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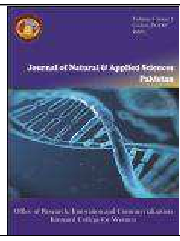

Applications of Chemically Modified Cellulose Filter Paper: A Review

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Abstract

Today, the chemically modified filter papers are used for the advanced and efficient research purpose as these filter papers have number of application. Especially they are used for the removal of heavy metals from the environment. Cellulose is one of those adsorbent that exists in high abundance, low cost and it is easily modified chemically. There are two approaches to the modification of cellulose first by direct chemical modification and second by the grafting approach in which a suitable polymer is exchange. The interconnected porous microstructure is present in cellulose paper that derived from pulp fiber layered networks. It can be chemically modified by the cellulose OH^- groups to offer catalytic function. The cellulose-g-GMA- imidazole used by the current study showed a relatively strong Cu(II), Pb(II) and Ni(II) adsorption capacities of 68.5, 71.9 and 45.2 mg g-1 as compared to other studies. Hence, the material used in the study can be favorably described as mid-range in terms of Pb(II) uptake relative to the other adsorbents. It is concluded that application of modified filter paper can be increased due to the success of its application majorly in the area of heavy metal removal.

1. Introduction

Filter paper is the basic material used for the filtrations purpose in almost every research. Today, the chemically modified filter papers are used for the advanced and efficient research purpose as these filter papers have number of application. Especially they are used for the removal of heavy metals from the environment. Advancement in the field of research equipment has been taken place with the passage of time especially nanotechnology has opened new pathways for more accurate and efficient research.

Nanotechnology is the new approach used in almost every field to enhance the treatment practices, it is also been used in every technology to deal with the component at very miniature level and treating the cause at the root. Integration of nanotechnology, mechanical and physio-chemical approach has created new pathway for the development of analytical technologies [1].

Before the development of the chemically modified filter paper multiple procedures were done to obtain the desired filtrate or the desired solvent. The time on other procedural application was also wasted but due to the modification of the filter paper many procedure were eliminated e.g. the multiple filtration procedure reduced to single filtration process and the efficiency and credibility of the research set the new standards for future research. The development of chemically modified filter paper also enhanced the research quality along with that many environmental remediation techniques were also applied due to its invention [1].

Due to global industrialization the pollution of heavy metals has increased rapidly. The release of heavy metals from industrial as well as domestic processes has become a source of pollution in terrestrial and aquatic environment. Contact with heavy metals causes number diseases in humans such as kidney impairment, behavioral changes, and anemia, damage to reproductive system, lower the immunity, damage to gastrointestinal tract and cognitive impairment. In recent years the researchers aimed to develop new low cost adsorbents from renewable resources for adsorption of heavy metals. Cellulose is one of those adsorbent that exists in high abundance, low cost and it is easily modified chemically. There are two approaches to the modification of cellulose first by direct chemical modification and second by the grafting approach in which a suitable polymer is exchange [1-2].

Another principle of the chemically modified filter paper is that it is also developed to be an antimicrobial material and its development deal with the diseases cause by the microorganisms. After the continuous research antimicrobial biomaterial is developed based on polymers. Recently antimicrobial textile fiber has also gained attention because of its high efficiency and effectiveness. These antimicrobial fibers either kill the bacteria or prevent bacterial proliferation ultimately, preventing bacteria to enter the human body [2].

2. Nanomaterial Functionalized Chemically Modified Cellulose Filter Paper and its Environmental Applications

Cellulose paper has been utilized for many purposes i.e. for writing, packaging etc. but most importantly it was used as the filter paper for quite some time now. It is composed of cellulose fiber pulp of porous quality. This pulp is made up of two main components i.e. pendant hydroxyl (OH) groups along with the β-anhydroglucose units and the presence of these components allows the opportunity for the modification in it to increase its applications range. One of the environmental friendly points of cellulose filter paper is that it is biodegradable which leads to more research on it. Its application are already diverse but an addition can done by modifying its basic parameters of sizes, flow rates, retention time, chemically modifying the existing cellulose structure and treating its intrinsic properties [3].

Chemically modified filter papers are used for the analytical applications along with that nanomaterial are coupled with it to enhance its productivity. Nano-materials are composed of both organic and inorganic components [4]. A nanostructure defines the modifications as the size, elemental composition, oxidation shape or state, morphology enhances the catalytic, oxidation/reduction or optical properties [5].

Nano-materials which are used for the modification of the cellulose paper includes: (i) metals like platinum (Pt), silver (Ag), palladium (Pd) and gold (Au), (ii) carbon materials like grapheme, carbon nanotubes and quantum dots, (iii) metal-oxides which includes titania (TiO_2), iron oxides (Fe_2O_3), silica (SiO_2) and ceria (CeO_2) [6]. Nanomaterial integration with the cellulose fibers also results in addition to new properties of the cellulose paper which includes fluorescence, redo functions and catalytic anti-bacterial functions and conductivity. Along with that this integration also increases thermal and mechanical stability of the cellulose paper [7].

There are majorly two techniques by which the Nano-material is fabricated in devices or on the filter paper. One way if to interface the cellulose paper with the pre-synthesized Nano-materials and other is the in-situ synthesis. These methods are quite complex as the assembly of Nano-structure should be appropriate and characterized, along with that its attachment with the selected receptor; response and sensing should be accurate [7-8].

2.1 Modification of Cellulose Filter Paper

Modification of the cellulose filter paper is not only done by the changing in the structural composition of the paper but instead sometimes the destructive approach is used in order to develop more application of the cellulose paper [9].

Pyrolysis of the modified filter paper is done i.e. providing the temperature 1000^{o}C to it in the absence of oxygen to form a carbon rich material. This material is then used for the development of the electrode which is then decorated with the copper Nano-particles (CuNPs). These electrodes demonstrated more electrochemical signals for the detection of the glucose content in the chemical preservatives and dyes [10].

Ionic liquids can chemically modify the surface of cellulose filter paper. Whatman filter paper is derived from the lignocellulose biomass. They have higher tensile elasticity due to their cellulose fiber structure and modification in it can be done through the approach of surface chemistry i.e. immobilization of its nanoparticles and increase the functionality of the hydroxyl group of the filter paper. Zinc Oxide Nano-particles (ZnONPs) coating is done on the filter paper with the help of ultrasound approach to show antibacterial activity. Higher catalytic characteristics are obtained by modifying the filter paper and colliding it with the nanomaterial solution: Graphene Oxide (GO), Multi-Walled Carbon Nanotubes (MWCNT) and Iron Oxide Nanoparticles (Fe_3O_4NPs) [11].

2.2 Application of Chemically Modified Filter Paper for Environmental Detection

Cellulose Nano-materials are used for the electrochemical detection. For the detection of Hydrogen peroxide (H_2O_2) (in wastewater) Silver Nano-particles (AgNPs) electrode are used which have a coating of octylamine on it. Secondly, for the detection of Mercury (II) ions (Hg^{2+}) chemically modified filter paper Gold Nano-particles (AuNPs) are used. Sodium Borohydribe presence allowed the reduction of rhodamine B (RhB) [12]. The Gold Nano-particles (AuNP) filter paper acted as the remediation tool and toxic ion detection. Copper (Cu), Nickel (Ni) and Lead (Pb) are also detected by these techniques with certain modification of the filter paper [13].

3. Chemically-Modified Cellulose Filter Paper as a Microstructured Catalytic Reactor

Techniques for the catalytic conversion of several chemical substances have played important roles in many industrial processes like the conversion of energy, environment purification, and useful chemicals production. The escalation of resource, environmental and energy problems are the main reason for an urgent need of developing catalytic material of high-performance that can efficiently promote chemical reactions. For various chemical reactions, the most promising catalysts are metal-based catalysts like metal complexes and metal nanoparticles [14-15].

Usually, the filter paper is used for various purposes in daily life such as laboratories etc., and it is a cellulosic material. By using a low-cost and high-speed papermaking process, paper materials can be produced from cellulose pulp fibers. The interconnected porous microstructure is present in cellulose paper that derived from pulp fiber layered networks. It can be chemically modified by the cellulose OH^- groups to offer catalytic function [15].

3.1 Cellulose Paper In-Situ Modification with Functional Groups by Using Silane-Coupling Technique

Silane coupling is commonly used for functionalize inorganic material like alumina and silica [16-17]. The modification of cellulose with functional groups in the paper form by silane coupling has been reported in many previous papers [18-19]. For example: amine-modified paper was prepared by following three steps. First, in a mixture of ethanol/water 80/20 (v/v), 3-aminopropyltrimethoxysilane was added and hydrolyzed to make reactive silanol groups. In the second step, cellulose filter paper was dissolved in the obtained solution for two hours and after that, at 40 °C solvent was evaporated for three hours under reduce pressure. Lastly, at 110 °C the resulting paper was treated thermally for three hours [20].

For the methacrylate-modified paper preparation, instead of ethanol/water and 3-aminopropyltrimethoxysilane, acetic acid aqueous solution and 3-(trimethoxysilyl) propyl methacrylate were used. The filter cellulose papers treated with 3-(trimethoxysilyl) propyl methacrylate and 3-aminopropyltrimethoxysilane contained methacryloxy groups and amino groups, respectively, in which by silane-coupling process, the functional groups were effectively introduced in-situ into cellulose paper where condensation reaction between C-OH of cellulose and Si-OH of silane-coupling agents produce Si-O-C bonds [20]. Even after the treatment of silane-coupling, the cellulose filter paper retained its particular porous interconnected microstructure. Silane-coupling technique is a useful and facile technique for the functionalization of paper and it can be used to produce polymers like polyethylenimine (PEI) and many functional groups in cellulose paper [19].

3.2 Amine-Modified Paper for Knoevenagel Condensation

Because of the many functions of amino groups, including the ability to adsorb CO_2 [21] and metal ions [22] and catalytic activity [23], it has been used widely for various processes, therefore, amine-modified cellulose filter paper is expected to have number of applications. The most convenient and important reactions for the formations of C-C bond is the Knoevengel condensation between active methylene compounds and ketones or aldehydes in the base catalyst presence [24-25]. For the production of α-cyanocinnamic acid ethyl ether, the amine-modified paper can be used as a base catalyst for ethyl cyanoacetate and benzaldehyde Knoevengel condensation and it is an essential intermediate in the antihypertensive drugs production [25].

In one of the studies, Knoevenagel condensation process was performed as follows [19]. In the process, 1.7 mmol of ethyl cyanoacetate and 2.0 mmol of benzaldehyde were dissolved in the 10 ml mixture of water and ethanol. A piece of diameter 33 mm of PEI-modified paper or NH_2- was then dissolved in the solution. At 25^{o}C, the reaction was completed with constant stirring at 150 rpm. For the analysis of desired product (α-cyanocinnamic acid ethyl ester) concentration, the reaction solution was determined at a given time by using gas chromatography (GC). The reaction was also completed by using the original cellulose filter paper, liquid diethylamine and chitosan powder [14].

3.3 Immobilized Lipase on Methacrylate-Modified Paper for Non-aqueous Transesterification

Enzymes, like lipases, due to their excellent catalytic activities are known as green catalysts [26]. Out of many enzymatic reactions, in non-aqueous media, reactions like lipase-catalyzed transesterification are widely used in many useful chemicals production by organic synthesis [27]. Enzymes, like lipases, in non-aqueous media are usually unstable and can be easily deactivated and aggregated, thus, enzymes are commonly immobilized on several supporting materials, including carbonaceous materials, ceramics, silica and resins and polymers, to provide stability and reusability in non-aqueous solution and to facilitate isolation of product [28].

Simple lipases adsorption on hydrophobic supports because lipases have moderately high hydrophobicity though these interactions is an efficient immobilization approach [29-30]. For the continuous and efficient target chemicals

production, the structured supporting materials use has been widely investigated [31].
Another study was conducted in which immobilization on cellulose paper was performed by soaking the paper in phosphate buffer solution of crude lipase powder. In the solution of lipase, a piece of methacrylate-modified paper and original paper was soaked with continuous stirring at 23°C by an orbital platform shaker for 12 hours. The obtained paper was then completely washed with the solution of phosphate buffer for 3 hours at 150 rpm of stirring rate. Then the paper was dried at room temperature in a desiccator. On methacrylate-modified paper, lipase immobilization yield was approximately 95%; however the original paper was approximately 30%. Lipase efficient immobilization is enabled by cellulose paper modification with methacryloxy groups [32].
The chemically modified catalytic filter paper can easily be reused and fit several reactor configurations. Moreover, in continuous flow reaction systems, the paper-specific porous interconnected microstructure gives greater productivity than in batch reactions. The additional cellulose paper advantages include production of high mass and sustainability. Cellulose is both lipophilic and hydrophilic and it is highly stable in many solvents [19].

4. The Use of New Chemically Modified Cellulose for Heavy Metal Ion Adsorption and Antimicrobial Activities

Due to global industrialization the pollution of heavy metals has increased rapidly. The release of heavy metals from industrial as well as domestic processes has become a source of pollution in terrestrial and aquatic environment [33]. Contact with heavy metals causes number diseases in humans such as kidney impairment, behavioral changes, anemia, damage to reproductive system, lower the immunity, damage to gastrointestinal tract and cognitive impairment [34]. In recent years the researchers aimed to develop new low cost adsorbents from renewable resources for adsoption of heavy metals [35]. Cellulose is one of those adsorbent that exists in high abundance, low cost and it is easily modified chemically [36]. There are two approaches to the modification of cellulose first by direct chemical modification and second by the grafting approach in which a suitable polymer is exchange [37].
Antimicrobial material has been developed to deal with the diseases cause by the microorganisms [38]. After the continuous research antimicrobial biomaterial is developed based on polymers [39]. Recently antimicrobial textile fiber has also gained attention because of its high efficiency and effectiveness. These antimicrobial fibers either kill the bacteria or prevent bacterial proliferation ultimately, preventing bacteria to enter the human body [40].

4.1 Thermal Stability

The comparison for thermal stability between natural cellulose and chemically modified cellulose (DTD) was carried out. The results showed that natural cellulose has better thermal stability as compared to chemically modified cellulose. The initial decomposition for natural cellulose and chemically modified cellulose were 270 °C and 150 °C. Hence, DTD can be used as an adsorbent at 150 °C; this is because of breaking down of pyranose ring during reaction [41].

4.2 Scanning Electron Micrograph (SEM) Analysis

Scanning electron micrograph analysis was carried out over natural cellulose and chemically modified cellulose (DTD). The results showed the greater capacity of adsorption over DTD this is because of the porous surface that have high capacity to trap metal ions over it. Due to these cavities in morphology allow the metal ions such as copper ions and lead ions to penetrate into the surface. The analysis showed that greater is the surface area greater would be adsorption of metal ions till they reach the saturation point in an aqueous media [42].

4.3 Effect of Dose on Adsorption

The dose of DTD was varied between 5mg to 25mg in the present study. The results showed that as the dose increased the rate of adsorption of metal ions of Cu^{2+} and Pb^{2+} also increased. However it reached a saturation point at 20mg of dose of adsorbent any further increase beyond this value allowed no removal of metal ions [42].

4.4 Effect of pH value on Adsorption

pH of the solution effect the process of adsorption. It affects the protonation and deprotonation of functional groups present at the active sites in adsorbents. The capacity of adsorption increases as the pH increases up to 6 however beyond 6 the capacity of adsorption begins to decrease. The study highlights that at low pH i.e. below 2 the percentage of removal of metal ions is >70%. This shows that DTD could efficiently adsorb metal ions at lower pH, this is very important characteristic of DTD feasible to be used in industrial processes [42].

4.5 Antimicrobial Activity

The chemically modified cellulose was tested by standard disc diffusion method using E.Coli and S. aures microorganisms. The result showed that natural cellulose showed no activity against these microorganisms however, chemically modified cellulose showed antimicrobial activity against these microorganisms. DTD showed such response because of presence methyl benzalaniline pendent groups linked in the cellulose chain. DTD possess medicinal importance due to its antimicrobial property [42].

5. Removal of copper, nickel and lead from wastewater using a modified cellulose material: a comparison

Several heavy metals like lead, nickel and copper are dumped into the wastewater from different sources of industries which includes acid mine drainage [43], metallurgical industries [44], electronic industries [45], and electroplating [46]. Most of the concentration of heavy metals is absorbed by plants, but taking up higher concentration can lead to the adverse lethal effects [47-48]. There are number of technologies that are used for the removal of heavy metals form waste water through the process of chemical precipitation [36], process of ion-exchange [49] the membrane technology [50], and process of adsorption [51]. Adsorption is considered as the most widespread process which is flexible both in operation and design and it able to re-use the treated effluents. Presently there are number of research on the removal of heavy metals through the use of naturally occurring adsorbents. Examples of such materials include chitosan [52] and cross-linked chitosan [53] in the removal of Cu(II) and cross-linked starch gel [54] for the removal of Pb(II) from wastewaters. Crini [55], are used for the removal of heavy metals for waste water. Our work is about [56-57] alteration of cellulose in two step reaction.

5.1 Preparation of Cellulose-g-GMA-imidazoleUnder

Nitrogen atmosphere cellulose of about 0.5 g was placed in glass joining apparatus with the deionized water of about 30 mL at 30^0C. Cerium Ammonium of about 0.05 and 10mL of nitric acid were added in cellulose and were allowed to react for 15mins. Then we added Glycidyl methacrylate monomer of about 0.35M, and allowed to react for 2 hours. After this reaction the product Cell-g-GMA was removed and for 12 hours it was extracted with acetone for the removal of GMA homopolymer. Then at 60^0C Cell-g-GMA was dried, and reacted with imidazole of about 3.0 g with 3.0 g of cellulose-g-GMA fibres at 70^0C in 120 mL solution of dimethyl formamide. It was then filtered, cleaned with water, extracted with methanol for 6 hours and at 70^0C it was dried in vacuum [57].

5.2 Adsorption Isotherms

By dissolving proper amounts of copper (II) sulphate (Cu(SO4), 5H2O (lead(II)nitrate), or nickel(II)sulphate (Pb(NO3)2), NiSO4.6H2O (Merck, Germany) in deionized water, a variety of Cu(II), Pb(II) and Ni(II) (20–2000 mg dm-3) adsorption solutions were prepared. After removing 25ml aliquot from each flask, it was placed separately in a 50ml plastic vial along with 0.2g of the adsorbent cellulose-g-GMA-imidazole. After that, all the vials were sealed and later on placed in a temperature regulated water bath at 23^oC for either 120mins for Cu(II) and Pb(II) or 400mins for Ni(II). Afterwards, they all were centrifuged at 4,000 rpm for 15 minutes. 10 cm^3 of each supernatant, after being removed was appropriately diluted with de-ionised water and analysed by atomic absorption spectrophotometry (AAS) (Varian SpectraAA220). In order to ensure the reproducibility and accuracy, blank solutions holding corresponding preliminary concentrations of either Cu(II), Pb(II) or Ni(II) but devoid of any additional adsorbent were prepared and put through the same processes [56].

5.3 pH Studies

For the purpose of studying effect of preliminary solution pH on Cu(II), Pb(II) and Ni(II), adsorption onto cellulose-g-GMA-imidazole was studied at 23 ◦C. By dissolving suitable amounts of the sulphate salt of each metal in deionised water, a 1000 mg dm−3 stock solution was prepared [55]. After this, a 25 cm^3 aliquot of this stock solution was extracted and placed in each of six 50 cm^3 plastic vials along with adding 0.2 g of the adsorbent (cellulose-g-GMA-imidazole). In order to yield pH values that varied from 2 to 7, the pH of the solution in all the vials was adjusted. The process of adsorption was then conducted for 60 min for Cu(II) and Pb(II) and in case of Ni(II), the process was proceeded for 400 min. The level of metal adsorption was measured for all the vials analogously in accordance with the adsorption isotherms methodology [57].

5.4 Adsorption

The adsorption isotherms for uptake of Cu(II), Pb(II) and Ni(II) on the celluloseg-GMA-imidazole material, at 23°C. The uptake of Cu(II), Pb(II) and Ni(II) extended to the degrees of 68.5, 71.9 and 45.2 mg g-1 correspondingly. When adsorption approach was applied to the isotherm data, it showed a strong relationship amid the Langmuir approach and the uptake of each metal ion [57].

5.5 Influence of pH

The following figure demonstrates the impact of preliminary solution pH was demonstrated on the adsorption each metal onto cellulose-*g*-GMA-imidazole at room temperature and during the varied pH between 2 and 7 [57].

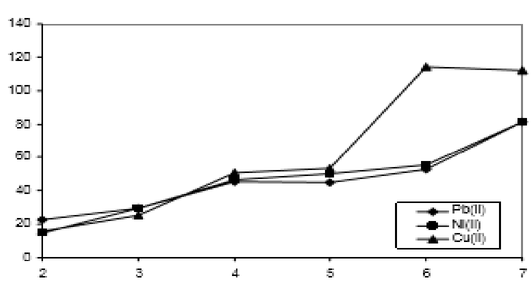

Fig 5.1: Influence of pH on metal uptake

The graph is divides into three regions; i.e. from pH 2 to 4, from pH 4-6 and from pH 5-7. In the first region, there clearly exists a competition for adsorption sites on the cellulose-*g*-GMA-imidazole amongst protons (H+) and the metal ions. There was a clear uptake of the metal ions that varied from 25-40%. The second region demonstrated a minimum influence of H^+ and maximum influence of Pb(II) and Ni(II). The last region showed a distinct increase in the uptake mainly due to the precipitation of Cu(II), Pb(II) and Ni(II) as their respective hydroxide species [55].

5.6 Kinetics of Uptake

In order to assess the kinetics of uptake, the effect of preliminary metal concentration on the rate of Cu(II), Pb(II) and Ni(II) uptake was measured. The equilibrium adsorption for Cu(II) and Pb(II) was attained within 40 min, whereas, Ni(II) uptake took considerably more time i.e. 400 minutes [53].

5.7 Regeneration of cellulose-g-GMA-imidazole

The degree to which adsorbed metal was recovered as compared to pH is demonstratedin below table. When metal loaded cellulose-g-GMA-imidazole sorbent was regenerated, varied results were observed [59]. With pH 1, there was a complete recovery of all metals. With increased pH value i.e. 2, there was a substantial drop in metal recovery and when the pH was further increased, the metal recovery continued to reduce more and more [54].

5.8 Comparison of Cu(II), Pb(II) and Ni(II) on alternative adsorbents

Table 4 shows the compares Cu(II), Pb(II) and Ni(II) uptake levels on the cellulose-g-GMA-imidazole material with the results of other research studies and is shown as follows. The cellulose-g-GMA-imidazole used by the current study showed a relatively strong Cu(II), Pb(II) and Ni(II) adsorption capacities of 68.5, 71.9 and 45.2 mg g-1 as compared to other studies. Hence, the material used in the study can be favorably described as mid-range in terms of Pb(II) uptake relative to the other adsorbents. Moreover, this material also demonstrated strong Ni(II) uptake as compared to the adsorbents used in other research studies [58].

6. Conclusion

Chemically modified filter papers are the future for the advanced research and many analytical technologies are also developed with their integration. Their major application includes the detection of heavy metal and their removal especially from the waste water. Application of modified filter paper can be increased due to the success of its application majorly in the area of heavy metal removal. It efficiency can be enhanced through the cellulose OH group or through the increase in the adsorption capacity of the modified cellulose filter paper. Along with the Nano-technology advancement the integration among this technique and filter paper modification has been taking place. This approach is aiding in separating the Nano-particles of selected criteria to filter easily. This technique will be effectively used in the wastewater treatment to gain clean water as we are going through the global crisis of water, this approach could be our savior. Hence this will help in making water clean for domestic purposes in the future on a large scale.

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Table 1: Recovery of adsorbed metals from Cellulose-g-GMA-imidazole.

pH	**1**	**2**	**3**	**4**	**5**	**6**
Cu(II)	96	28	12	10	9	9
Pb(II)	99	36	19	22	6	6
Ni(II)	100	34	16	14	13	14

Table no 2: Comparison of Cu, Pb and Ni on alternative base

Adsorbent	**Cu(II)**	**Pb(II)**	**Ni(II)**
Cellulose/Cysteine	22	28	8
Sawdust/Acrylic acid	104		97
Cellulose-g-GMA-Imidazole	68.5	71.9	45.2
Clinoptilolite	25.4	124	0.9
Chabazite	5.1	6.0	4.5
Chitosan	16.8	16.4	2.4
Cross-linked chitosan	62.5		
Cross-linked starch gel		433	