conducted for three different induced concentrations (0.01 mg/L, 0.03 mg/Land 0.05 mg/L) and three adsorbent dosages (1 mg, 5 mg, 10 mg, 20 mg) as a function of time.

Concentration of metals after adsorption with copolymer was determined on Flame Atomic Absorption spectrophotometer (AA 220, Varian) using Hollow Cathode Lamp. The batch experiment was reported with lead and Chromium at three different concentrations (30, 50 and 70 mg/L) and at different adsorbent doses (1 mg, 5 mg, 10 mg and 20 mg).

The percent or the removal (in percentage) of dyes, metals and PAHs was calculated using the following relation:

$$R\ (\%\ age) = 100\ \frac{(C_i - C_o)}{C_i}$$

3 RESULTS AND DISCUSSION

Keeping the objective to remove a wide range of organic and inorganic pollutants from the environment, Direct co-condensation approach is adopted for the synthesis of co-polymers, as this process is easier, convenient and efficient (Da, na [7] et al., 2011).

3.1 FTIR INTERPRETATION OF COPOLYMERS

The recorded FTIR spectra of raw cabbage show characteristic peak at 3354–3601 cm^{-1} assigned to the absorption of N–H and O–H stretching (Bao [4] et al., 2013) while the characteristics peaks of β- Cyclodextrin was observed at 1033 $cm^{-}1$, 860cm-1 and 1157cm^{-1} are due to anti-symmetric stretching of C-O-C and vibrational stretching of –C=C- (Li [19] et al., 2011). FTIR spectra of raw starch indicated at 1670cm^{-1} and 1411cm^{-1} of C-H or C-O vibrating absorptions suggests intramolecular bonds (Wang [35] et al., 2012).

The synthesized β-CCD Copolymer was characterized by the presence of peak at 2960.83cm^{-1} indicates the presence of Hydrogen free -NH-COO-,-NH2- and –COOH groups. FTIR of β-CCDE show the CH_2–Cl and C-Cl rocking and wagging band at 707–526 cm^{-1}confirm the formation of polymer with the addition of ECH. This is also supported by Gidwani [13] et al., 2014.

Copolymer synthesized from starch, when analysed under FTIR prompted the free and bonded N-H stretch vibration at 3463 $cm^{-1}$and urethane - urea linkage is observed at 1712 cm^{-1}(Mostafa [21] et al 2011).After modification (with epichlorohydrin) of the above mentioned copolymer epoxy group absorption band at 931cm^{-1}-860 $cm^{-1}$is assessed. The terminal and internal epoxy groups at 763 cm^{-1} and 669$cm^{-1}$are also identified by (Yu [38] et al., 2003).

3.2 SCANNING ELECTRON MICROSCOPY OF SYNTHESIZED COPOLYMERS

The modified β-Cyclodextrin copolymer with epichlohydrin shows (see Figure: 1)interesting morphological features, like wider cavities, globular shape and roughness of surface due to the presence of cross linker that will contribute the availability of more spaces to entrap the incoming pollutant and enhanced surface area for adsorption. The sizes ranges form 50-80 nm. (Khatoon [17] et al., 2013).The starch based copolymer was modified with epichlorohydrin will exhibit some features distinctive of cross-linking agent which shows generation of more wider spaces, whereas the basic constituents of copolymers are more strongly and closely networked due to cross-linking phenomenon. As a result, the copolymer clusters into larger agglomerates. This is reflected by the relatively larger size of the synthesized copolymer ranging from 60-131nm (Ding [11] ***et*** al., 2011).

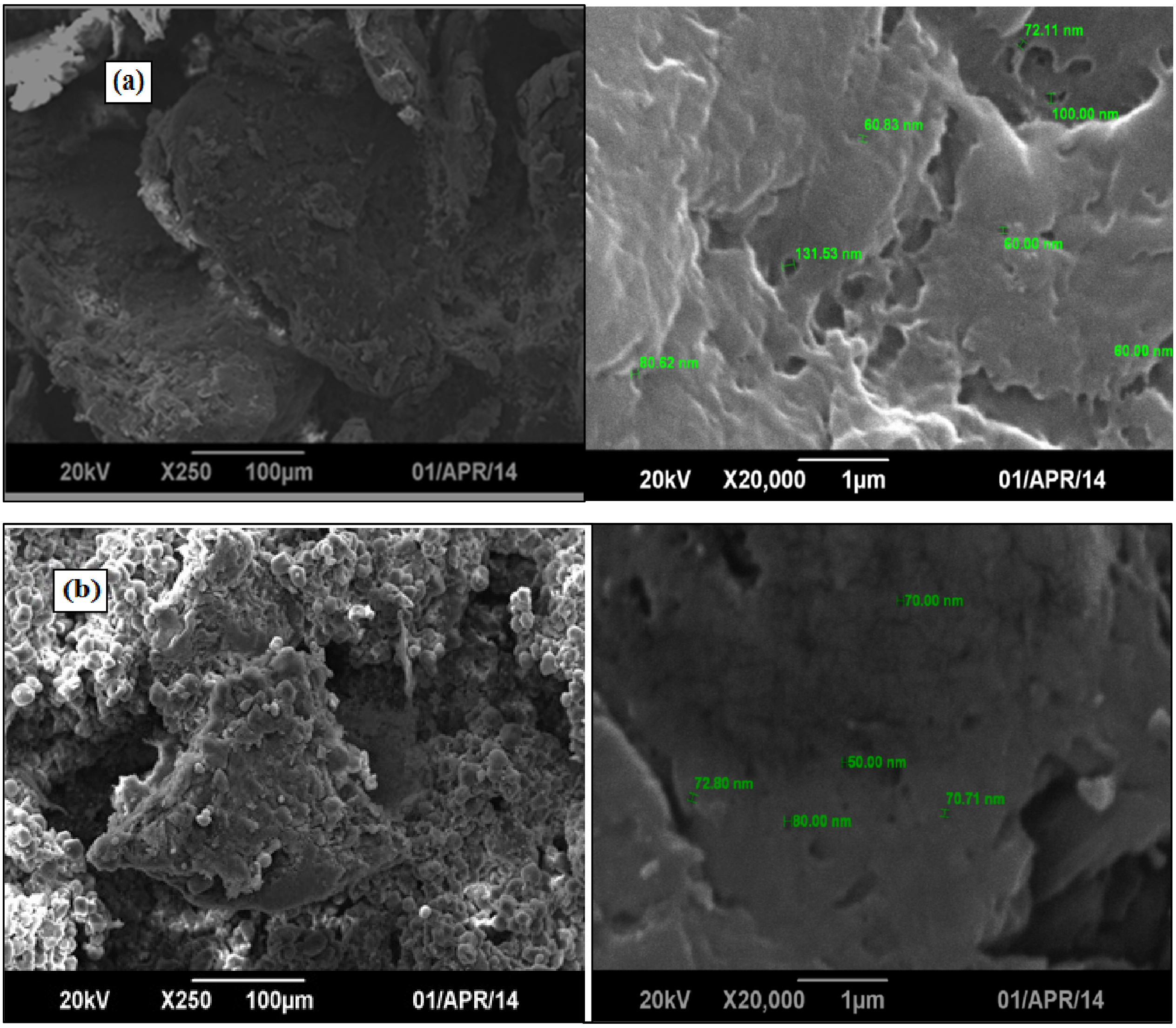

Figure: 1. SEM images of modified (a) β-Cyclodextrin (b) Starch based Copolymers

3.3 XRD ANALYSIS OF SYNTHESIZED COPOLYMERS

The synthesized copolymers when impinged with X-rays show that β-Cyclodextrin copolymer diffracts to a much limited range with maximum intensity at 2θ of 21.66^0. It indicates the material is preferably amorphous due to loss of regularity throughout the polymeric chains (Raoov [26] et al., 2014) and wide spacing (d >4) inhibits scattering of incoming rays. Further, very small sized grains (0.064 nm) may provide another hindrance to diffraction process (Stalin [32] et al., 2014).The starch based copolymers show a marginal increase in degree of crystallinity but modification with epichlorohydrin slightly reduces the intensity of diffracted peaks which is attributed towards the amorphization of the structure (Kumar [18] et al., 2014). During crystallization of Cyclodextrin, some water molecules inculcates into Cyclodextrin cavity while other act as integral part of crystal structure (Das [8] et al., 2013).

Further d-spacing is contributing to comparable size of crystallites after modification of starch based co-polymers. The wider spacing depicts the synthesized copolymers having characteristics of both crystalline and amorphous (Mulla [22] et al., 2012).

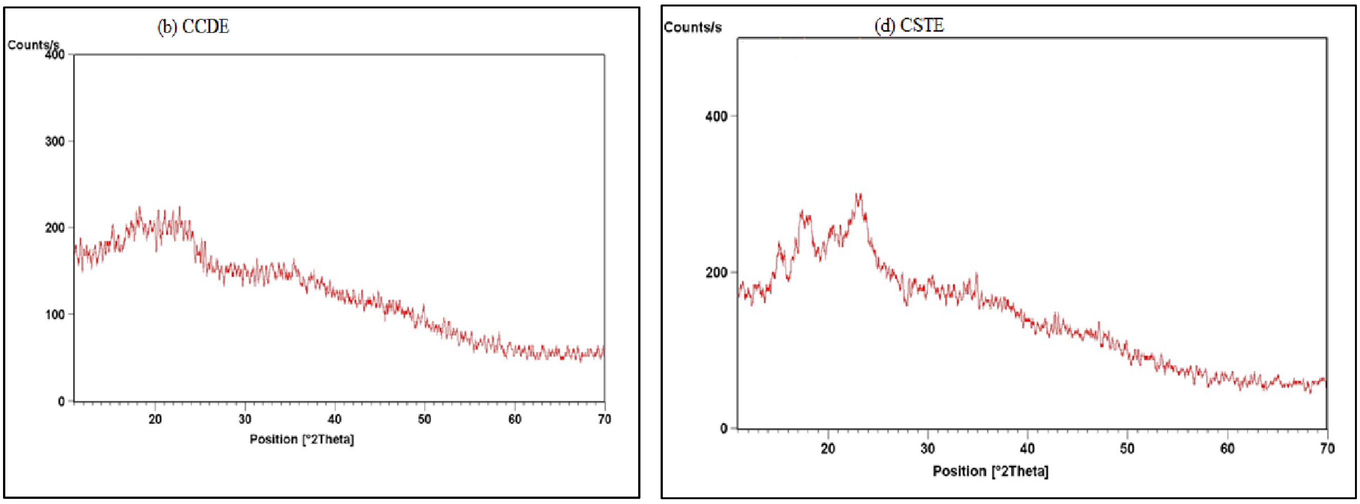

Figure: 2. XRD of synthesized copolymer (b) CCDE (d) CSTE

3.4 EFFECT OF DOSE

The adsorption efficiency of modified β-Cyclodextrin based copolymers indicates that higher percent (94) removal of crystal violet was observed at high dose of adsorbent (20 mg).This indicates that efficient removal of crystal violet is due to increase in adsorbent surface area and active sites results in availability of more binding site for desorption.

3.5 EFFECT OF TIME

The contact time for the removal of crystal violet by both adsorbents (CSTE and CCDE) was determined. It is suggested that that adsorbent mass has impact on contact time to reach the equilibrium. Smaller the dose longer it will take time to attain equilibrium (60 min), higher the doses lesser it will take the time to attain equilibrium 30 min (S[29] et al., 2014). The results indicate that the modified copolymers show maximum desorption between 10 min-20 min due the activity of cross linker. Maximum adsorption was observed at (5 min-10 min).This trend is supported by Vanitha [34] et al., 2014 reported a considerable increase in percent removal of crystal violet with the increase in contact time will attains equilibrium at 30 min.

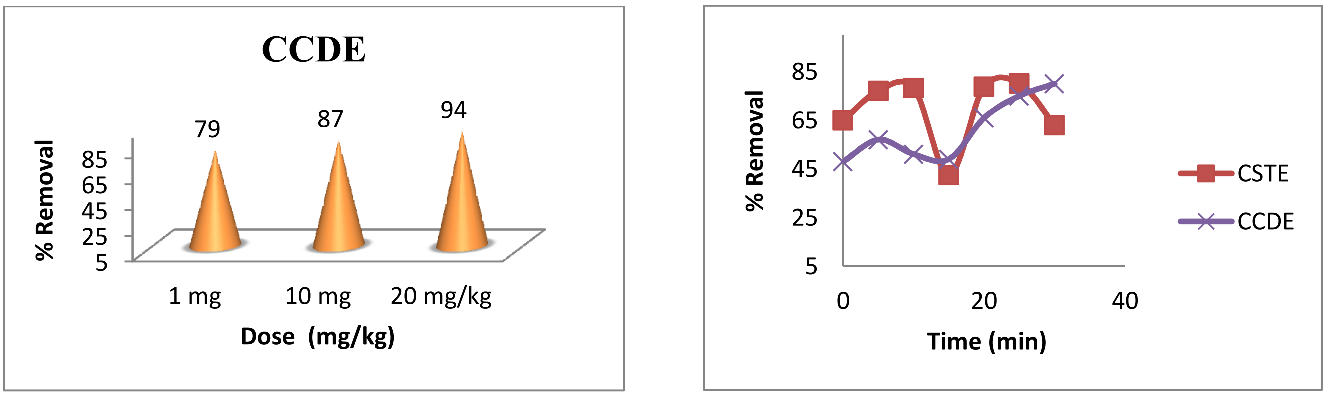

Figure: 3. Removal (% age) of crystal violet

4 CONGO RED

4.1 EFFECT OF CONCENTRATION

The modified β-Cyclodextrin based adsorbent reveals its higher adsorption capacity for the removal of Congo dyes because β-Cyclodextrin act as a host that allow Congo red (guest) to entrap within its cavities and adsorption sites remain unsaturated during adsorption. It enhances the sorption capacity due to the presence of intermolecular hydrogen bonding between hydroxyl group in β-Cyclodextrin and amide group as a result of the addition of pyridine and cabbage (Rima[27] et al., 2013) strongly bonded with the sulfonate group of azo dyes. The trend follow in adsorption of Congo red shows increased with the increase in concentration as it is supported by (Panic [24] et al., 2013).

4.2 EFFECT OF CONTACT TIME

The effects of contact time on the removal efficiency of modified starch and β-Cyclodextrin based adsorbents were examined. The maximum removal of Congo red was observed between 5 min-15 min and attains equilibrium after 20 min. This is followed by similar trend by clay based materials as adsorbents (Meroufel [20] et al., 2013).The adsorption of congo red is rapid in the initial time (within 10 min) after which larger amount of dye adsorb with the increase in initial concentration. Similar trend is observed by S [29] et al., 2014 who reported the adsorption of methylene blue which depends upon the initial concentration.

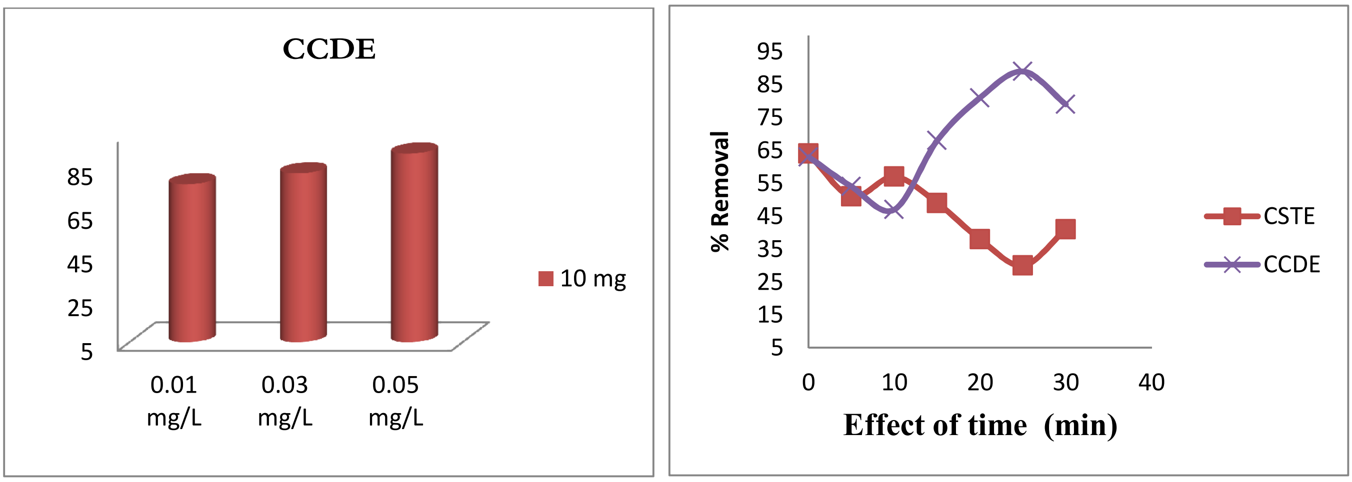

Figure: 4. Removal (% age) of Congo Red

5 REMOVAL OF POLYAROMATIC HYDROCARBONS (PYRENE AND ANTHRACENE)

5.1 EFFECT OF DOSE

The free sites on the surface of adsorbents are responsible for the efficient removal of polluting moieties. Due to increase in dose number of active sites and surface area increase which allows more adsorption of pollutants. The bar graph (Figure: 5) represents 93% removal efficiency at 20 mg dose. This shows that percent removal increase with the increase in amount of dose. CCDE show higher percent removal because the removal capacity of CCDE depends upon molecular species of pyrene in aqueous solution. Due to higher mass of adsorbent (20 mg) the neutral species in the pyrene which are more hydrophobic and weakly polar gradually inco-operates in to the CCDE cavities (Yu [38] et al., 2003).

5.2 EFFECT OF CONTACT TIME

The percent removal of any pollutant depends upon the time of contact. Longer the pollutant become intact with the adsorbent higher will be its removal. The removal trend shown in (Figure: 5) suggest that both modified adsorbents reveals different percent removal on the basis of it properties such as surface area and active sites on the surface of adsorbent which increase with the time and mass of adsorbent. CSTE attains equilibrium at 20 min and maximum removal was observed between (5 -15 min) while CCDE show equilibrium till 25 min and then decrease sharply.

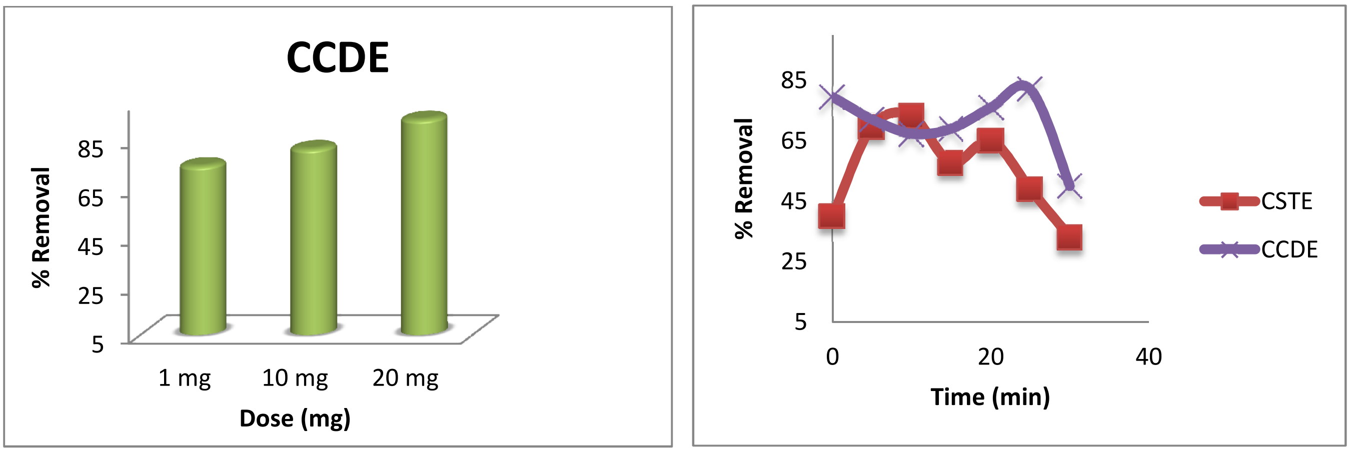

Figure: 5. Removal (% age) of Pyrene

5.3 EFFECT OF DOSE

Comparatively to pyrene which shows highest removal at highest dose. Dissimilarity in trend was observed for the removal of anthracene which depicts the optimum removal of anthracene at 1 mg followed by 20 mg. This is due to the fact that maximum removal was 86% percent because cross-linking ability enhances the adsorption at initial dose which later on further enhance the active sites due to the increase in dose which shows 93 % removal.

5.4 EFFECT OF CONTACT TIME

The trend in the graph show that percent removal of anthracene increase with the increase of time because longer contact time will favours the adsorption of anthracene at much faster rate. The maximum removal was observed between 5-20 min. Later on CST, CSTE, CCDE will attain equilibrium after 25-30 min while CCD show desorption after 25 min.

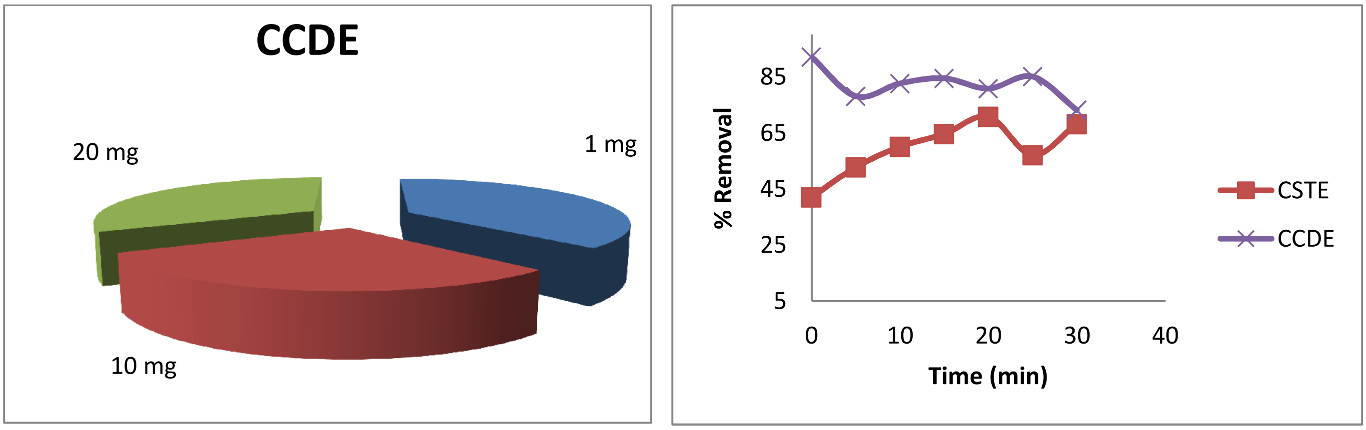

Figure: 6. Removal (% age) of Anthracene

6 REMOVAL OF METALS(LEAD AND CHROMIUM)

6.1 EFFECT OF DOSE

The efficient removal of lead was observed at initial dose which reveals the significant efficiency of β-Cyclodextrin based adsorbents because they provide large surface area for the incoming metal to entrap within the cavities while the opposite trend was observed for Chitosan based adsorbent whose percent removal increase with the increase in adsorbent dose. This fact that lead adsorbs at low dose rather than at higher dose due to its low ionization energy is supported by (Shanmugapriya,[31] et al., 2013) who also observed that Ni get removed from the adsorbent surface at higher dose. It is observed that there is decrease in removal percentage with the increase in dose due to the aggregation and non-availability of active sites on the adsorbent surface (B [3] et al., 2011).

6.2 Effect of Contact Time

Increase in time results in probability that more and more time will be available for metal ion to remain intact with the adsorbent surface and form complexes at the surface which favours more removal of pollutants. This shows that adsorption increase with the increase in contact time (see Figure: 7) because in bulk solution all adsorbents show decrease in boundary layer resistance to mass transfer results in increase in kinetic energy of hydrated ions so more and more lead ions become mobile in solution than on adsorbent surface. The highest adsorption was observed between 10 min and 20 min for CCDE due to high cross- linked complexation between adsorbent and adsorbate while remaining adsorbents sow equilibrium between 5-25 min (Xia [36] et al., 2003).

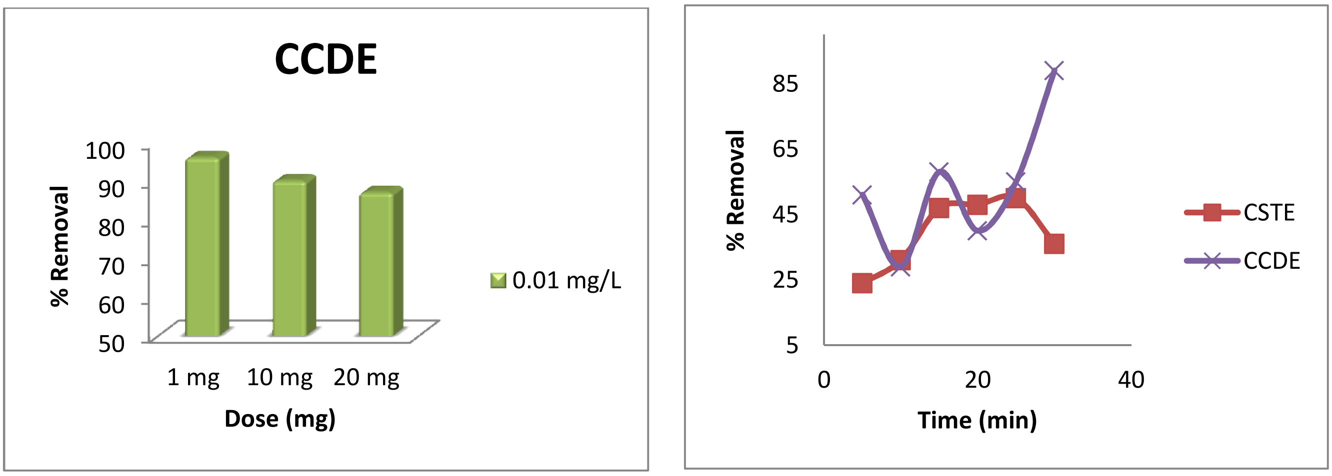

Figure: 7. Removal (% age) of Lead

6.3 Effect of concentration

Three different concentrations (30 mg/ L, 50 mg/Land 70 mg/L) were selected to determine the removal efficiency of Chromium by applying synthesized copolymers as adsorbents. The β-Cyclodextrin based modified copolymers shows its optimum removal efficiency at 50 ppm which decrease with the decrease in concentration because the active sites at the surface are occupied by the epichlorohydrin which results in high cross-linked structures that ultimately affect the adsorption phenomena. The percentage adsorption increase after some time and then decrease with the increasing concentration (Khatoon [17] et al., 2013).

6.4 Effect of contact Time

The effect of time was investigated to check the increase in removal efficiency with the increase in contact time because it allows more time for metal ion to form complex. The efficient removal was observed at the initial stage (5-10 min) because whenever metal and adsorbent become intact so more and more active sites are occupied. This shows that all adsorbents show quick adsorption and desorption phenomena towards the removal of chromium. CSTE attain equilibrium whereas CCDE show decreasing trend due to non-availibity of the adsorptive sites at the surface of β-Cyclodextrin based adsorbents as shown in Figure: 8 (Kanwal [15] et al., 2012).

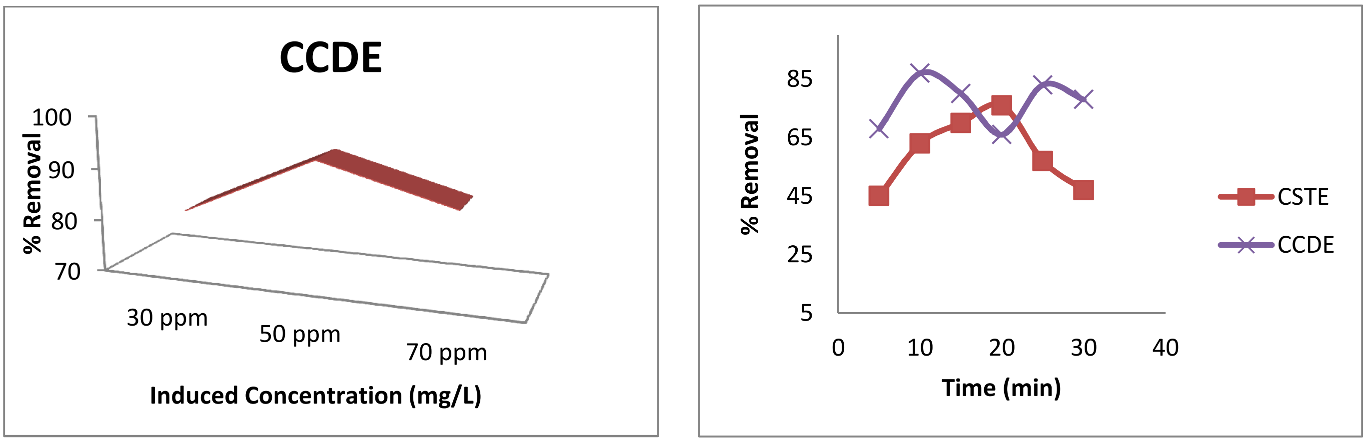

Figure: 8.Removal (% age) of chromium

7 EXTRACTION AND DETERMINATION OF PCBS IN TRANSFORMER OIL

7.1 EXTRACTION METHOD

Transformer oil is first extracted by adding 10 ml of dimethyl sulfoxide and water mixture, repeated extraction with 8 ml and 5 ml, discard oil layer of sample by adding 10 ml of water. Second extraction is carried out by by adding 10 ml of hexane, repeated extraction with 8 ml and 5 ml. Discard DMSO: H_2O mixture layer by concentrating 1 ml organic layer in rotary evaporator. This organic layer is eluted with 10 ml hexane by pouring it in separatory funnel. Discard 10 ml of hexane by collecting 25ml which is then passing through anhydrous sodium sulphate. This is than concentrated in rotary evaporator. Later on it can be spiked with 1.5 µg of internal standard.

7.2 DETERMINATION OF PCBs BY BATCH ADSORPTION EXPERIMENTS

Batch adsorption experiment was carried out by preparing three different working solutions at three different concentrations (0.01 mg/L, 0.03 mg/L and0.05 mg/L) with three different doses of following such as adsorbents (CST, CSTE, CCD, and CCDE).Concentration of PCBs was determined on UFLC against Arocolor-1260 mixture as standard. (Ryoo [28] et al., 2007) reported that Arocolor-1260 can be removing more rapidly by reducing the concentration of PCBs.

Detrimental effect of persistent organic pollutants on human beings and environment leads towards the idea of their efficient removal by utilizing greener sources (synthesized natural and synthetic copolymers) from waste transformer oil. Calibration curve was obtained by using standard solution of three known concentrations in order to determine the concentration of PCBs quantitatively. Stock solution was prepared by dissolving dichlorobiphenyl in 50 ml of hexane. Further working solutions were prepared by diluting the stock solution. Results reveal that raw transformer oil (RTO) contain highest concentration of PCBs (8.9%) because it contain different other constituents along with the PCB supported by the literature that waste transformer oil contain 0-60% PCBs while remaining contain other toxic moieties such as PAH, sulphur etc (Toader [33] et al., 2011) but after extraction the percentage was reduced to 6.4% which confirms that specifically the PCBS were extracted from the remaining residual constituents in the raw transformer oil. It is evident from the literature that the most toxic PCB is dichlorobiphenyl whose peak appears in chromatogram within 0-10 min (Dietrich [10] et al., 2005).

Batch adsorption experiment was designed to investigate the removal efficiency of synthesized modified copolymers and selective determination of PCB can be determined by comparing the chromatogram of the purified extracts with those obtained from standard solution (Yoo [37] et al., 2007).

7.3 RESULTS AND DISCUSSION

The results suggest that highest percent removal was observed for modified β-Cyclodextrin based copolymer because chlorine atoms obtrude from the PCBs planar molecule due to solid inclusion complexes with aromatic compounds such as PCBs (Friedman [12] et al., 2008).The starch based copolymers shows its least significant removal efficiency because after modification with cross-linker it reduces the surface area for the adsorption of PCBs so ultimately it reduces the adsorption ability (Aken [1] et al., 2010). The optimum concentration of PCBs in transformer oil can be quantified by two parameters Limit of detection, limit of quantification by using the following equations:

LOD =33(SD/S)…… (i)

LOQ =10(SD/S)…… (ii)

The calculated values after putting values in the equation gives 3.16576 for LOD and 9.59322 for LOQ which suggest that the method adopted for the extraction of PCBs from transformer oil is more sensitive and reliable to adopt because it show significant reduction in PCBs quantity after removal with the synthesized copolymers.

The trend towards the removal efficiency of synthesized natural and synthetic copolymers is as followed: CSTE >CCDE.

7.4 KINETIC STUDIES

Different kinetic models including first order, pseudo first order, and pseudo second order and intra particle diffusions equations were applied to determine the mechanism involved in adsorption process. The kinetic parameters for the removal of heavy metals, dyes, PAHs by different natural and synthetic copolymers as adsorbents. The kinetics follows the pseudo second order. Similar results were also observed in different studies.

7.5 ADSORPTION ISOTHERMS

The value of Langmuir and Freundlich isotherm model constants for heavy metals dyes, PAHs and PCBs using different adsorbents. Adsorption kinetics of various pollutants (dyes, metals and PAHs) were studied following kinetic models Pseudo second order, First order, Inter-particle diffusion, Freundlich and Langmuir isotherm models for the selection of linear best fit model. The results show that the adsorption of various pollutants are best described by Pseudo-second order, Freundlich and Langmuir isotherm models with high correlation coefficient values(R^2)(0.9968,0.999 and0.9992) while Inter-particle diffusion is best fit in case of methyl orange with maximum correlation coefficient 0.9166 (Ketcha [16] et al., 2011).

8 CONCLUSION

It is concluded from the above study that this research is new portal towards the greener synthesis of material for the remediation of environment in economical way. This study is based on the synthesis of eco-friendly copolymers at low cost to remedy the environment suffered from toxic moieties in environment which ultimately enters the food chain and effect human beings and aquatic species and the replacement of toxic solvent with the cleaner and safer solvent. Toluene diisocyanate, the most toxic solvent in the environment is replaced by the least toxic acetic acid whereas the cabbage is added as a biosource to enhance its degradable properties.

It is proposed that the synthesized copolymer is good and cheaper alternate towards the replacement of non-biodegradable plastics after studying its thermal behaviour in the present research.

After the applications of synthesized Copolymers in pollutant removal it is proposed that they are efficient economical adsorbents for the dyes, PAH, heavy metals and PCBs (from waste transformer oil).Among all adsorbents modified β-Cyclodextrin based and non-modified Copolymers reveals its significant removal efficiency at optimum dose and concentration. It gives 80-90% removal for dyes 60-70% removal for metals, 50-60% for PAHs and 5% for PCBs (Total concentration of PCBs in Transformer oil (T.O) is 8%.

It is suggested that Copolymers after modification removes the toxic pollutant at considerable rate which confirms that the properties of synthesized copolymers are further enhanced due to cross-linking with epichlorohydrin.

On the basis of the results of the batch adsorption experiments, it is suggested that pseudo-second order, Langmuir and Freundlich isotherm are best fit for studying the adsorption kinetics of different pollutants on copolymers.

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