“ADSORPTION MECHANISM OF CELLULOSE AND ITS DERIVATIVES ONTO VARIOUS SOLID SURFACES”

THESIS

SUBMITTED TO

BABASAHEB BHIMRAO AMBEDKAR UNIVERSITY
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BABASAHEB
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ASHOK KUMAR
Ph.D. Research Scholar
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PROFESSOR KAMAN SINGH

DEPARTMENT OF APPLIED CHEMISTRY
SCHOOL FOR PHYSICAL SCIENCES
BABASAHEB BHIMRAO AMBEDKAR UNIVERSITY
(A Central University)
VIDYA VIHAR, RAEBARELLI ROAD, LUCKNOW-226025, UTTAR PRADESH (INDIA)
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Summary

Cellulose has been recognized as one of the most widely, abundant naturally occurring biopolymers in the world. Human beings had used cellulose as an extension of their hands for millions of years, even before the beginning of hominization because of its wide availability (cellulose is the major constituent of plant material), and cellulose is a relatively low-cost polymer. Cellulose has a component of at least a third of advanced plants: 40-60% (in weight) of dry wood, and more than 90% of raw cotton (99.9' %) of purified cotton) and flax. It is a homopolymer of anhydroglucose, with the glucose residues linked in a β -1, 4 fashion (Figure 1), It has a general formula $(C_6H_{10}O_5)n$ consisting of a linear chain of several hundred to many thousands of $\beta(1\rightarrow4)$ linked D-glucose units. The molecular studies reported that due to presence of several functional hydroxyls (-OH) in the polymeric chain of cellulose, it is well known polyhydroxy alcohol. These groups (hydroxyls) allowed numerous chemical modifications to obtained derivatives. The hydroxyl groups of cellulose can be partially or fully reacted with the various reagents to obtain various derivatives with useful properties. Most of the chemically modified cellulose polymers were known as cellulose esters and cellulose ethers (sometimes referred to as "classical cellulose derivatives"). Generally, cellulose derivatives (CDs) like microcrystalline cellulose (MCC), carboxymethylcellulose (CMC), hydroxyethylcellulose (HEC), etc, could be obtained by either mechanical or chemical processing or both. The CDs exhibit characteristics like biodegradability, high aspect ratio, sustainability, high modulus, high surface area, surface functionality, high chemical resistance, renewable, excellent crystallinity, water stability, improve stability of the drug, good lubrication, rapid disintegration, good flowing properties and good binding properties. Because of these properties, CDs have been widely used for various applications in several areas like mineral processing, petroleum, textile & dyeing, papermaking, food, pharmaceutical, cosmetics, ceramic, leather paints & lacquers, building materials, mosquito, repellent, toothpaste, battery, detergent and tobacco industry.

Nowadays the relevance of understanding the adsorption behaviour of polymers like CDs at solid-liquid interfaces has been generally recognized. A detailed understanding of adsorption characteristics of CDs was needed to develop new applications of CDs. Our understanding of the adsorption/binding behaviour of the CDs at the solid-liquid interface has been increasing year by year as significant work has been devoted to the adsorption of CDs onto the various solid surfaces. Several binding mechanisms have been developed, but as yet no common mechanism has received general acceptance. Thus, the associated problems have received adequate attention. Herein, cellulose its derivatives (CDs) namely, carboxymethylcellulose, sodium carboxymethylcellulose (NaCMC) and hydroxyethylcellulose (HEC) were mainly selected as adsorbates.

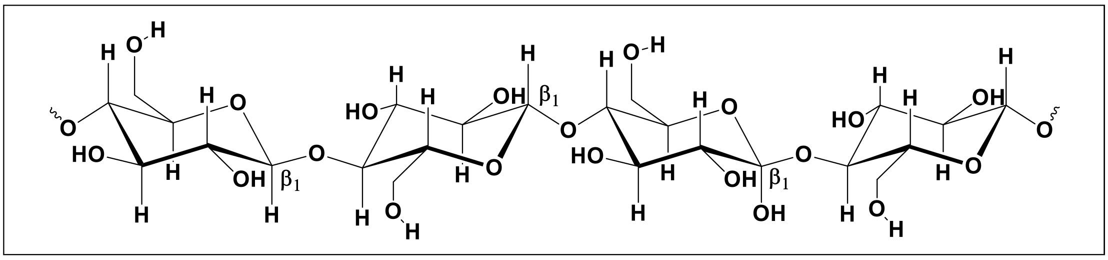

Figure 1. Structure of cellulose (repeating unit of glucose) shows the D-glucose units are linked through β-1, 4 bonds.

The prime objective of this research was to establish an understanding of the binding mechanism of CL, Na-CMC and HEC onto various solid surfaces and to determine the most desirable conditions to increase the applicability of selected polymers in various fields. The solid surface was probed with various physicochemical parameters such as zeta potential, specific surface area, pore diameter, pore-volume, particle size distribution and mesoporous nature employing various in-depth characterizations techniques. The effect of various parameters like concentration of polymers, the dose of adsorbents, pH, salt concentration, concentration of urea and dimethyl sulfoxide (DMSO), contact time, temperature, and sonication, etc. during adsorption experiments were investigated. For the validation of the adsorption data, various adsorption isotherm models were modeled. Based on the results, it was suggested that the physicochemical binding aspects of selected polysaccharides/polymers onto solid surfaces was stabilized by H-bonding and other weak noncovalent interactions and such alteration could play a noteworthy role in the field of food, pharmaceutical, and industrial applications particularly in mineral processing by gaining a more developed understanding of the mechanism of CDs adsorption onto various solid surfaces. The theoretical aspects were also investigated employing density functional theory (DFT) for some selected CDs. Since, a detailed study of the synthesis, characterization and application of new adsorbents (solid surfaces) for adsorption behaviour of CDs from their aqueous solutions have been carried out and presented in the thesis. The thesis consists of mainly seven chapters with some appendices as mention below:-

Chapter 1: Introduction and review of literature
Chapter 2: Experimental methods and characterization techniques
Chapter 3: Adsorption behaviour of carboxymethylcellulose onto mesoporous carbon derived from mustard cake
Chapter 4: Adsorption behaviour of carboxymethylcellulose onto functionalized accurel
Chapter 5: Physiochemical aspects for the adsorption behaviour of sodium carboxymethylcellulose onto mesoporous granular fine quart surface from its aqueous solutions
Chapter 6: Adsorption behaviour of cellulose, sodium carboxymethylcellulose and hydroxyethylcellulose onto activated kaolin
Chapter 7: Conclusions and prospects
Appendices
Appendix-I: List of publications
Appendix-II: List of national, international, conferences, congress, symposia, conventions, webinars and workshops
Appendix-III: List of honours, recognitions and awards
Appendix-IV: Plagiarism report

The study broadly followed the scheme as given above. The summary of the research work carried out is as follows:-

Chapter 1 describes basic information related to cellulose and its derivatives (CDs) and adsorption process. From the reported literature, it was concluded that there are various applications of polysaccharides like CDs due to their characteristics properties. The applications of CDs have been widely recognized in various industries like textile & dyeing, papermaking, food, pharmaceutical, cosmetics, ceramic, leather, paint & lacquers, petroleum, building materials, mosquito-repellent, toothpaste, battery, detergent and tobacco industry [10-12]. However, there was a lack of understanding of the interaction mechanism between the polysaccharides (CDs) and solid surfaces which has hindered its possible applications, hence, adsorption of polysaccharides onto solid-liquid interface has been a topic of long-standing debate. The present study provided substantial proofs and a systematic understanding of the adsorption behaviour of CDs onto various solid surfaces.

Chapter 2 presented the experimental methods and characterization techniques to characterize the synthesized adsorbents from various raw materials. It also deals with detailed methodology like physical and chemical activation methods for the preparation of adsorbent and solid-liquid interphase analysis (SLIA) for CDs onto prepared solid surfaces (adsorbents). The following instrumental techniques that have been employed for the characterization of adsorbate and adsorbents during research work and are discussed in details in this section.

- Fourier-transform infrared spectrometer (FTIR) to identify functional groups and the types of chemical bonds in molecules with sample preparations
- Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectrometer for the identification of functional groups and the types of chemical bonds in molecules without sample preparations
- Scanning electron microscope (SEM) to observe the surface morphology of the samples
- Energy dispersive X-Ray analysis (EDX) for elemental composition analysis of the samples
- Elemental mapping analysis (EMA) for effective microanalysis in the surface texture of the samples
- Powder X-ray diffraction ($_P$XRD) to determine crystallinity and phase analysis of the samples
- Brunauer–Emmett–Teller (BET) surface area analyzer for specific surface area, pore diameter, pore-volume, particle size distribution, mesoporous nature of adsorbents
- X-ray photoelectron spectrometer (XPS) for analyzing the surface chemistry of materials (CDs and adsorbents)
- Thermogravimetric analysis (TGA) for thermal behaviour of CDs and adsorbents

- Advanced high-intensity ultrasonicator (AHIU) for sonication process and homogenization of the samples
- Zeta-potential analysis for measuring the surface charge on adsorbent at different pH environment.
- Ultraviolet-visible (UV-Vis) spectrophotometer for the determination of the residual concentration of CDs at a specific wavelength

In chapter 3, the synthesis of the mesoporous mustard carbon (MMC) was described by earlier reported methods (Figure 2). The typical surface area (S_{BET}) of the MMC was 16.576 m^2 g^{-1}. The average pore diameter and total pore volume of MMC were found to be 12.432 nm and 0.051 cm^3g^{-1}, respectively and confirm the mesoporous nature of the MMC as per the IUPAC classification of materials. The adsorption of CMC onto MMC was found to be affected by process parameters such pH and ionic strength, etc.

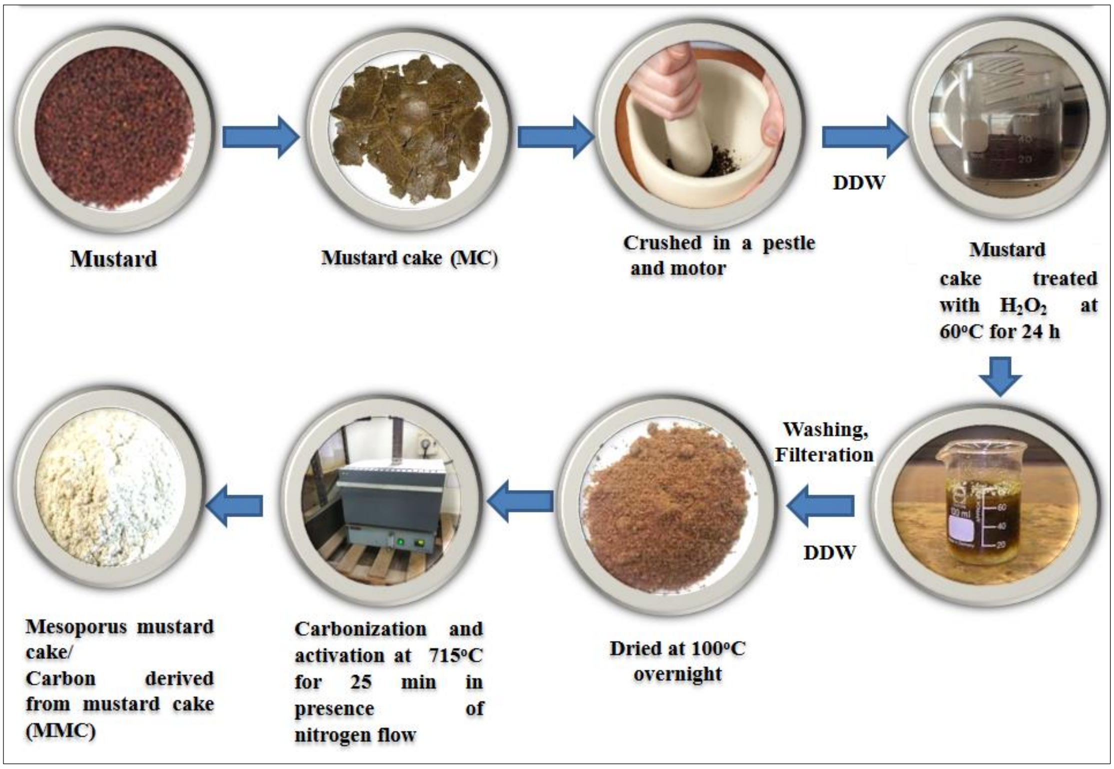

Figure 2. Graphical representation of the synthesis of MMC by carbonization method

These findings indicated that the electrostatic force plays an important role in CMC binding at MMC/water interfaces. The findings of the ATR-FTIR study helped to detect spectral differences associated with hydrogen bonding between CMC and

MMC. The differences in the ATR-FTIR bands in the 1000–1080 cm^{-1} area were important, owing to the C–O stretch coupled to the C–C stretch and O–H disability, confirming strong bond formation due to hydrogen bonding of CMC onto the MMC/water interface. Since urea functions as a hydrogen bond breaker, the presence of urea during adsorption greatly reduced the amount of CMC adsorption on MMC. This finding further favoured a hydrogen bonding-based system rather than a hydrophobic one. Since the adsorption free energy (-22.561 kJ mol^{-1}) of CMC evaluated is similar to that of hydrogen bond formation, Langmuir adsorption isotherm study endorses hydrogen bonding as the dominant force for CMC adsorption (Figure 3).

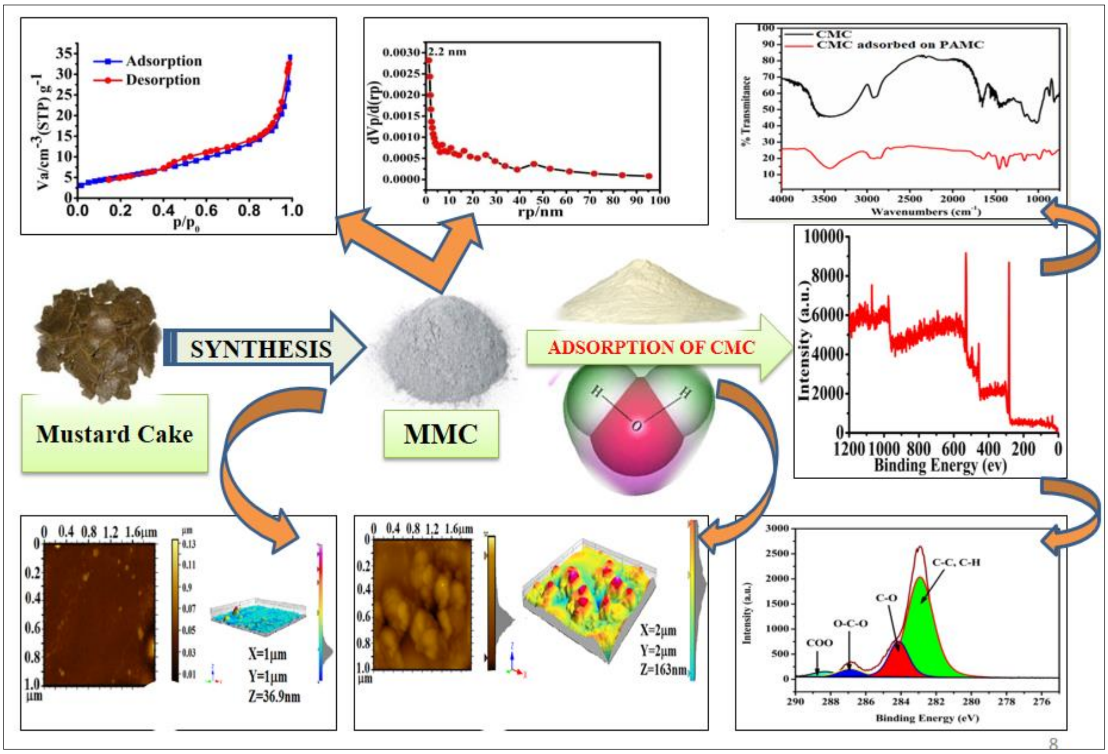

Figure 3. Graphical abstract illustrating adsorption mechanism CMC onto MMC

The survey scan and high resolution of C1S XPS spectra confirmed that the OH groups on the MMC surface associate with the CMC carboxylate ion. Thus, the current research provided significant evidence to show without doubt that CMC adsorption on the MMC/water interface was governed by electrostatic interaction and hydrogen bonding and influenced by experimental conditions.

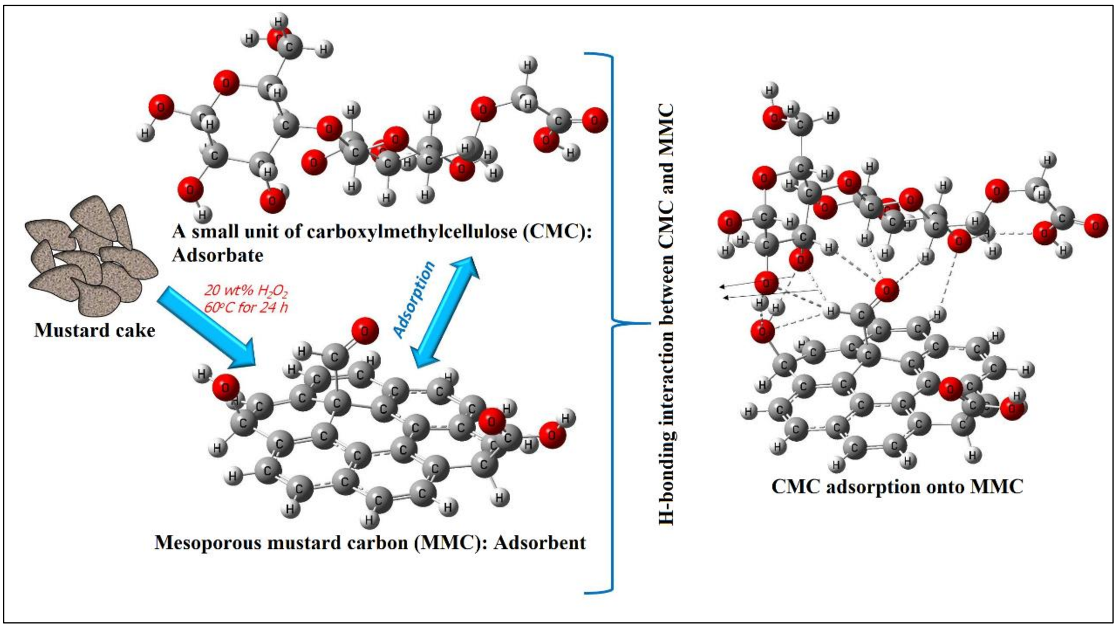

Figure 4. Schematic graphical representation of an overall summary of the adsorption mechanism of CMC onto MMC

This adsorbent-adsorbate model (Figure 4) was supposed to pave a new path towards a deeper understanding of molecular aggregation mechanisms in food and industrial applications, based on theoretical investigations.

The interpretation of the adsorption behaviour of carboxymethyl cellulose onto functionalized accurel polymeric surface was discussed in this chapter. The polypropylene (PP) (Trade name-Accurel) inactive material was dried for 24 hrs under vacuum. To get functionalized accurel (FA), the dried PP was treated with an oxidizing solution containing a 1:1:2 (by weight) mixture of H_2SO_4, CrO_3, and double-distilled water; in the 500 ml volumetric flask with a thermometer [22]. After the treatment for 5 min, the new adsorbent (FA) was obtained from the slurry under stirring (30 ppm) at atmospheric pressure and 70°C, on a thermostat. The sample was washed first with double distilled water and then with acetone and finally, the MPP was ground and passed through a 100 mesh sieve and stored in a desiccator for further use (Figure 5). The physiochemical parameters of FA such as specific surface area (S_{BET}) =34.472 m^2/g, pore volume (Vp) =0.07-0.121 cm^3/g, total pore volume (Vtp) = 0.115 cm^3/g, mean pore diameter = 13.692nm and pore diameter =39.402nm determined by BET analysis. The particle size and pXRD studies confirmed that FA possessed mesoporous and crystalline nature, respectively. It was found that the adsorption of CMC on FA affected by the change of various factors like the initial concentration of CMC, dose of FA, pH, ionic strength (0.1mol/L), temperature (℃), presence of urea (0.1mol/L) and sonication (20 kHz).

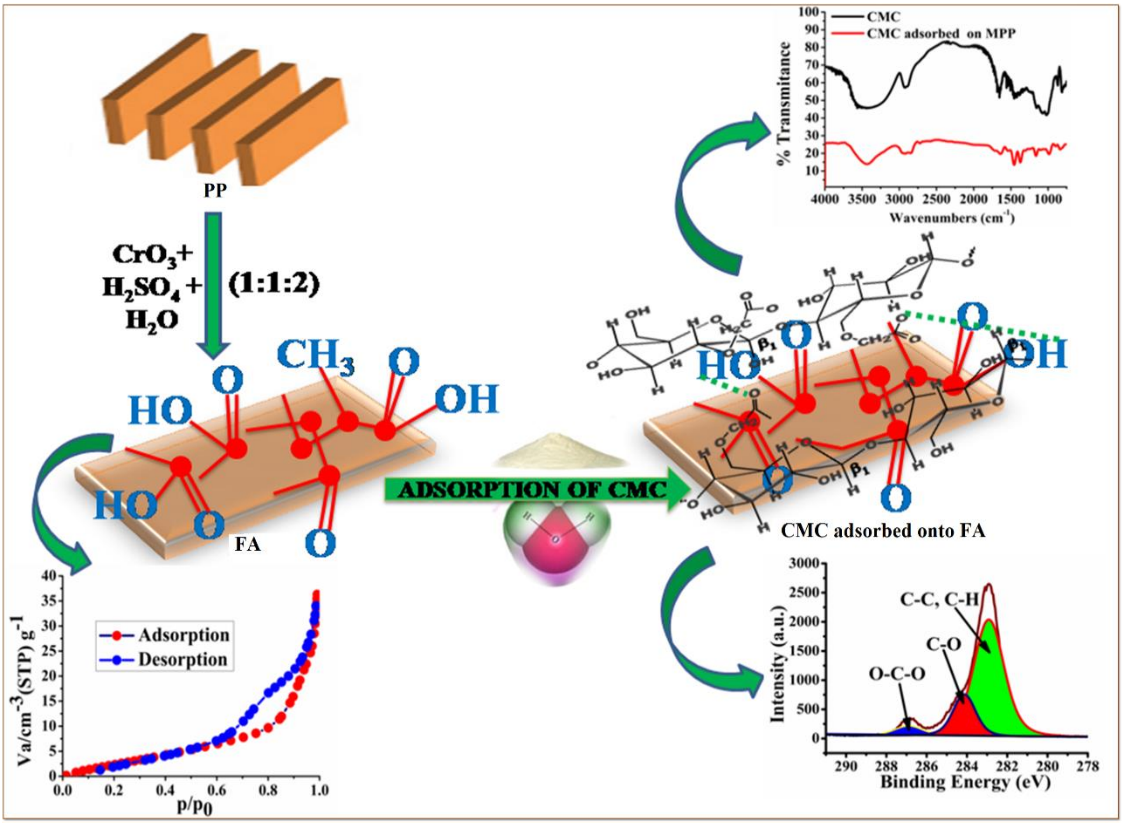

Figure 5. Graphical abstract of synthesis of FA and adsorption of CMC onto it

These observed results concluded that the non-covalent force played a significant role in the binding of CMC at FA/water interfaces. The results obtained from the FTIR analysis provided useful information on spectral changes which are attributed to hydrogen bonding between CMC and FA as evidenced by changes in the IR frequencies of some main functional groups -OH, C=O, C-O, C-H, and –COOH in which the C–O stretch coupled to the C–C stretch and O–H deformation which were significant and thus supports strong hydrogen bonding of CMC on FA surface. The effect of urea and sonication during adsorption of CMC onto FA confirmed that the amount of adsorption of CMC onto FA was reduced significantly and suggested that the hydrogen bonding is a predominant force responsible for the occurrence of adsorption of onto solid surface rather than hydrophobic force.

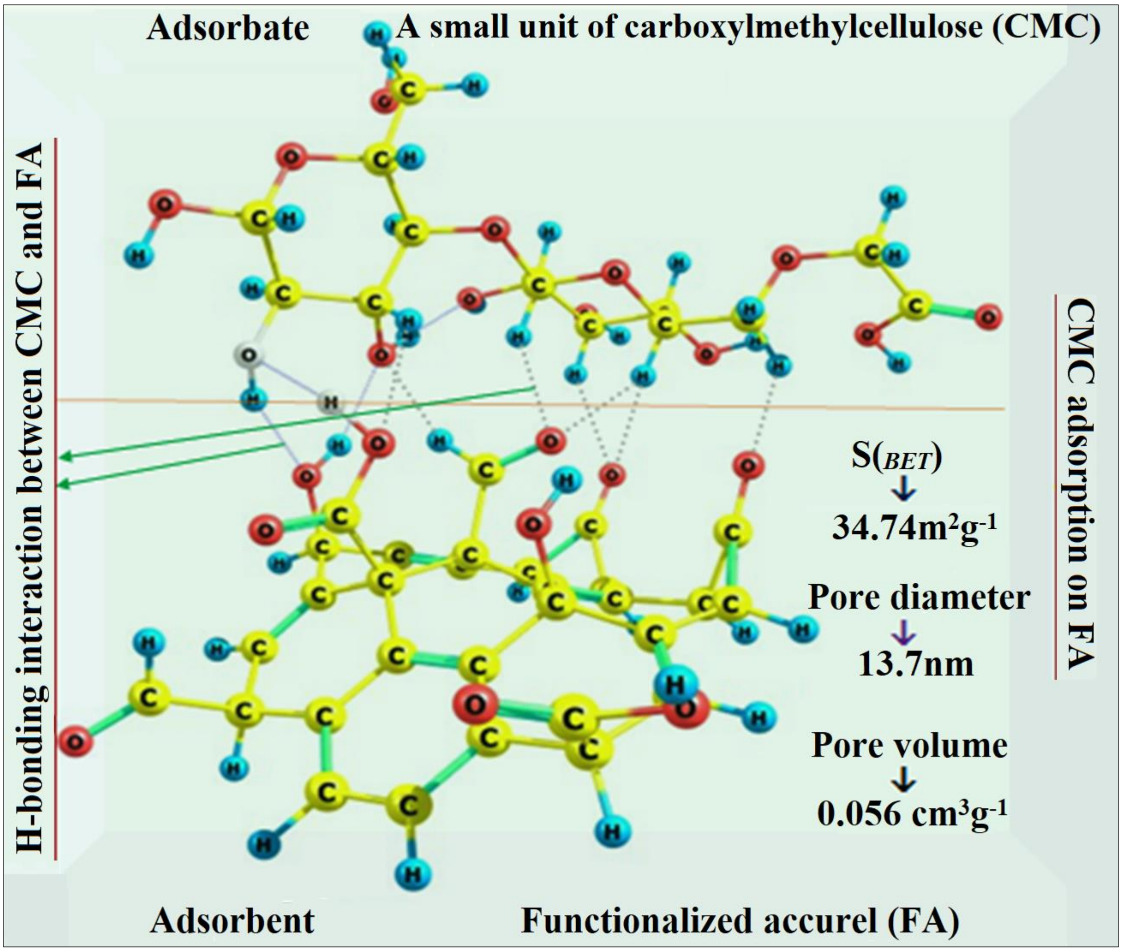

Figure 6. Theoretical graphical interaction between CMC and FA

The batch shaking adsorption experiments with various parameters were tested and the equilibrium isotherm data were fitted with Freundlich, Langmuir, Temkin and Jovanovic model of adsorption and compered by linear regression coefficient (R^2) which obeyed the order as Langmuir (R^2=0.9933)> Freundlich (R^2=0.9830)>, Temkin (R^2=0.9428)> Jovanovic (R^2=0.8667). The adsorption free energy of CMC is close to that of physical adsorption suggesting H-bonding to be a dominant force for polysaccharide (L2 type) adsorption. XPS analysis illustrated the binding of -OH groups available onto FA surface much interacts with carboxylate ions of the CMC and confirmed that the hydrogen bonding is responsible for the occurrence of the adsorption. Thus, the present study provides substantial evidence to prove beyond doubt that adsorption of CMC onto FA surface governs by hydrogen bonding and other weak non-covalent interactions. Moreover, the theory-based quantum mechanical calculations provided a better understanding of the adsorbate – adsorbent binding features and to understand better such molecular agglomeration systems

(Figure 6**)**, this model could overlay a new insight to explore the adsorption aspect of CMC onto solid surfaces.

Chapter 5 deals with the physiochemical aspects for the adsorption behaviour of sodium carboxymethylcellulose onto mesoporous granular fine quartz (MGFQ) from its aqueous solutions (Figure 7). The MGFQ was successfully prepared from supplied granular fine quartz earlier reported method. Briefly, the supplied granular fine quartz was washed using double distilled water and dried in an oven at optimized temperature (120°±2C) for 2-3h to remove all the volatile impurities and undesired impurities present on the surface. After drying, the sample was sieved to obtain the uniform size and kept in a desiccator for further characterization and experimental use. After in-depth characterization of this material results confirms its mesoporous nature, now it was termed as mesoporous granular fine quartz (MGFQ).

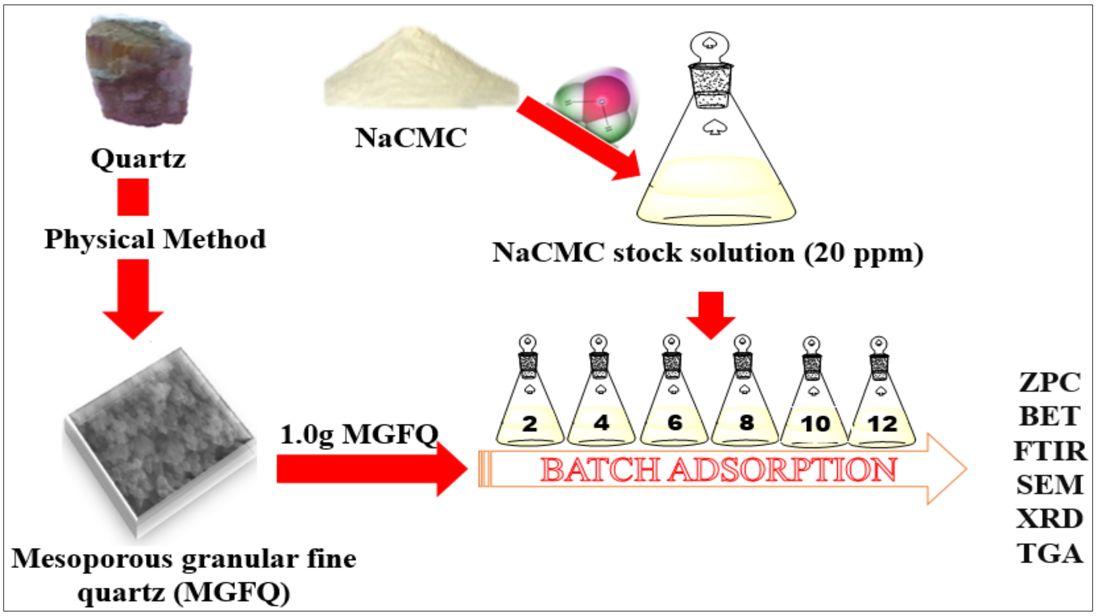

Figure 7. Graphical abstract for synthesis of MGFQ and the adsorption behaviour of NaCMC onto it from their aqueous solutions

The physiochemical characterizations (Table 1) and experiments confirm that MGFQ has very efficient potential adsorptive properties (Table 2). It was observed that the adsorption of NaCMC on MGFQ remarkably affected by the change in adsorptive optimized conditions such as pH, ionic strength, and sonication and presence of alcohols**.** These observed results concluded that hydrogen bonding plays a significant role during the adsorption. The FTIR spectral changes that appeared nearby 1104

cm^{-1} and 1076 cm^{-1} provided sufficient evidence to confirm strong hydrogen bonding responsible for the occurrence of adsorption of NaCMC onto activated kaolin. The chemical structure of NaCMC was relatively open and has low steric effect for interaction with the functional groups present on MGFQ. The adsorption mechanism was associated with hydrogen bonding between active chemical functions of MGFQ (Si-O-H) and carboxylates ions of NaCMC. These Si-O-H localized active sites bind with the carboxylate ion of NaCMC to form hydrogen bonding. In the aqueous system, carboxylic functions of NaCMC developed affinities with most of the Si-O-H of the MGFQ. The adsorption of NaCMC on adsorbent was a result of the interaction of Si-O-H and carboxylate ion of the adsorbate. However, adsorbent being porous assists to enhance the surface area which provides the more active sites on the adsorbent. More active sites on the adsorbent (MGFQ), there could be more interaction between Si-O-H of MGFQ and –COOH groups of NaCMC. Experimental data of the present work were excellently fitted to the Freundlich equation since the regression analysis gave high correlation coefficients $R^2>0.99$, as shown in Table 2. The adsorption models were computed and the correlation coefficient (R^2) obeyed the order as Freundlich ($R^2=0.9830$)> Langmuir ($R^2=0.9933$)>Temkin ($R^2=0.8663$)>Jovanovic ($R^2= 0.9428$). Thus, these physicochemical adsorption aspects of NaCMC onto MGFQ provides substantial evidence to prove beyond doubt that adsorption mainly occurs *via* hydrogen bonding followed by some electronic interactions.

Chapter 6 deals with the interpretation of the adsorption behaviour of polymers namely cellulose (CL), sodium carboxymethylcellulose (Na-CMC) and hydroxyethylcellulose (HEC) onto kaolin activated by physical method (Figure 8). This study demonstrated that activated kaolin was prepared from supplied kaolin only by one physical step and utilized to adsorption for HEC, CL and Na-CMC. The physiochemical characterizations and experiments confirm that activated kaolin has very efficient potential adsorptive properties. It was observed that the adsorption of polymers on activated kaolin remarkably affected by the change in adsorptive optimized conditions such as concentration, dose, pH, contact time and temperature.

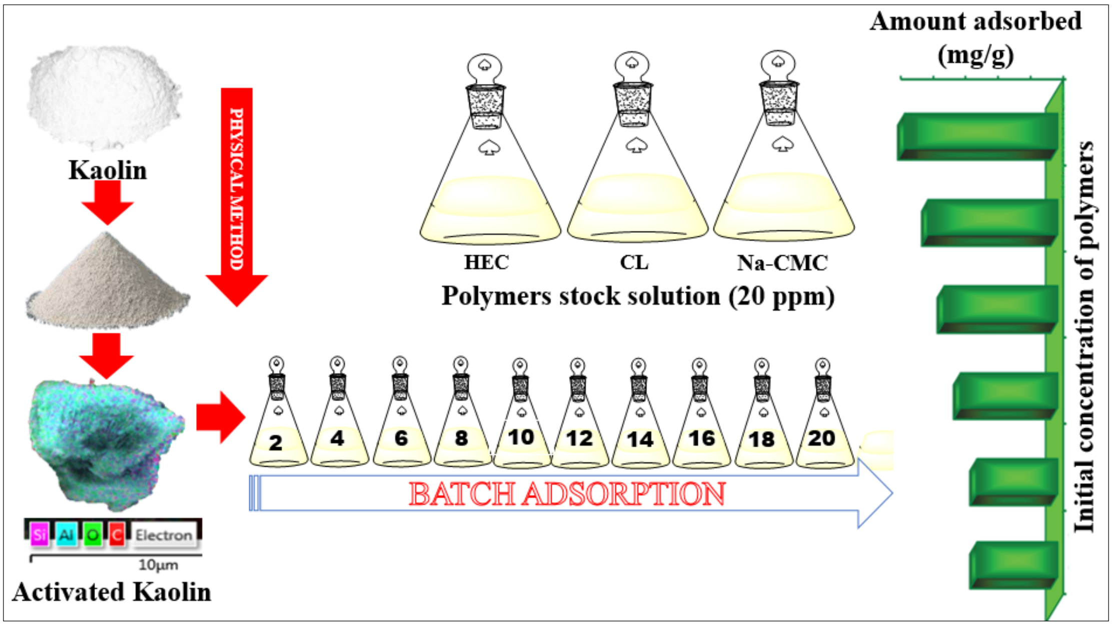

Figure 8. Graphical abstract showing adsorption behaviour of HEC, CL, Na-CMC onto activated kaolin

The adsorption of aforesaid polymers shows some remarkable shifting in Si-O stretching at bands 1114 and 694 cm^{-1} which may be attributed to the formation of new hydrogen bonds between Si-O of activated kaolin and carboxylate ion of Na-CMC, hydroxyl ion of CL and HEC. The chemical structure of Na-CMC was relatively open and has a low steric effect for interaction with the functional groups present on activated kaolin rather than HEC and CL. The adsorption mechanism governed by hydrogen bonding between active chemical functions of activated kaolin (Si-O-H) carboxylates ions of Na-CMC. These Si-O-H localized active sites bind with the carboxylate ion of Na-CMC to form hydrogen bonding. In the aqueous system, carboxylic functions of Na-CMC developed affinities with most of the Si-O-H of the Na-CMC. The adsorption of Na-CMC on activated kaolin was a result of the interaction of Si-O-H and carboxylate ion of the adsorbate. However, adsorbent being a porous assist to enhance the surface area which provides the more active sites on the adsorbent. More active sites on the adsorbent, there could be more interaction between Si-O-H of the adsorbent and –COOH groups of Na-CMC. However, for HEC and CL, such interactions were not observed significantly. Experimental data of the present work were excellently fitted to the Langmuir equation since the adjusted R^2 gave high correlation coefficients R^2>0.99. Thus, this exploration of adsorption behaviour of aforesaid polymers onto activated kaolin provides substantial evidence to prove beyond doubt that adsorption mainly occurs *via* hydrogen bonding followed by some electronic interactions.

Chapter 7 gaves an overall summary of the present work. The adoption of polymers such as cellulose, carboxymethylcellulose, sodium carboxymethylcellulose and hydroxyethylcellulose onto various adsorbents (mesoporous mustard carbon, functionalized accurel, mesoporous quartz and activated kaolin) were conducted employing FTIR, ATR-FTIR, SEM, EDX, EMA, PXRD, BET, XPS, TGA, AHIU, ZPA and UV-Vis techniques. The mesoporous mustard carbon (MMC) was derived from the mustard cake by chemical method. The BET analysis revealed that MMC had a specific surface area (S_{BET}) of 16.576 m^2g^{-1}. The electrokinetic measurements indicated that the MMC interface was negatively charged at ZPC value 9.8 which favoured CMC adsorption at a specific pH value (pH=3.0). The adsorption free energy of CMC was found as -22.561 $kJmol^{-1}$ which was in close agreement with H-bond energy revealing hydrogen bonding to be a dominant force for CMC (L2 type) adsorption. The optimized titled model, adsorbent-adsorbate complex (MMC-CMC) as considered in the theoretical study, is structured by mild to moderate noncovalent (intra- and intermolecular) interactions to assess the intermolecular interaction(s) between the MMC and CMC and was stabilized by these interactions. Based on binding energies (BEs), the FMO-based HOMO-LUMO gap, natural population analyses, the Bader's QTAIM-based parameters, and a recent measure reported recently as hydrogen bond strength based on interaction coordinate (HBSBIC) with the deployment of computational B3LYP and M06-2X using 6-31+G basis set, the structural, stability, electronic, and charge transfer features were described.

The binding aspects of CMC to functionalized accurel (FA) prepare from polypropylene-based accurel (MP1001) was also investigated. For the functionalization of accurel (MP1001) oxidation method was adopted. The BET study was used to evaluate the physicochemical parameters of FA, such as specific surface area (S_{BET}) =34.472 m^2/g, pore volume (Vp) =0.07-0.121 cm^3/g, total pore volume (Vtp) = 0.115 cm^3/g, mean pore diameter = 13.692nm, and pore diameter =39.402nm. The equilibrium isotherm data were fitted with Freundlich, Langmuir, Temkin, and Jovanovic models of adsorption and compared by determination coefficient (R^2), with Langmuir (R^2=0.9933)> Freundlich (R^2=0.9830)>, Jovanovic (R^2= 0.9428)> Temkin

(R^2 =0.8663). The hydrogen bonding between the carbonyl group of CMC and functional groups (-OH) of FA in the regions 288-280 eV and 1772-1676 cm^{-1} was verified by IR and XPS changes before and after adsorption, respectively. A theoretical model was used in this report to explain the type, nature, and intensity of interaction(s) involved in the adsorbent-adsorbate complex (FA-CMC). The geometric, stability and electronic feature studies have been conducted using the optimised structure, binding /interaction energy, HOMO-LUMO gap, natural population analyses, and Bader's quantum theory of atoms in molecules (QTAIM) related parameters with the deployment of the DFT dispersion-corrected (DFT-D) and DFT approaches. The molecular electrostatic potential surface (MESP) map was used to find the reactive sites of the above entities. The binding aspects of the adsorbate (CMC) onto the polymeric surface of the adsorbent FA were exercised through CMC aggregation stabilized by H-bonding and other weak noncovalent interactions.

Further, the mesoporous granular fine quartz (MGFQ) was derived from quartz by physical method. The MGFQ was utilized for the adsorption of NaCMC from its aqueous solution employing several aforesaid characterization techniques. The physiochemical parameters of MGFQ such as specific surface area (S_{BET}) =11.34 m^2/g, pore volume (Vp) =0.09 cm^3/g, total pore volume (Vtp) = 0.09 cm^3/g, mean pore diameter =32.52 nm were determined. The TGA analysis revealed that NaCMC could be used for adsorption at optimized temperatures (251°C). The equilibrium isotherm data were computed employing the Langmuir, Freundlich, Temkin and Jovanovic models of adsorption and compared by linear determination coefficient (R^2). The computed R^2 values obeyed the order as Freundlich (R^2=0.9984)> Langmuir (R^2=0.9194)>Temkin (R^2 =0.8899)>Jovanovic (R^2= 0.8709). The infra-red spectral changes in the region 1104 cm^{-1} and 1076 cm^{-1} associated NaCMC adsorption onto MGFQ which was stabilized by H-bonding and some other weak noncovalent interactions depending on the solution optimized conditions.

Furthermore, the adsorption behaviour of three polymers such as cellulose (CL), sodium carboxymethylcellulose (Na-CMC) and hydroxyethylcellulose (HEC)) onto activated kaolin was conducted. The activated kaolin was derived from supplied kaolin by a physical method and characterized by various characterization techniques. The specific surface area (S_{BET}) of activated kaolin (AK) was S_{BET} =18.57 m^2/g. The electrophoresis measurements at pH 7.0 revealed that activated kaolin possesses a positive surface. Moreover, the experimental data were computed employing several isotherm models such as Freundlich, Langmuir, Elvoich and Halsey for the adsorption of CL, Na-CMC and HEC onto activated kaolin from aqueous solutions. The adjusted R^2 values suggested the results were in favour of the data collected from the adsorption experiment. The equilibrium data of CL, Na-CMC and HEC onto activated kaolin was found to best fit the Langmuir equation since the adjusted R^2 gave high correlation coefficients R^2>0.99 than HEC and CL.

These studies confirmed that the mechanism of adsorption of aforesaid polymers onto various solid surfaces was attributed to the hydrogen bonding. The result of the present study could be extended to systems of significant importance. Finally, the alternate adsorbents have been used for explaining systematic understanding of the binding mechanism of CDs. They will not only be beneficial for the industries but also the surrounding environment from the potential toxicity caused by inorganic dispersant and depressants (used in mineral processing). Thus, the use of studied adsorbents may contribute towards the sustainability of the environment also. Undoubtedly, adsorbents used in this study for the adsorption of CDs could offer a lot of probable benefits for the future prospectus.

Appendices

Appendix-I includes a list of all publications

Appendix-II consists of national, international, conferences, congress, symposia, conventions/ webinars and workshops

Appendix-III includes the prestigious honours, recognitions and awards

Appendix-IV consists of plagiarism report

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