Decontamination of Manganese and Phenol from Aqueous Media by Sunflower Stems

Samir K.[a]; Ibrahim M. B. M.[b]; A. K. Sher[c]

[a] Pharmacy Department, University of Malakand, Chakdara, N.W.F.P., Pakistan [b] Biotechnology Department, University of Malakand, Chakdara, N.W.F.P., Pakistan [c] University of Malakand, Chakdara, N.W.F.P., Pakistan

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Samir K.,[1] Ibrahim M. B. M.,[2] and A. K. Sher[3]
[1]Pharmacy Department, University of Malakand, Chakdara, N.W.F.P., Pakistan
[2]Biotechnology Department, University of Malakand, Chakdara, N.W.F.P., Pakistan
[3]University of Malakand, Chakdara, N.W.F.P., Pakistan

Development of new economically feasible eco-friendly products from agricultural wastes for the removal of pollutants from water is the objective of many researchers. In this study, attempts have been made to use sunflower stems for the removal of Mn(II) and phenol from water. An ion-exchange resin was fabricated through the hydrolysis of graft copolymer of pretreated sunflower stem with acrylamide that was made by Fe^{2+}/H_2O_2 initiator. Factors affecting the grafting reaction, such as grafting time and temperature as well as initiator and monomer concentration, were studied. The hydrolysis under basic/acidic conditions was also studied. In addition to grafting, the charring of sunflower stem was studied at 400°C. Our results showed that the optimum condition for grafting was sunflower stem: monomer = 1:3, at 30°C, weight of $Fe^{2+}/2g$ bleached sunflower stem = 0.5g, and grafting time 2h. The maximum removal capacity for Mn(II) was found with the alkali and acidic hydrolyzed grafted sunflower stem, while the charred sunflower stem had the highest efficiency for removal of phenol from water.

Keywords: adsorption, grafting, manganese, phenol, sunflower stem

INTRODUCTION

The contamination of surface and ground water by various organic compounds as well as heavy metals due to the rapid development of chemical and petro chemical industries over the past several decades, which are difficult or impossible to remove by conventional biological treatment processes, led many researchers to identify effective and

inexpensive adsorbents for these contaminations. Phenol is a class of organics which is resistant to biodegradation and soluble in water [1,2]. In addition, one of the prevalent contaminates in water is metal ions that come from a wide variety of sources including abandoned hard rock and coal mines, highways and large parking-lot runoff, and the natural erosion of minerals. In natural conditions, iron and manganese mostly occur in the form of hydrocarbons, sulphates, chlorides, combinations with humus compounds and sometimes in the form of phosphates. In contact with air, these elements precipitate from water in the form of dark deposits, and water becomes turbid and dark brown.

The occurrence of these elements always creates some problems during water treatment. The occurrence of iron and manganese causes water-pipe networks to become overgrown. At much higher concentrations, both iron and manganese also have a negative influence on people and animals [3]. Although there are many methods for removing phenol and metal ions from aqueous solution, such as oxidation, precipitation, ion exchange, and solvent extraction, adsorption is a well-established and powerful technique for treating domestic and industrial effluents [4,5]. On the other hand, many organic materials exhibit ion-exchange properties. These include polysaccharides and carbonaceous materials such as cellulose and charcoal. Although they exhibit a very low ion-exchange capacity compared with synthetics, they are widely available at a very low cost and normally used as general sorbents, with their ion-exchange properties being a secondary consideration. For example, Roger found that tree bark can be used as a competitive adsorbent for removing substantial amounts of iron, aluminum and manganese from acidic coal mine drainage [6]. Mahvi et al. has used rice husk and rice husk ash for adsorption of phenol from aqueous solution [7].

As previously mentioned, the main limitations of natural organic ion exchangers are their low exchange capacity compared with other materials; they also are nonselective. To improve exchange capacity and selectivity, some naturally occurring organic ion exchangers are modified. For example, cellulose-based anion exchangers may be modified by the introduction of carboxyl, amino, or other functional groups [8,9]. So, the sorption parameters of natural materials can be modified by a chemical and/or thermal treatment too [10,11].

In Pakistan, sunflower is planted in four provinces. Its growing sites in Pakistan are Badin, Thatha, Mirpur Khas, and Umarkot Nawabshah in Sindh, and Sialkot, Bahawalpur, Vehari, Lodhran, Multan, Narowal, Rajanpur, and Layyah in Punjab. The area and production in 2005–2006 was 344.13×10^3 hectares and 595×10^3 tons, respectively [12]. In addition, sunflower stems are mostly used

in Pakistan for burning or heat-generating purposes, which releases large quantities of smoke, soot, ash and carbon dioxide into the air with detrimental environmental effects. Sunflower stem consists almost entirely of cellulose, hemicellulose (xylans, arabans, and poly-uronides) and lignin [13]. So, the biomass of sunflower stem can be used as a feedstock for the production of a variety of cellulose derivatives for various broader applications by chemical modification.

The aim of this study is to explore the possibility of the utilization of sunflower stems and their products for removing Mn(II) as well as phenol from aqueous solution. The selection of sunflower stem as a source of cellulose is due to sunflower being one of the principal sources of edible oils produced in Pakistan. The utilization of sunflower stem products as an adsorbent would solve both a disposal problem and also access to cheaper material for adsorption in water pollutant control systems. For these reasons the selection of sunflower stem for this study was bridging the economy and the environmental.

EXPERIMENTAL

Materials

Air-dried whole sunflower stems (SFS) were collected from Talash, Dir Lower NWFP, Pakistan, and were ground in a Wiley mill to pass a 4-mm screen. The constitutive analysis of this material is presented in Table 1.

Treatment of Sunflower Stem

Prehydrolysis

Acid hydrolysis of SFS was performed to remove as much hemicellulose as possible. 50 g of oven-dry SFS meal of known moisture content was weighed accurately and placed in a 1 L round-bottom flask. The sample was hydrolyzed in tenfold amount of HCl solution under reflux for 3 h based on the liquor-to-material ratio of 10:1. HCl concentration was calculated to be 10% of raw material. After hydrolysis, the SFS was washed by water to neutrality.

TABLE 1 Analysis of SFS and BSFS

Contents %	Wax and resin	Lignin	α-Cellulose	Hemicellulose	Ash
Sunflower Stem	4.7	28	33.9	26.1	9.2
Bleached Sunflower Stem	–	11.92	64.8	17.2	1.5

Alkali Treatment

Alkali treatment was performed under the same condition of prehydrolysis, using 18% NaOH based on the raw material in place of HCl, giving unbleached SFS (UBSFS).

Bleaching

5 g of dry UBSFS (with known humidity) was weighed and transferred to a 100 mL reagent bottle. Distilled water (95 mL), glacial acetic acid (0.5 mL) and sodium chlorite (1.0 g) were successively added. The reagent bottle was heated on a thermostatic bath adjusted to a temperature of 70–80°C, and stirred for 2 h. Then, additional glacial acetic acid (0.5 mL) was added, followed by sodium chlorite (1.0 g), and the reaction continued at the same range of temperature for more than 2 h. At the end of the second step, the flask was cooled. The content was filtered on a Büchner filter and washed with distilled water, giving bleached SFS (BSFS) [14].

Grafting

BSFS was grafted with acrylamide according to Gehui et al. [15]. About 2.0 g of BSFS and a certain mass of $FeSO_4 \cdot 7H_2O$ were added into a reagent bottle containing 40 mL of distilled water, stirred at ambient temperature for 15 min, filtered, and then washed with distilled water four times. The filter cake was put into the reagent bottle with the addition of certain weight of acrylamide and certain volume of H_2O_2, agitated, and kept at a certain temperature for a specific time period. The contents of the glass vessel were filtered after the reaction was over and washed with distilled water until the filter liquor was colorless and clean. The product was dried at 60–70°C, weighed, and extracted with distilled water [16] in a soxhlet device for 48 h to dissolve the formed homopolymer, giving grafted bleached SFS (GBSFS). The grafting parameters were calculated based on the following equations [17]:

$$\text{Graft yield \%} = \frac{B - A}{A} \times 100$$

$$\text{Graft conversion \%} = \frac{B - A}{D} \times 100$$

$$\text{Total conversion \%} = \frac{C - A}{D} \times 100$$

$$\text{Homopolymer formation \%} = \frac{E}{D} \times 100$$

$$\text{Grafting efficiency \%} = \frac{B - A}{C - A} \times 100$$

where, A is the weight of the original cellulose, B is the weight of the product after copolymerization and extraction, C is the weight of the product after copolymerization, D is the weight of the monomer, and E is the weight of the homopolymer.

Hydrolysis of the Graft Copolymer

Approximately 2 g of GBSFS was added into a 100 mL round flask containing 50 mL of 1.5% HCl or 1.5% NaOH water solution and refluxed for 2 h. It was then filtered and washed by distilled water until the pH of the filter liquor was about 7, and dried at 50–60°C giving AlHGSFS and AcHGSFS, respectively.

FTIR Spectra

BSFS, GBSFS, AlHGSFS, and AcHGSFS samples in KBr pellets were characterized by using Shimadzu Prestige -21 FTIR spectrophotometer.

Charring

Dried SFS was charred at 400°C for 3 h in a muffle furnace and then powdered, giving charred SFS (CSFS).

Adsorption

Mn(II) and phenol sorption experiments were carried out under batch conditions. The load was 1 g of dry sorbent/100 ml of solution. The adsorption was investigated at a room temperature by pouring metal or phenol containing solution onto sorbent in a tight reagent bottle. The contents were equilibrated on a horizontal mechanical shaker (IKA® AS 1301 USA) for 4 h at 400 rpm, then centrifuged at 4000 rpm for 10 min for phase separation. The supernatant was analyzed for the residual concentration of Mn(II), by persulfate method [18], or phenol by aminoantopyrine method [19], spectrophotometrically at 525 nm or 460 nm, respectively, using a UV-visible spectrophotometer (Nicolet evolution 300).
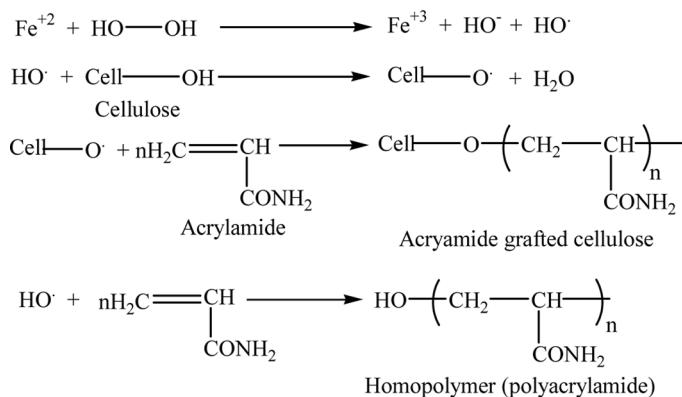
RESULTS AND DISCUSSION

Grafting

The free radical grafting of BSFS with acrylamide in the presence of $FeSO_4 \cdot 7H_2O$ is shown in Scheme 1 [20].

Effect of Initiator Usage

The effect of $FeSO_4 \cdot 7H_2O$ concentration on grafting parameters is gathered in Figure 1. Increasing the initiator concentration and

$$Fe^{+2} + HO\text{---}OH \longrightarrow Fe^{+3} + HO^- + HO^·$$

$$HO^· + Cell\text{---}OH \longrightarrow Cell\text{---}O^· + H_2O$$
Cellulose

$$Cell\text{---}O^· + nH_2C\text{===}CH \longrightarrow Cell\text{---}O\text{---}(CH_2\text{---}CH)_n$$
$$\quad\quad\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad CONH_2 \quad\quad\quad\quad\quad\quad\quad CONH_2$$
Acrylamide   Acryamide grafted cellulose

$$HO^· + nH_2C\text{===}CH \longrightarrow HO\text{---}(CH_2\text{---}CH)_n$$
$$\quad\quad\quad\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad\quad\quad CONH_2 \quad\quad\quad\quad\quad\quad\quad CONH_2$$
Homopolymer (polyacrylamide)

SCHEME 1 Free radical grafting procedure of cellulose with acrylamide.

increasing the number of grafling sites on the cellulose backbone, in the presence of monomer, induced grafting. Maximum grafting has been observed at $0.2\,g$ $Fe^{+2}/2\,g$ BSFS. Further increasing the concentration resulted in a decrease of the graft yield, because at higher concentration more Fe^{+3} ions are produced which act as the chain terminator [21]. By increasing the initiator concentration more than $0.2\,g$, the graft conversion and graft efficiency were slightly decreased,
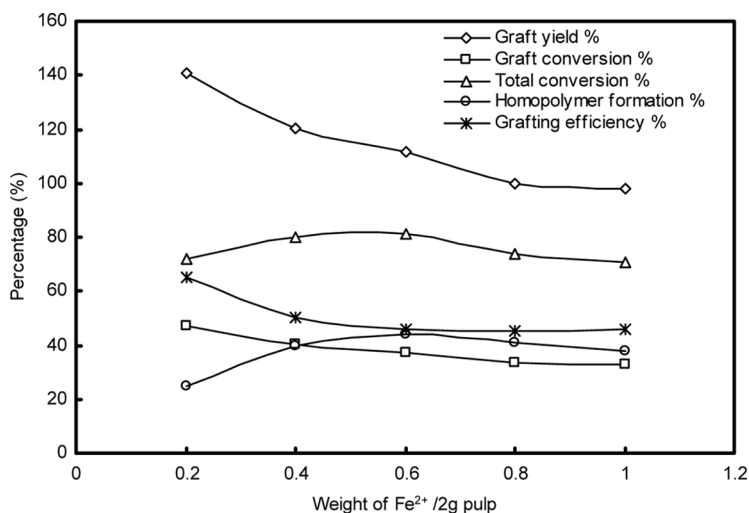

FIGURE 1 Effect of usage of Fe^{2+} on graft copolymerization of sunflower stem with acrylamide (Pulp:monometer $= 1:3$, grafting temp. $30°C$, grafting time $2\,h$).

but the polymerization % was slightly increased. This can be explained as increasing of the initiator more than 0.2 g caused a retardation of monomer diffusion through cellulose chains, accelerating the rate of termination. On the other hand, the increase in the initiator leads to initiation of many chains, which enhances the chance of mutual initiation of growing polymeric chains. These factors increase the formation of homopolymer and cause a fall in graft yield [22].

Effect of Usage of Acrylamide

Four different BSFS to monomer ratios (wt/wt), 1:1, 1:2, 1:3 and 1:4, were used to study the effect of monomer concentration on grafting parameters (Figure 2). The results show that as the monomer concentration increased from 1:1 to 1:4 there is an increase in graft yield. The initial rise in graft yield with monomer concentration is expected as there is a higher amount of the acrylamide available for copolymerization. But above 1:3 the excess monomer concentration did not result in graft copolymerization product. This is considered to be due to the fact that under a given initiator concentration, the available number of active sites for grafting is constant and the acrylamide molecules compete for the limited sites for grafting. Thus at high monomer
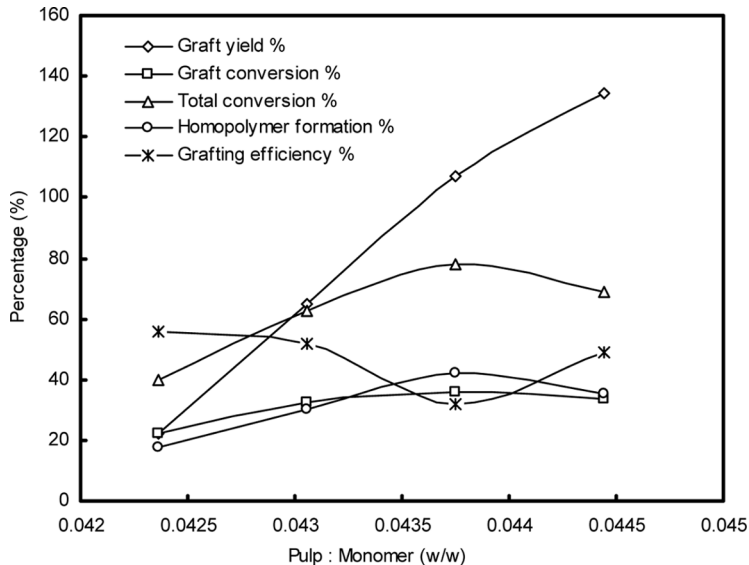

FIGURE 2 Effect of usage of acrylamide on graft copolymerization of sunflower stem with acrylamide (Weight of $Fe^{2+}/2$ g pulp $= 0.5$, grafting temp. $30°C$, grafting time 2 h).

concentration there is an excess of the monomer molecules relative to the available sites for graft formation hence more of the monomer molecules participate in homopolymerization. Figure 2 also shows that the graft efficiency decreased with increasing monomer concentration. This may be due to an increased formation of the homopolymer as the concentration of the monomer is increased. Even though the reaction conditions were chosen to maximize the formation of the copolymer, the formation of homopolymers may not be prevented. In addition, the fraction of the monomer that resulted in graft copolymerization is highest at low concentrations. At this relatively low concentration the few monomer molecules available are readily converted to copolymers. As the acrylamide concentration increased, however, more acrylamide forms homopolymers, resulting in lower conversion to the graft copolymer. This confirms an earlier observation that higher concentration of the monomer results in more molecules of the monomer being available to form the homopolymers [23].

Effect of Grafting Time

The duration of acrylamide grafting on BSFS varied from one-half h to 4 h. The results are shown in Figure 3. It is clear from the figure
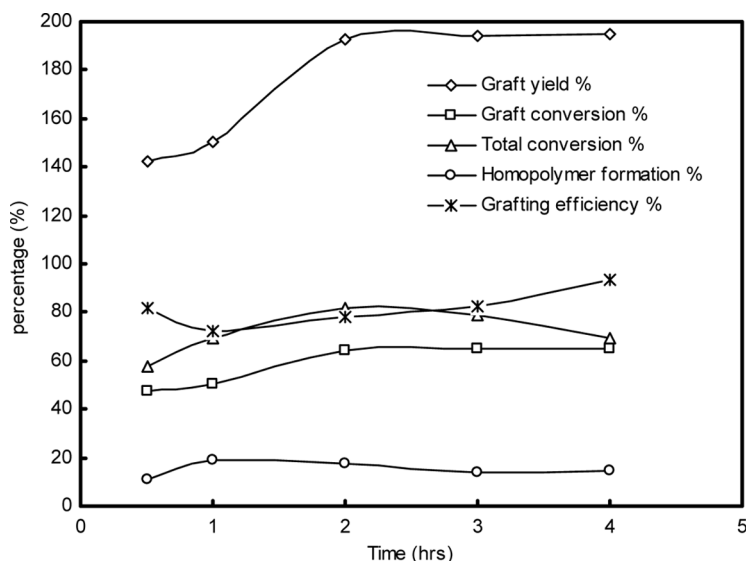

FIGURE 3 Effect of grafting time on graft copolymerization of sunflower stem with acrylamide (Pulp:monometer $= 1:3$, grafting temp. $30°$C, weight of $Fe^{2+}/2$ g pulp $= 0.5$).

that the grafting rate increases fast at initial up to 2 h and then slowed down with time and leveled off after 3 h. Also, homopolymer formation increases and levels off after 2 h. So, the grafting efficiency increases with increasing grafting time. This increase by increasing grafting time can be attributed to the swellability of cellulose, formation of free radical species and their subsequent reaction with cellulose to form macromolecules, as well as the mobility of acrylamide molecules and their collision with cellulose macroradicals for initiation of grafting.

Effect of Grafting Temperature

The grafting parameters of GBSFS with acrylamide at different temperatures (30–70°C) are depicted in Figure 4. The increased grafting by increasing the grafting temperature from 30 to 40°C is a direct consequence of enhancing diffusion and mobility of monomer within cellulose structure, the swelling of cellulose as well as the formation of active sites necessary for grafting. However, the decreased grafting by increasing the grafting temperature above 40°C can be attributed to the oxidation of free radicals which leads to termination of growing macroradicals.
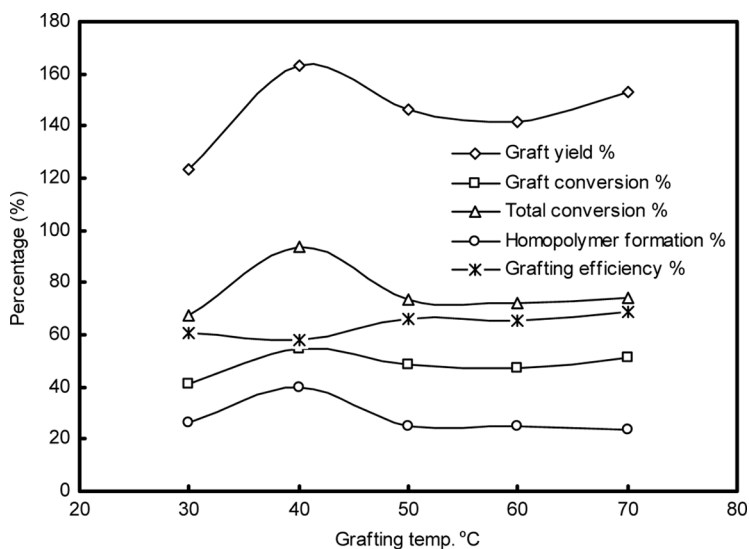

FIGURE 4 Effect of grafting temp. on graft copolymerization of sunflower stem with acrylamide (Pulp:monometer = 1:3, weight of $Fe^{2+}/2$ g pulp = 0.5, grafting time 2 h).
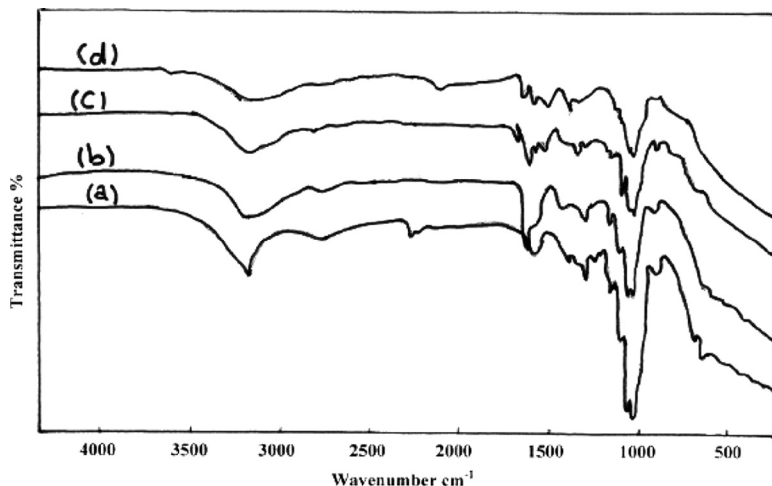
FIGURE 5 IR spectra of (a) BSFS, (b) GSFS, (c) AlGSFS, and (d) AcGSFS.

FTIR Analysis

Infrared spectra of BSFS, GBSFS, AlHGSFS and AcHGSFS are shown in Figure 5. The absorbency of different bands and IR specification of the same samples were measured (Table 2). The OH band at $3400 \, cm^{-1}$ was broadened by grafting. This indicates a reaction of acrylamide monomer with OH group of cellulose. In the same time, the spectrum of GBSFS showed a characteristic band at $1568 \, cm^{-1}$ which is peculiar to NH of $-CONH_2$ group [24] this band is absent in BSFS, thereby indicating the formation of polyacrylamide grafted cellulose. The intensity of this band decreased by hydrolysis, meaning a conversion of $-CONH_2$ to $-COOH$. Another proof is that the absorbance of C=O

TABLE 2 IR Specifications of BSFS, GSFS, AlGSFS and AcGSFS

Function group	Wavenumber (cm^{-1})	Absorbance			
		Bleached pulp	Grafted pulp	Acid hydrolysis	Basic hydrolysis
$-OH$	3400	6	4	4	2.4
$NH/-CONH_2$	1568	–	5.5	3.5	2
$CO/-CONH_2$	1650	2.5	7.5	2.7	1
$-C-O-C-$	1115	16	8.5	6.5	5
1650/1115%	–	0.16	0.88	0.78	0.20
$-COOH$	1715	–	–	1.0	1.5

of the amide group at $1650\,cm^{-1}$ [25] increased by grafting and decreased by hydrolysis. Also, the ratio of band intensity at wavenumber $1650\,cm^{-1}$ to that at $1115\,cm^{-1}$ increased by grafting due to the increase of incorporated $CONH_2$ group onto cellulose, while this ratio in HGSFS is less than that in GBSFS due to conversion of $-CONH_2$ to $-COOH$ which appeared at $1715\,cm^{-1}$. The relative absorbance of $-C-O-C-$ band at $1115\,cm^{-1}$ decreased by grafting and hydrolysis. This means that some degradation of cellulose occurred during grafting and hydrolysis.

Adsorption

Effect of Mn(II) Concentration on the Efficiency of Adsorbents

To evaluate the efficiency of adsorbents, solutions of different concentrations, namely 1, 5, 10, 20, and 30 mg/L, were used. The adsorption % and removal % of Mn(II) were achieved as presented in Figures 6 and 7, respectively. From Figure 7 it is seen that the removal % decreased with increasing Mn(II) concentration in case of all adsorbents, and the rate of decrease is higher when using SFS, UBSFS, and GBSFS than other sunflower products.

Low Mn(II) concentrations, namely 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 mg/L, were taken to study the efficiency at low concentrations
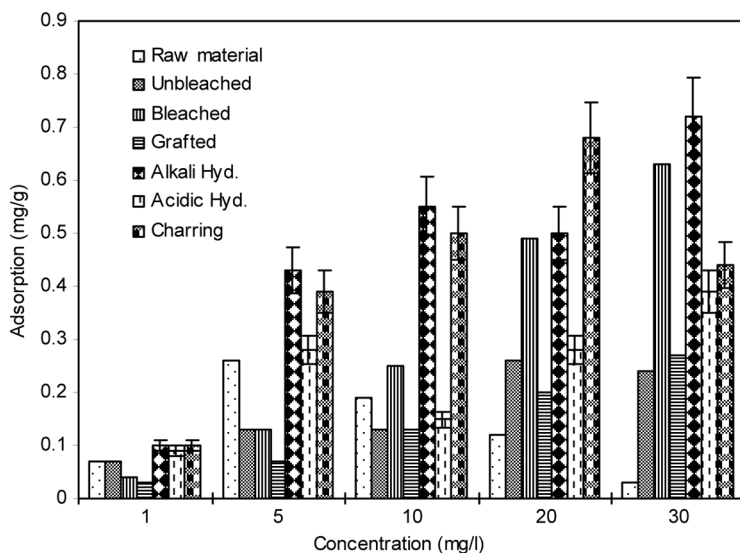

FIGURE 6 Adsorption of Mn by different materials. (mg/g = mg of adsopted Mn/1 g material).
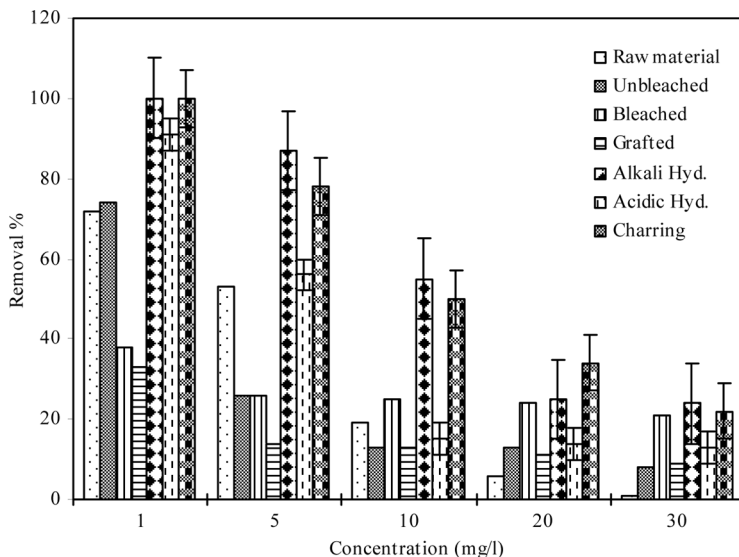
FIGURE 7 Removal % of Mn by different materials.

(Figure 6). From this figure it is seen that the highest adsorption appeared with AlHGSFS and AcHGSFS as well as CSFS. Also, the removal % decreased with increasing Mn(II) concentration and reached 87, 56, and 78% for AlHGSFS, AcHGSFS, and CSFS, respectively. But the actual amounts of Mn(II) adsorbed per unit mass of adsorbents increased with increasing Mn(II) concentration, from 0.05 to 0.435, 0.281, and 0.390 mg Mn(II)/1 g adsorbent when using AlHGSFS, AcHGSFS, and CSFS, respectively. It means that the adsorption is highly dependent on the initial concentration of Mn(II). At lower concentration the ratio of the initial number of Mn(II) ions to the available surface area is low so that the fraction adsorption becomes independent of the initial concentration. However, at high concentration the available sites of adsorption become fewer and hence the removal % of Mn(II) is more dependent upon initial concentration [26].

On comparing the adsorption efficiency of sunflower products under the same adsorption conditions and same Mn(II) concentration, AlHGSFS >CSFS >AcHGSFS. These results may be explained as follows: the hydrolysis of GSFS converts the amide groups into carboxylic groups, which is more drastic in alkaline medium than in acidic medium. Thus the available sites for the adsorption of ions (−COOH) is higher in AlHGSFS than in AcHGSFS, which is consistent with the FTIR analysis (Table 2 and Figure 5). The high efficiency of CSFS
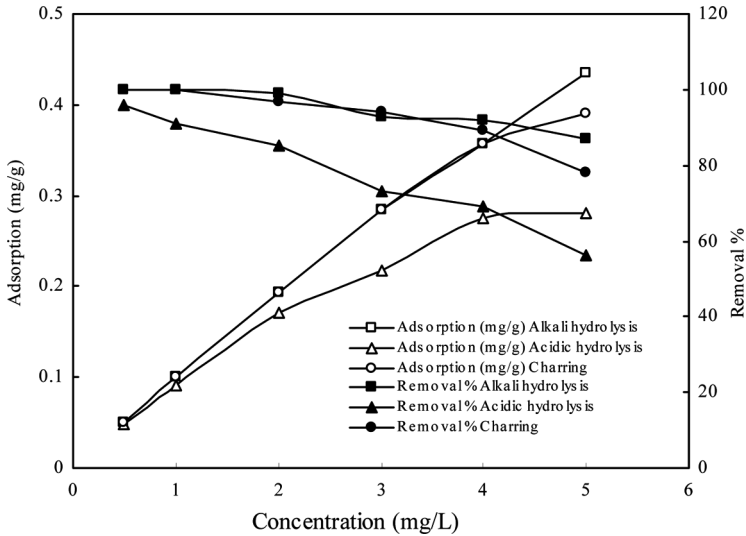
FIGURE 8 Adsorption of Mn (II).

may result from microporous structure, while the lower, adsorption efficiency of raw material and UBSFS is due to high content of lignin. The reason why some fibers have high ion-exchange capacity and some do not is not well understood at present.

Effect of Phenol Concentration of the Efficiency of Adsorbents

The adsorption and removal % of phenol from aqueous solution of concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 mg/L by SFS, AlHGSFS, AcHGSFS, and CSFS are presented in Figure 9. As can be seen from this figure, four adsorbent materials demonstrated different affinities for the adsorption of phenol from aqueous solution. While maximum adsorbed amounts, adsorbed by 1 g of SFS, AlHGSFS, and AcHGSFS, are 0.041, 0.05, and 0.037 mg phenol, respectively, it is 0.06 mg with CSFS. While the removal % decreased with increasing initial phenol concentration, the amounts of adsorbed phenol by 1 g adsorbents increased. The highest adsorbed amounts and removal % per unit mass of CSFS can be attributed to the greater specific area and the microporous structure of charred product compared with other products [27]. Also, the higher efficiency of HGSFS than SFS itself can be attributed to the decrystallization and increased amorphous phase by chemical treatment and hydrolysis, increasing the active surface area of the adsorbent.
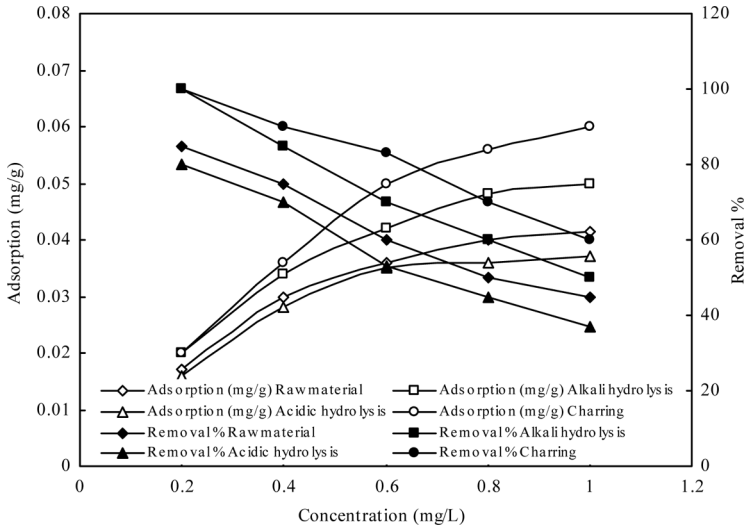
FIGURE 9 Adsorption of phenol.

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