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Potential use of bagasse and modified bagasse for removing of iron and phenol from water

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ABSTRACT

The potential of bagasse, chemically modified and thermally charring bagasse for iron and phenol adsorption were studied. Graft copolymerization of acrylonitrile onto cellulosic material derived from bagasse in heterogeneous medium can be initiated effectively with Fe^{+2}/H_2O_2. The effect of initiator and monomer concentration as well as grafting time and temperature were investigated. The grafted products were evaluated with FTIR and their iron and phenol adsorption from water.

The results obtained for both phenol and iron adsorptions were dependent on the nature of adsorbent, which had been changed according to the type of modification carried out on bagasse adsorbent. The extent of iron adsorption is less than that of phenol for all adsorbents and for certain adsorbent (phenol or iron) the ranking of adsorbent efficiency is charred > grafted > bleached > unbleached > raw material.

The results showed that the equilibrium data for iron and phenol-sorbent systems fitted the Freundlich model best within the concentration range studied.

1. Introduction

High cost of activated carbon and conventional adsorbent encouraged researcher to pay attention for alternative adsorbent produced from lignocellulosic materials.

Literature survey shows large number of alternative adsorbents to replace activated carbon. Both, the industrial wastes as well as some natural resource material such as, fly ash and coal, peanut hulls, rubber, peat, lignin, have been tested for this purpose. (Brown, Jefcoat, Parrish, Gill, & Graham, 2000; Eichenmuller, Bunke, Behrend, Buchholz, & Gotz, 1997; Srivastava, Singh, & Sharma, 1994).

Laszlo and Dintzis have shown that lignocellulosics have ion-exchange capacity and general sportive characteristics, which are derived from their constituent polymers and structure. The polymers include extractives, cellulose, hemicelluloses, pectin, lignin and protein. These are adsorbents for a wide range of solutes, particularly divalent metal cations (Kamel, Hassan, & El-Sakhawy, 2006). Sawdust and wood fiber have been used to remove cadmium, nickel or copper from aqueous solution (Acemiodglu & Alma, 2001; Min, Han, Skin, & Park, 2004; Shin & Rowell, 2005; Vaughan, Seo, & Marshal, 2001). Isolated Kraft lignin has been used to remove copper and cadmium (Verma, Swaminathan, & Subrehmnyam, 1990). Soybean hulls, sugar beet pulp and tea leaves have also been used to remove metal ions from water (Laszlo & Dintzis, 1994; Reddad, Gerente, Andres, Ralet, & Thibault, 2002). Peat moss has been largely used for adsorption of heavy metals and dyes from waste water due to its excellent ion exchange properties. It has been used for the purification of contaminated waste water and it had a good adsorbing capacity for heavy metals (Allen, Brown, McKay, & Flynn, 1992). Kenaf has been used for adsorbing toxic heavy metals, nickel, and copper from aqueous system (Allen, McKay, & Khader, 1988).

Cellulose can be modified to introduce a number of different functional groups such as carboxymethyl and amines, to which ions can bind either by chemical or physical adsorption (Nada & El-Wakeel, 2006). Bleached bagasse; carboxymethylated and hydrolyzed cyanoethylated bagasse pulp has been used to investigate the influence of metals incorporation with cellulose fibers. In another study, the adsorption of Cu(II) from aqueous solution was studied using oxycellulose and cationic oxycellulose as adsorbent (Kamel, Abou-Yousef, & El-Sakhawy, 2004). In addition to being the basis of traditional ether and ester derivatives, cellulose can be modified by cross-linking or by preparing so called graft copolymers. Grafting copolymerization onto cellulose induces physical changes, since the introduction of side chains leads to different structural characteristic in the raw material (Flaquie, drigo, & Ribes, 2000). By grafting polymer branches can be created to the cellulose backbone without destroying the desirable properties of the

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original cellulose fibers. Graft copolymerization has been applied to a number of cellulosic materials, including cotton, rayon, paper, cellophane, and wood. Grafting by monomers produce products have advantages over conventional ion exchangers due to chemical resistant, low cost of preparation and they also provide a large hydrophilic surface area (Chauhan & Lai, 2003; Gitisudhe, Prufulla, & Samal, 2005). Although cellulose can be grafted homogeneously using soluble cellulose derivatives or suitable solvents, grafting is usually performed in a heterogeneous system and is greatly influenced by the physical structure of the cellulose. The vast majority of grafting methods involve polymerization of vinyl monomers of type $CH_2{=}CH{-}X$ where X is an inorganic moiety, such as halide, $-CN$, $-NO_2$, or organic substituent.

The objective of this study is to explore the possibility of utilization of bagasse and modified bagasse for removing of iron as well as phenol from aqueous solution. The selection of bagasse for this study was based on low cost raw material and environmental impact.

2. Experimental

2.1. Materials

Bagasse (Ba) was obtained from a local vendor after extraction of juice, washed with water, air dried and then cut into small pieces. The raw material was in a Wiley mill to pass a 4-mm screen.

2.2. Prehydrolysis

Raw material (RM) was hydrolyzed with 2% H_2SO_4, based on the raw material, using liquor to material ratio of 15:1 under refluxed for 4 h.

2.3. Alkali treatment

The prehydrolyzed bagasse was treated with 5% NaOH under the same condition of acidic prehydrolysis giving unbleached bagasse (UBa).

2.4. Bleaching

Bagasse was bleached by 5% sodium chlorite (based on dry weight) and 0.5 ml glacial acetic acid with liquor ratio of 1:15 (wt:vol.) at 80 °C for 3 h and washed with distilled water (Browning, 1967). Bleached bagasse (BBa) of 68.7, 10.6, and 5.2 α-cellulose, hemicellulose, and lignin respectively was obtained.

2.5. Grafting

BBa grafted with acrylonitrile (AN) according to Gehui, Zhanqian, Zhifeng, and Liansheng (2002). About 2.0 g of BBa and a certain mass of $FeSO_4{\cdot}7H_2O$ were added into reagent bottle containing 40 ml of distilled water stirred at ambient temperature for 15 min, filtered, and then washed with distilled water for four times. The filter cake was put into the reagent bottle with the addition of certain weight of AN 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 and washed with distilled water until the filter liquor was colorless and clean. The product was dried at 60–70 °C, weighted, and extracted with distilled water in a soxhlet device for 48 h to dissolve the formed homopolymer giving grafted bagasse (GBa) (Abd-Alla, Mohamed & Hesham, 2007). The grafting parameters were calculated based on the following equations:

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

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

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

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

$$\text{Graft efficiency } (\%) = \frac{B-A}{C-A} \times 100$$

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

2.6. Hydrolysis of the grafted bagasse

GBa was hydrolyzed by 25 volume of 1.5% HCl or NaOH under reflux for 2 h giving acidic hydrolysis grafting bagasse (AcGBa) and alkali hydrolysis grafting bagasse (AlGBa) respectively.

2.7. Charring

Dried bagasse was charred at 400 °C for 3 h in a muffle furnace and then powdered giving charring bagasse (CBa).

2.8. FTIR spectra

IR spectra of KBr powder-pressed pellets were recorded on using Shimadzu Prestige-21 FTIR Spectrophotometer.

2.9. Adsorption

Iron 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 tight reagent bottle. The contents were equilibrated on a horizontal mechanical shaker (IKA® AS 1301 USA) for 4 h at 400 rpm, centrifuged at 4000 rpm for 10 min for phase separation. The supernatant was analyzed for the residual concentration of iron by persulfate method and for phenol by aminoantopyrine method spectrophotometrically at 525 or 460 nm respectively using UV–visible spectrophotometer (Nicolet evolution 300) (George, 1996).

3. Results and discussion

3.1. Grafting

Several redox systems have been used to generate free radicals on cellulose molecules to initiate copolymerization one of these is Fe^{2+}/H_2O_2 which releases hydroxyl radical through one-electron transportation as follows:

$$Fe^{2+} + HO{-}OH \rightarrow Fe^{3+} + HO^{-} + HO^{\bullet}$$

Hydroxyl radical initiates the graft copolymerization between bagasse and AN. Also it initiates the homopolymerization of AN monomers as in Scheme 1.

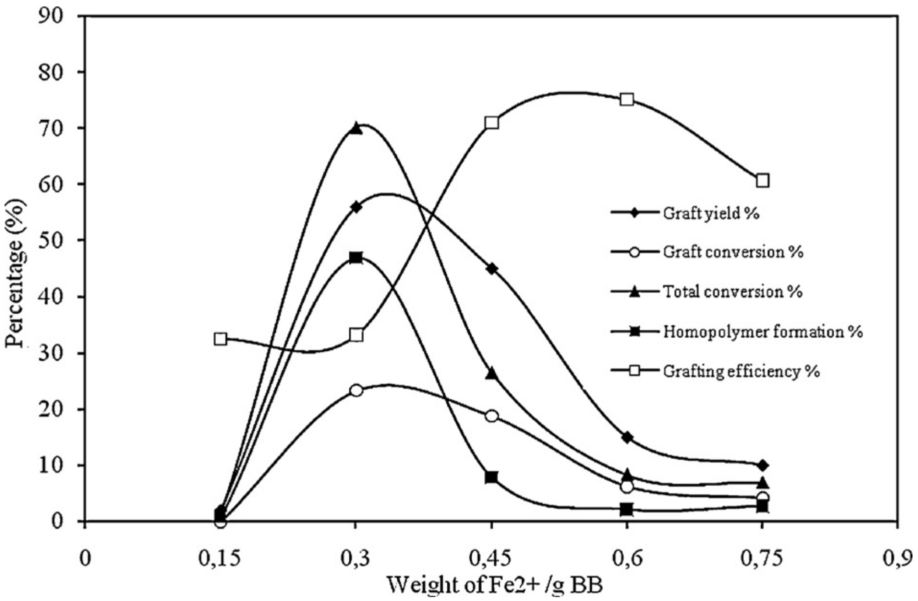


Fig. 1. Effect of usage of Fe^{2+} on graft copolymerization of BB with AN (BB:AN = 1:3, grafting temp. 30 °C, grafting time 2.5 h).

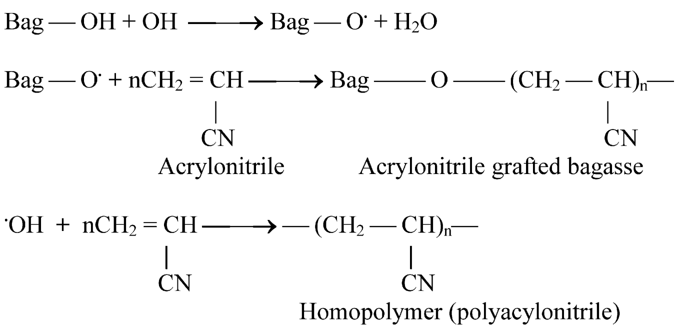
3.1.1. *Effect of initiator usage*

The molar ratio of initiator plays an important role in obtaining high grafting yield. To study the effect of initiator, the AN grafting of bagasse was carried out at 30 °C for 2 h with BBa to AN ratio 1:3 (g:ml) while initiator dose was varied from 0.15–0.75 g/g BBa.

From Fig. 1 it is clear that, the optimum ratio for the maximum graft yield, graft conversion, total conversion as well as homopolymer formation has been found to be at 0.3 g, while maximum grafting efficiency obtained at 0.45 g. Increasing the grafting with increasing the initiator concentration from 0.15–0.45 g refer to the formation of a large number of grafting sites which in the presence of monomer induced grafting. While increasing the initiator concentration beyond this limit lead to a retardation of monomer diffusion through cellulose chain, increasing the termination step. Also increasing the initiator concentration may be lead to initiate many chains which enhances the chances of mutual initiation of growing polymeric chains and this result a decrease in the graft yield (Bhattacharya & Misra, 2004).

3.1.2. *Effect of AN dosage*

Using 2 h grafting time at 30 °C with 0.3 g initiator/g BBa, the effect of monomer variation was studied and the results are shown in Fig. 2. The results show that, graft yield, total conversion, as well as homopolymer formation increase with increasing monomer ratio and reached maximum values at 1:2.5 (g:ml) and shows decreasing trend with further increasing in monomer concentration. While graft conversion reached maximum (66.25%) at 1:2 beyond this concentration it has been decreased.



$$\text{Bag—OH} + \text{OH} \longrightarrow \text{Bag—O}^{\cdot} + \text{H}_2\text{O}$$

$$\text{Bag—O}^{\cdot} + n\underset{\substack{|\\ \text{CN}}}{\text{CH}_2=\text{CH}} \longrightarrow \text{Bag—O—}(\text{CH}_2\text{—}\underset{\substack{|\\ \text{CN}}}{\text{CH}})_n\text{—}$$

$$^{\cdot}\text{OH} + n\underset{\substack{|\\ \text{CN}}}{\text{CH}_2=\text{CH}} \longrightarrow \text{—}(\text{CH}_2\text{—}\underset{\substack{|\\ \text{CN}}}{\text{CH}})_n\text{—}$$

Scheme 1. Free radical grafting of BBa with AN.

The enhancement of grafting by increasing monomer concentration to optimum value could be ascribed to the greater availability of monomer to grafting sites. However the decrease trend of graft yield and grafting efficiency beyond optimum monomer concentration may be due to the competition between homopolymerization and graft copolymerization (Lai & Guo, 1991) or, to the difficulty of the initiator to approach the cellulose back bone to create new sites for grafting due to the over crowding of the monomer in the reaction mixture.

3.1.3. *Effect of grafting time*

The effect of varied grafting time (0.5, 1, 2, 3, and 4 h) on grafting was studied at 30 °C using 0.3 g initiator/g BBa with monomer ratio 1:3 (g:ml). The results are presented in Fig. 3. The graft yield, graft conversion, total conversion as well as homopolymer formation and grafting efficiency were found to increase rapidly during the first 2 h of reaction then increasing rate gradually slowed down. The increase in grafting yield is accounted for the increase in number of available grafting sites in the initial stages of the reaction (Hon, 1982). Since there is a large excess of monomer even after the longer reaction time (2 h), the leveling off after 2 h is presumably due to initiator exhaustion.

3.1.4. *Effect of grafting temperature*

The effect of varied temperatures (30, 40, 50, 60 and 70 °C) on graft copolymerization of AN onto BBa for 2 h with using 1:3 (g:ml) monomer ratio and 0.3 g initiator/g BBa was studied; the results are gathered in Fig. 4.

The optimum grafting temperature has been found to be 50 °C. The dependence of grafting parameters on grafting temperature can be ascribed to higher rate of initiator dissociation as well as transition of monomer from the aqueous phase to cellulose phase, resulting in considerable improvement in the grafting (Sharma, Kumar, & Soni, 2003). With further increase in grafting temperature beyond 50 °C, the radical termination reaction might be accelerated, leading to decrease of graft parameters (Fig. 4).

The above results show that, temperature is one of the important factors that control the kinetics of the graft copolymerization, and thermally charring bagasse. The maximum graft yield obtained at

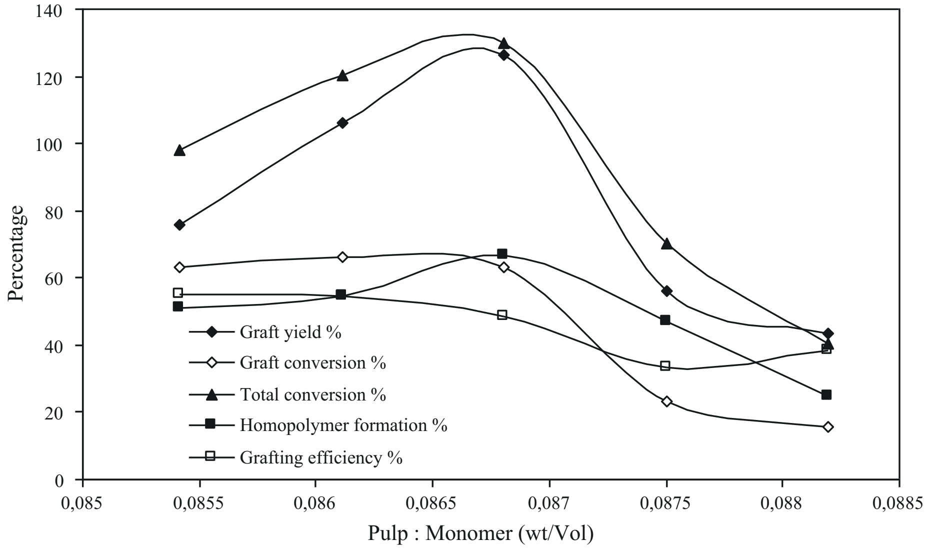


Fig. 2. Effect of AN concentration on graft copolymerization of BB with AN (grafting temp. 30 °C, weight of Fe^{2+}/gBB = 0.3, grafting time 2.5 h).

50 °C may be contributed to the ceiling temperature of AN grafted bagasse. The ceiling temperature is defined as the temperature at which the rate of addition is equal to the rate of the elimination reaction for a given system (Olfat & Altaf, 1991).

3.2. Adsorption of iron and phenol

According to the data obtained in Tables 1 and 2, it can be observed that the extent of adsorption from solution increases with concentrations of adsorbates (phenol, iron), but it is probable that a limit is attained by adsorbent surface in solution. Also, results obtained for both of phenol and iron adsorptions are dependent on the nature of adsorbent according to the type of modification carried out on bagasse.

It is obvious that the interpretation of the adsorption efficiency of any system studied depends on the nature of interaction between the fibrous structure of adsorbent and the adsorbate in the aqueous medium. According to the swelling phenomenon, it can be concluded that the factors that enhance the swellability of fibrous adsorbent are the deriving forces for enhancing the adsorption efficiency. Thus, the low adsorption efficiency of bagasse, as raw material, is referred to the poor swellability of it. The swellability of bagasse increases by sodium hydroxide treatment to form alkali cellulose. The penetration of adsorbates into alkali cellulose has been enhanced by Van der Veals forces between the adsorbate dipoles and dipoles of alkali cellulose formed along the cellulose structure. Modified bagasse via bleaching process excesses polar groups on fibrous adsorbent due to effect of bleaching process. These polar groups act in the direction of enhancing the interactions between the adsorbates and adsorbent surface.

The entrance of polymer chain through the grafting of bagasse may change the lattice dimensions to great extent, and hence, the disordered regions through the cellulosic structure have been increased. Also, the existence of —CN group in the grafted polymer enhances the adsorption efficiency of the adsorbent to higher level. The highest adsorption efficiency had been manifested by charred bagasse. This may be attributed to dramatic change in pore size distribution and the total available surface area.

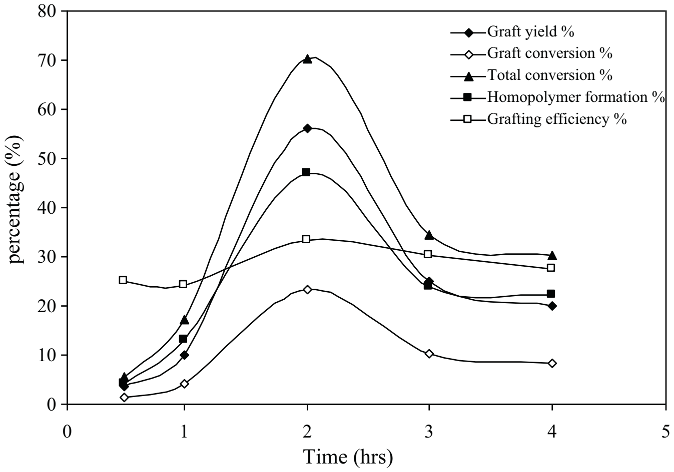


Fig. 3. Effect of grafting time on graft copolymerization of BB with AN (BB:AN = 1:3, grafting temp. 30 °C, weight of Fe^{2+}/gBB = 0.3).

3.3. Adsorption isotherm

Several models have been published in the literature to describe experimental data of adsorption isotherms. Analysis of the isotherm data is important in order to develop an equation that accurately represents the results and which could be used for design purposes. In this work Freundlich isotherm models (Yang, 1998) were used to describe the relationship between the amount of iron and phenol adsorbed and their equilibrium concentrations for Ba, UBa, BBa, GBa, AlGBa, AcGBa, and CBa.

Application of Freundlich adsorption equation on the data in Tables 1 and 2 was considered to find the relation between the extent of adsorption of phenol and iron cation on different modified bagasse samples.

The experimental method employed by shake a definite weight of adsorbent with known volume of solution under investigation. Since the process of adsorption is almost invariably reversible and definite equilibrium is reached in a short time depending on the concentration of solution, the adsorbent samples employed were allowed to settle and clear liquid had been analyzed. The amount of phenol or iron adsorbed was calculated from the difference between the initial and final concentrations of the employed solution.

The classical adsorption isotherm in the form:

$$\frac{x}{m} = KC^{1/n} \tag{1}$$

Table 1
Removal amount of phenol (μg/g).

Solution conc. (μg/l)	RM	UB	BB	GB	AlGB	AcGB	CB
100	6.75	8.35	13.40	23.40	20.00	33.33	30.00
200	37.50	48.20	60.00	86.70	106.78	40.00	118.40
300	75.36	92.34	115.20	183.00	159.99	120.00	211.80
400	103.56	98.24	185.32	234.20	193.40	246.72	284.00
500	213.80	75.05	203.70	295.50	200.00	313.50	320.00

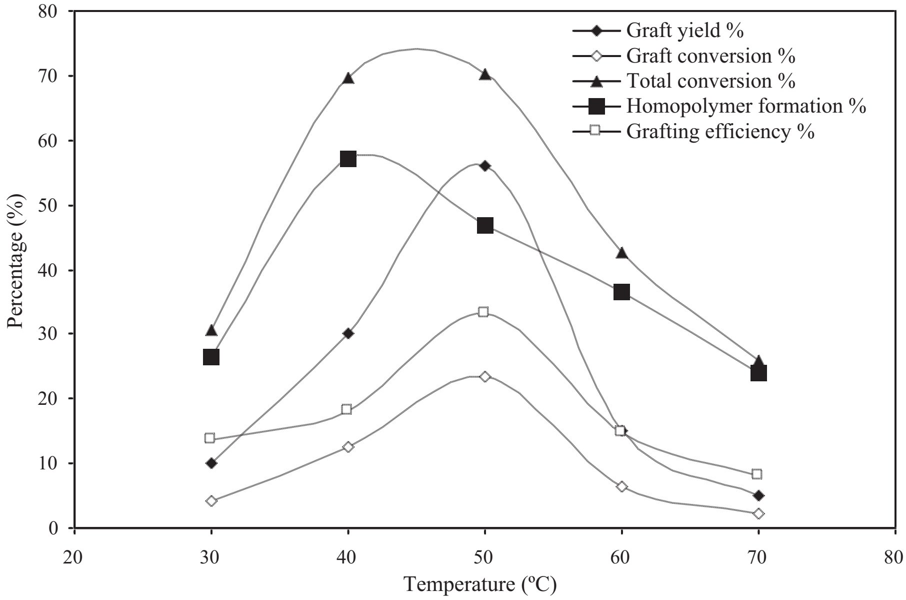


Fig. 4. Effect of grafting temperature on graft copolymerization of BB with AN (BB:AN = 1:3, weight of Fe^{2+}/gBB, grafting time 2.5 h).

Table 2
Removal amount of iron (μg/g).

Solution conc. (μg/l)	RY	UB	BB	GB	AlGB	AcGB	CB
100	5.51	11.11	22.33	5.66	38.88	27.88	16.67
200	27.80	55.66	78.88	39.00	100.00	105.54	67.00
300	53.64	104.40	93.60	80.40	144.54	161.10	105.60
400	65.80	193.76	151.88	128.88	211.08	222.20	166.40
500	104.00	211.00	186.50	160.64	211.11	200.00	195.00

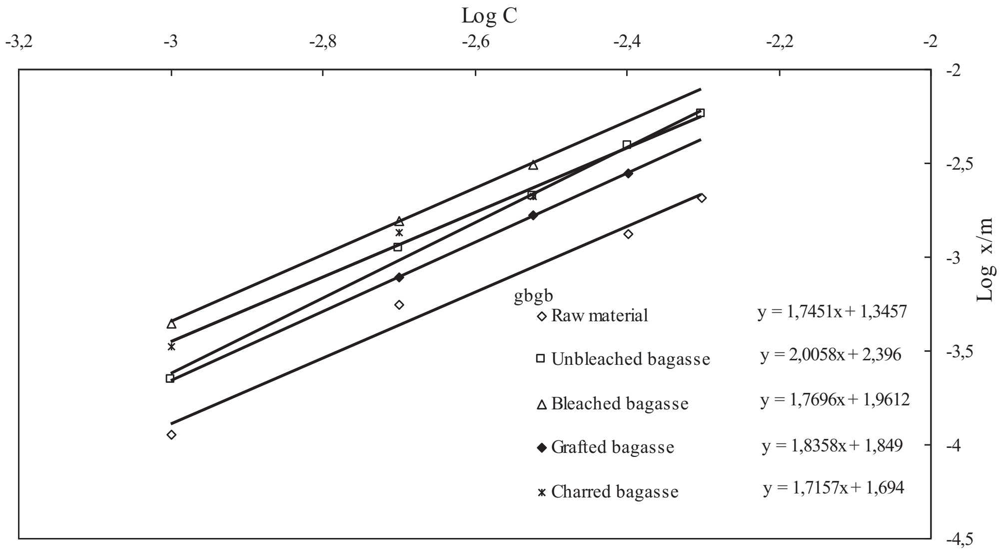


Fig. 5. Adsorption of iron on modified bagasse.

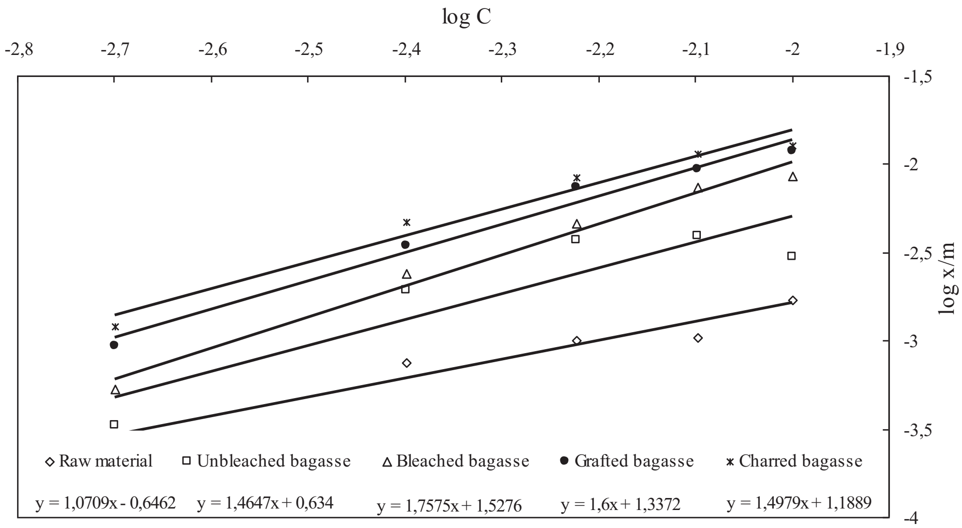


Fig. 6. Adsorption of phenol on modified bagasse.

or

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C \quad (2)$$

where C is the equilibrium concentration of solution (g/l), x is the amount of adsorbate (g) and m is the mass of adsorbent

Figs. 5 and 6 had been plotted for adsorption of iron and phenol respectively, from aqueous solutions by bagasse as raw material and different modified bagasse samples mentioned above.

According to Eq. (2), a straight line has been obtained for each adsorption process of definite adsorbent and k, n constants that characterizes each adsorption system have been calculated. The results showed that the equilibrium data for iron and phenol-sorbent systems fitted the Frenudlich model best within the concentration range studied.

4. Conclusion

The results show that, graft yield, total conversion, as well as homopolymer formation increase with increasing monomer ratio and reached maximum values at 1:2.5 (g cellulose:ml monomer). Grafting efficiency were found to increase rapidly during the first 2 h of reaction and the optimum grafting temperature has been found to be 50 °C.

Extent of adsorption from solution increases with the increase of adsorbates concentrations (phenol, iron). The extent of iron adsorption is less than that of phenol for all adsorbents. Also, results obtained for both of phenol and iron adsorptions are dependent on the nature of adsorbent according to the type of modification carried out on bagasse.

The results showed that the equilibrium data for iron and phenol-sorbent systems fitted the Frenudlich model best within the concentration range studied.

References

Abd-Alla, M. A. N., Mohamed, Y. A., & Hesham, M. F. (2007). Synthesis and characterization of grafted cellulose for use in water and metal ion sorption. *Bioresources*, *3*(1), 46–51.

Acemiodglu, B., & Alma, M. H. (2001). Equilibrium studies on the adsorption of Cu(II) from aqueous solution onto cellulose. *Journal of Colloid Interface Science*, *243*, 281–284.

Allen, S. J., Brown, P., McKay, G., & Flynn, O. (1992). An evaluation of single resistance transfer models in the sorption of metal ions by peat. *Journal of Chemical Technology and Biotechnology*, *54*, 271–276.

Allen, S. J., McKay, G., & Khader, K. Y. H. (1988). Multi-component sorption isotherms of basic dyes on peat. *Environmental Pollution*, *52*(1), 39–53.

Bhattacharya, A., & Misra, B. N. (2004). Grafting: a versatile means to modify polymers: Techniques, factors and applications. *Progress in Polymer Science*, *29*(7), 767–814.

Brown, P., Jefcoat, I. A., Parrish, D., Gill, S., & Graham, E. (2000). Evaluation of the adsorptive capacity of peanut hulls pellets for heavy metal in solution. *Advances in Environmental Research*, *4*, 19–29.

Browning, B. L. (1967). *Methods of wood chemistry* New York: Interscience. , p. 395.

Chauhan, G. S., & Lai, H. (2003). Synthesis of graft copolymer of acrylamide and comonomer onto cellulose. A study of the effect of comonomer on the polymer properties, structure and properties. *Polymer and Polymer Composites*, *11*, 1–7.

Eichenmuller, B., Bunke, G., Behrend, K., Buchholz, R., & Gotz, P. (1997). Adsorption of acenaphthene on porous organic polymers. *Journal of Environmental Engineering, ASCE*, *123*, 836–841.

Flaquie, L., drigo, L. C., & Ribes, G. (2000). Biodegradation studies of cellulose and its vinyl copolymer by thermal analysis and mechanical spectroscopy. *Journal of Applied Polymer Science*, *76*, 326–335.

Gehui, W., Zhanqian, S., Zhifeng, L., & Liansheng, W. (2002). Preparation for graft copolymers of sawdust/vinyl monomers and their application for removal of dye. *Journal of Applied Polymer Science*, *83*, 2390–2396.

George, P. F. (1996). Photocatalytic destruction of phenol and salicylic acid with aerosol-made and commercial titania powders. *Chemical Engineering Communications*, *151*(1), 251–269. http://www.informaworld.com/smpp/title

Gitisudhe, G., Prufulla, K. S., & Samal, R. K. (2005). Graft copolymerization onto wool fiber. Grafting of acrylamide onto fibres initiated by potassium monopersulfate/Fe(II) redox polymer. *Journal of Applied Polymer Science*, *40*, 471–480.

Hon, D. N. S. (1982). *Graft copolymerization of lignocellulosic fibers* Washington, DC: ACS Symposium Series., p. 101.

Kamel, S., Abou-Yousef, H., & El-Sakhawy, M. (2004). Copper(II) ions adsorption onto cationic oxycellulose. *Energy Education Science and Technology*, *14*(2), 51–57.

Kamel, S., Hassan, E. M., & El-Sakhawy, M. (2006). Preparation and application of AN-grafted cyanoethyl cellulose for the removal of Copper(II) ions. *Journal of Applied Polymer Science*, *100*, 329–334.

Lai, Y. Z., & Guo, X. P. (1991). Variation of the phenolic hydroxyl group content in wood lignin. *Wood Chemistry and Technology*, *25*, 467.

Laszlo, J. A., & Dintzis, F. R. (1994). Crop residues as ion-exchange materials. Treatment of soybean hull and sugar beet fiber (pulp) with epichlorohydrin to improve cation-exchange capacity and physical stability. *Journal of Applied Polymer Science*, *52*, 521–528.

Min, S. H., Han, J. S., Skin, E. W., & Park, J. K. (2004). Improvement of cadmium ion removal by base treatment of juniper fiber. *Water Research*, *38*, 1289–1295.

Nada, A. M. A., & El-Wakeel, N. A. (2006). Molecular structure and ion exchange of amidoximated cellulosic materials. *Journal of Applied Polymer Science*, *102*, 303–311.

Olfat, Y. M., & Altaf, H. B. (1991). Ionic xanthate method of grafting. Part 1. *Nordic Pulp and Paper Research Journal*, *4*, 184–189.

Reddad, Z., Gerente, C., Andres, Y., Ralet, M. C., & Thibault, J. F. (2002). Ni(II) and Cu(II) binding properties of native and modified sugar beet pulp. *Carbohydrate Polymers*, *49*, 23–31.

Sharma, B. R., Kumar, V., & Soni, P. L. (2003). Graft copolymerization of AN onto Cassia tora gum with ceric ammonium nitrate–nitric acid as redox mixture. *Journal of Applied Polymer Science*, *90*, 129–136.

Shin, E. W., & Rowell, R. M. (2005). Cadmium ion sorption onto lignocellulosic biosorbent modified by sulfonation: The origin of sorption capacity improvement. *Chemosphere*, *60*, 1054–1061.

Srivastava, S. K., Singh, A. K., & Sharma, A. (1994). Studies on the uptake of lead and zinc by lignin obtained from black liquor – A paper industry waste material. *Environmental Technology*, *15*, 353–361.

Vaughan, T., Seo, C. W., & Marshall, W. E. (2001). Removal of selected metal ions from aqueous solution using modified corncobs. *Bioresource Technology*, *78*, 133–139.

Verma, K. V. R., Swaminathan, T., & Subrehmnyam, P. V. R. (1990). Heavy metal removal with lignin. *Journal of Environmental Science and Health*, *25*(2), 242–265.

Yang, C.-H. (1998). Statistical mechanical on the Freundlich isotherm equation. *Journal of Colloid and Interface Science*, *208*, 379–387.