

Research Article

Use of Forestry Wastes for Biosorption of Dyes and Cr (VI)

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The pine cone and oak cups pulp were used as low-cost adsorbents for the removal of basic (Basic Red 18) and acidic (Acid Red 111) dyes and Cr (VI) from aqueous solutions. The adsorbents were modified by HNO_3 to improve their biosorption capacity. The adsorbents were characterized using scanning electron microscopy and FTIR spectroscopy. The zeta potential was determined as a function of the pH, in order to explain the effect of pH on electrostatic adsorption ability of biosorbent. Modification of adsorbents with nitric acid led to an increase in accessibility of some functional groups on the surface or a decrease in negativity of surface charge. The modification of pine cone increased its adsorption capacity for the basic dye, whereas the modification of oak cups pulp decreased the adsorption ability for basic dye to some extent. The adsorption isotherms fitted the Langmuir model. The adsorption capacities were found to be 142.85, 158.73, and 156.20 mg g⁻¹ for modified and raw pine cone and oak cups pulp, respectively. The acidic dye and Cr (VI) adsorptions were much lower compared to basic dye on all tested adsorbents. The results indicated that the forest wastes (pine cone and oak cups pulp) were an attractive candidate for basic dyes from aqueous solution.

1. Introduction

The biosorption of organic and inorganic toxic contaminants from waste water has greatly increased because an inexpensive and more easily available adsorbent would make the removal of pollutants an economically viable alternative [1, 2]. Numerous studies on adsorption properties of forestry and agricultural wastes, as naturally occurring and low-cost adsorbents, have been documented. A number of lignocellulosic wastes have been tried for dye and metal removal. These include wood sawdust [3, 4], orange peel [5, 6], tobacco dust [7], tea waste [8], hen feathers [9], sunflower seed hull [10], palm kernel fibre [11], coir pith [12], peanut hull [13], grape stalks [14], soya cake [15], soy meal hull [16], sugar beet pulp [17], and Canola hull [18]. In addition, a number of studies exist on the modification of the agricultural wastes to increase their adsorption capacity. Gupta and Rastogi, have reported excellent biosorption capacity of acid-treated algal biomass for the removal of lead, cadmium and hexavalent chromium [19]. The chemically treated *P. oceanica* fibres with nitric acid and phosphoric acid had showed enhancement in the reactive dye removal due to the protonation of the biomass surface for acidic attacks [20]. Similarly, treatment

of narrow-leaved cattail with formaldehyde + sulfuric acid increased the sorption ability for direct and reactive dyes due to the increase of positively charged molecules on the surface of adsorbent [21]. The modification of wood shavings with Na_2CO_3 and Na_2HPO_4 increased the adsorption ability for the basic dye (Methylene Blue), whereas the modification of with HCl decreased the sorption ability for Methylene Blue to some extent [22]. In addition, the biosorbent having high cationic sorption capacity was obtained by thermochemically modification of biomass with citric acid [23].

In this study, forestry wastes (pine cone and oak cups pulp) were used for dyes and Cr (VI) removal and acid pretreatment of biomass was adopted to improve their removal, efficiency. The Anatolian vegetation is very rich on account of species of trees. The oak trees are widely found and distributed on the Aegean region of Anatolia. The acorn cups of Turkish oak (*Quercus alegilops*) containing high percentage of hydrolysable (pyrogallol) group of tannin are internationally called as “Valonea.” The matured acorn cups are picked between October and March, dried and sent to the extract factory. The Valonea is treated with hot water in order to leach the tannin. The vegetable extract obtained from Valonea is named as “Valex” and used in leather manufacture

as tanner while the residue from extraction (oak cups pulp) is disposed by incineration. On the other hand, *Pinus pinea* L. is an economically important tree in the Mediterranean area, mainly in Spain, Portugal, Italy, Greece, Albania, and Turkey and has a significant role in soil conservation, landscape architecture, and for its edible seeds. Its plantation has been highly promoted by European policy of the forestation of croplands. Turkey has 35 000 ha of stone pine forest, and pine cones are widely used as a domestic fuel in forest villages or are retained in forest.

The aim of this study is to investigate the potential of cone of stone pine (*Pinus pinea* L.) and oak cups pulp waste acorn as alternative low-cost adsorbent for basic and acidic dyes and Cr (VI) metal ion. Although biosorption using various low-cost biomass materials has been widely studied, there has not been any report on oak cups pulp and pine cone.

2. Materials and Methods

2.1. Preparation of Adsorbent. The oak cups pulp valex residue was supplied by Valex plant in Salihli/Izmir, the cones of *Pinus pinea* L. was supplied from a forest in the Izmir area. Both two biomass samples were air dried and ground and sieved to particle size 0.20–0.5 mm. Some properties and composition of biosorbents are given in Table 1.

Both the oak cups pulp (OC) and pine cone (PC) samples were washed with distilled water to remove the surface-adhered particles and water soluble materials and was dried at 110°C overnight. Modified oak cups pulp (OC-N) and pine cone (PC-N) were prepared by suspending the sorbent material in 1 M HNO₃ solution for 24 hours at room temperature rinsing with deionized water and drying at 110°C overnight [20].

Basic and acidic dyes used in this study were Basic Red 18 and Acid Red 111. All the dyes (Bayer) were used as received. Their chemical structures are given in Figure 1. Hexavalent chromium solutions were prepared by dissolving appropriate amounts of potassium dichromate (K₂Cr₂O₇, Merck).

2.2. Adsorbent Characterization. The electrophoresis method was used to determine the zeta potential of the adsorbents, by using Zeta-Meter 3.0+ equipped with a microprocessor unit [24]. In order to obtain suspended particles in the solution of 0.025 g 50 mL⁻¹, dry biosorbents were shaken in bidistilled water for 24 hours at room temperature. Then, the zeta potential of the particles was measured as a function of pH between 2 and 10 without addition of electrolytes in bidistilled water (<2.0 μS/cm). The pH of dispersions was adjusted by adding either HCl or NaOH solutions.

Attenuated total reflectance infrared (ATR/IR) spectra of the biosorbents were taken by using a spectrophotometer (Spectrum 100, Perkin-Elmer). The scanning electron microscope (SEM) analyses were done by JSM-6060 JEOL instrument.

2.3. Batch Sorption Experiments. Batch experiments were carried out in 250 mL of Erlenmeyer by shaking a fixed mass of dry samples with 100 mL of adsorbate solution for the

desired concentration, pH, and contact times. The pH was adjusted, adding either HCl or NaOH. The filtrates were analyzed for residual acidic and basic dyes concentrations using the UV-visible spectrophotometer (UV-160A, Shimadzu) at 504 and 484 nm, respectively. For residual Cr (VI) concentrations, the filtrates were analyzed by a reaction with 1,5-diphenylcarbazide followed by absorbance measurement at 540 nm using the UV-visible spectrophotometer.

In order to obtain the adsorption isotherm 100 mL of the test solutions of various dye (10–150 ppm) and Cr (VI) (10–20 ppm), concentrations were added to predetermined amount of adsorbent in Erlenmeyer, and the suspensions were shaken at 150 pm for an experimentally predetermined time to establish the equilibrium, after adjustment of pH. In all sets of experiments, each test was carried out in duplicate and the average results are presented. The results were reproducible, and the standard deviations were found to be ±2.4%.

3. Results and Discussion

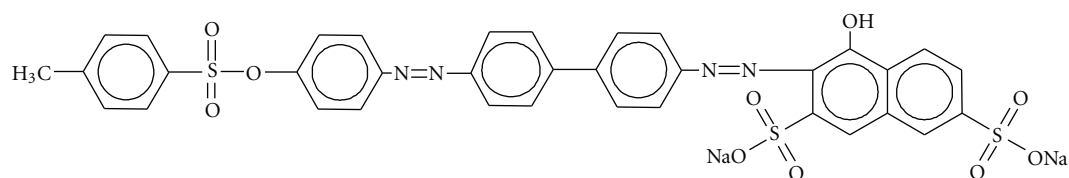
3.1. Characterization of the Adsorbents. Fourier transform infrared spectral analysis of natural and modified biosorbents displayed a number of absorption peaks corresponding to different functional groups indicating their complex structures. The spectrum of all tested adsorbents are given in Figure 2 and band assignments of typical IR spectrum are summarized in Table 2. It has been seen that all include common bands with some differences from the comparison of all the spectra.

It is worth noting that the spectra of modified sorbents did not differ significantly from the spectrum of unmodified sorbents. Similar result was obtained by Janoš et al. who compared the sorption capability of the modified wood with that of the unmodified wood for dyes [22].

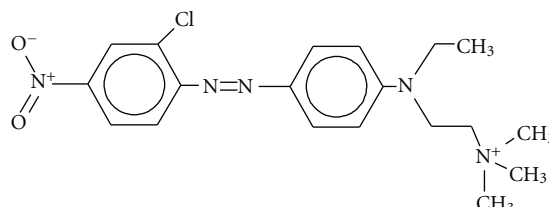
The most significant difference in adsorbents is that the C=O stretching band in PC-N, it appears at 1718 cm⁻¹ (corresponding to stretching in carboxylic acid). The displacement to lower wave numbers may be attributed to hydrolysis of esters in natural pine cone during modification with HNO₃ [25]. According to the FT-IR results, we can conclude that pine cone and oak cups pulp maintained its functional groups in the bulk after modification with HNO₃.

The polar functional groups, such as alcohols, carboxylic acids, and phenolic hydroxides in lignocellulosic materials groups may contribute to the occurrence of charged sites on the surfaces of biomass [7]. The surface charge of the biomaterial plays an important role in electrostatic adsorption on the biosorbent. The surface charge of adsorbents was investigated measuring zeta potential (ZP). ZP is variable with the surface potential and the thickness of electric double layer. The degree of repulsion between charged particles in dispersion is indicated by the zeta potential.

Figure 3 shows the variation of zeta potential as a function of pH. As seen from Figure 3, the surface of all biosorbents was negative, and the negativity increased as the pH of the solution increased slightly from 2.0 to 10. This suggests that deprotonation or/and ionization of acidic functional groups of the lignocellulosic material increased by increasing the pH of solution.



Acid Red 111



Basic Red 18

FIGURE 1: Chemical structure of investigated dyes.

TABLE 1: Properties of biosorbents.

	Ash (wt%)	Lignin (wt%)	Cellulose (wt%)	Hemicellulose (wt%)	Extractives (wt%)
Pine cone	0.9	31.4	47.2	15.7	4.8
Oak cups pulp	7.2	34.3	12.3	43.6	2.6
PC-N	0.18				
OC-N	1.09				

The negative charge values should be favorable to the attraction between active sites in adsorbent and positive charges of adsorbate, resulting in an electrostatic interaction. Although FTIR spectra suggested that chemical treatment procedure did not change substantially the lignocellulosic structure it, however, changed surface charge of the sorbents.

The zeta potential plots show differences between the natural and modified biosorbents. Unexpectedly, the surface charge of modified biosorbents was less negative than that of natural biosorbents. In the case of untreated material, polar functional groups due to the holocellulose and lignin are covered by noncellulose compounds. It is expected that the acid treatment removing of these compounds led to an increase in the negative zeta potential by the improved accessibility of anionic groups [26]. But in this study, we obtained opposite result. It was reported that the electrokinetic potential of fibers, depends on the chemical constitution and polarity of the fiber surface, the microstructure of the fiber and its swelling behavior in water [27]. Swelling increases the size of the active surface on adsorbent which led to an increase in the negative charge. The modification process might decrease the hydrophilic behavior of the fiber surface. Therefore, the surface charge of PC-N and OC-N is less negative than that of PC and OC.

The SEM micrographs of PC, PC-N, OC, and OC-N show typical lateral rack type of structure (Figure 4). It should be noted that all of the biosorbents exhibited only a color change, which could be observed with even naked eye, after the modification process.

3.2. Basic Dye Adsorption. The pH is one of the most important factors in the adsorption of dye. This is partly due to the fact that hydrogen ions themselves are strong competing adsorbates, and partly that pH of the solution influences surface charge of adsorbent. The influence of pH on the removal of Basic Red 18 was studied at different contact time over a pH range 6.0–10.0 at which the color was stable.

It is well known that adsorption of basic dyes is unfavorable at acidic pH due to the presence of excess H^+ ions which compete with the dye cation for adsorption sites [8]. However, the number of the negatively charged sites on adsorbent increases as the pH of the system increases, favoring the adsorption of dye cation due to electrostatic attraction. Figure 5 shows the effect of pH and contact time on dye removal. The dye uptake on PC was increased by the increasing pH. A similar trend was reported for the adsorption of dyes such as malachite green onto sawdust [23] and hen feathers [9], Methylene Blue and Red Basic 22 onto prehydrolysed beech sawdust [4], methyl violet onto seed hull [10], and Methylene Blue onto palm kernel fibre [11].

On the other hand, it was observed that the dye uptake increased with the contact time. As shown in Figure 5, the adsorption of Basic Red 18 was rapid within the first 6 h of contact time and then was gradual until equilibrium. It was established that within the eight hours, almost 93% of adsorption was achieved at pH 10. The equilibrium time of 8 h and the pH 10 were found to be sufficient for further studies. The influence of pH on the removal of Basic Red 18 by

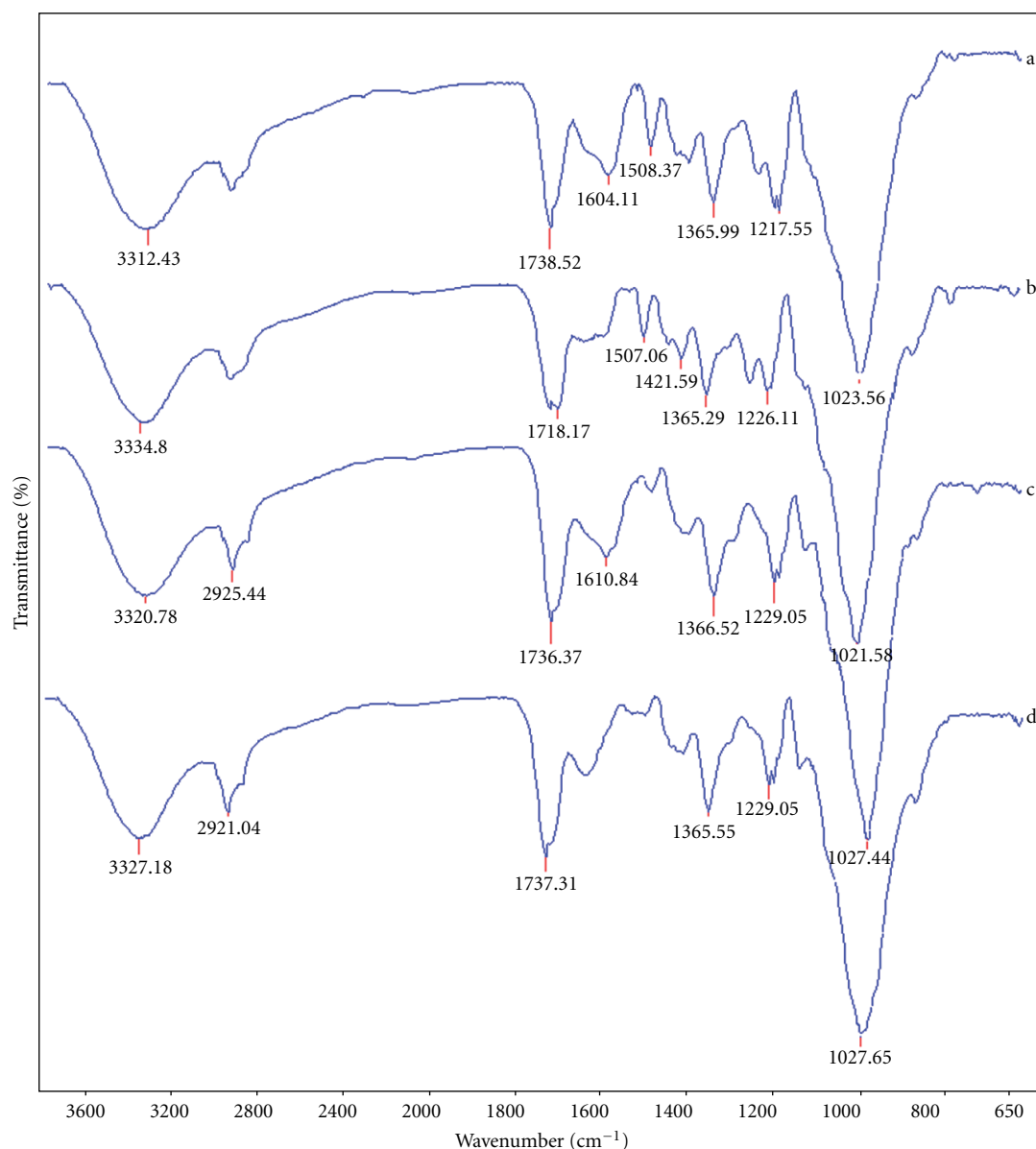


FIGURE 2: FT-IR spectra of PC (a), PC-N (b), OC (c), and OC-N (d).

OC was also investigated at different contact times between 2 and 24 hrs (not presented here). In contrast to PC, the dye up take on OC was independent of the pH between 6 and 10. The same trend has also been reported in the removal of basic dye by some other materials [5, 10, 12, 28]. There was an approximately 10% variation in adsorption capacity for the contact times between 4 and 24 hrs. Therefore, in order to maximize the cost-effectiveness of adsorption operation, it was decided not to extend the adsorption for larger period than 4 hrs. It is worth nothing that the optimum contact time was independent of the pH. This observation showed that an external surface mass transfer or film diffusion process may also control the sorption process as well as chemical sorption process. For the adsorption of Basic Red 18 on OC,

the equilibrium time of 4 hrs and the pH 6 were found to be sufficient for further studies.

In the case of modified pine cone (PC-N), dye uptake considerably increased above pH 8 (Figure 6). The uptake of dye by PC-N occurred faster than PC, corresponding to 93.0% removal at an equilibrium time of 4 hrs. It is clearly understood that the number of available adsorption sites area increased by the modification of PC with HNO_3 treatment, although its surface is less negative than that of native pine cone. The relative increase in the removal of dye after contact time of 4 hrs for PC-N was not significant, and hence, it was fixed as the optimum contact time.

On the other hand, the dye uptake on OC-N was not considerably changed by increasing of pH as in the case of

TABLE 2: The main atomic groups and structures of adsorbents.

Wavenumber (cm^{-1})	Infrared absorption and structures	PC	PC-N	OC	OC-N
1021–1023	C–O deformation	+	+	+	+
1217–1229	C–O stretching (phenols)	+	+	+	+
1366	C–H bending (methyl group)	+	+	+	+
1736–1738	C=O stretching (esters)	+	–	+	+
1718	C=O stretching (carboxylic acid)	–	+	–	–
2920–2925	C–H stretching (aliphatic structures)	+	+	+	+
3312–3335	–OH (phenols, alcohols, and carboxylic acids)	+	+	+	+

TABLE 3: Parameter of the Langmuir adsorption model of dyes and Cr (VI) (at $25 \pm 0.2^\circ\text{C}$).

Adsorbents	Basic Red 18			Acid Red 111			Cr (VI)		
	$S_M \text{ mg g}^{-1}$	$K_L \text{ L mg}^{-1}$	R^2	$S_M \text{ mg g}^{-1}$	$K_L \text{ L mg}^{-1}$	R^2	$S_M \text{ mg g}^{-1}$	$K_L \text{ L mg}^{-1}$	R^2
PC	142.85	0.26	0.96	7.54	0.09	0.97	7.16	16.24	0.99
PC-N	158.73	0.75	0.99	7.92	0.49	0.98	4.19	0.30	0.98
OC	156.20	0.32	0.97	7.99	0.16	0.98	6.54	1.91	0.97
OC-N	133.33	0.24	0.99	9.95	0.14	0.99	7.48	14.85	0.99

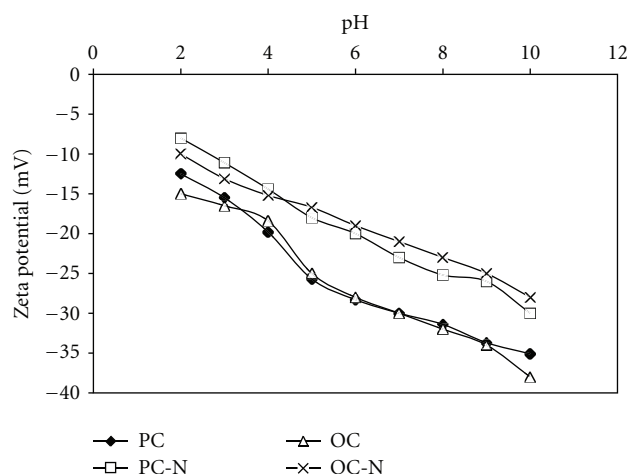


FIGURE 3: The zeta potential curves as a function of pH for raw and modified PC and OC.

OC. Since 100% removal was obtained for a contact time of 4 hrs at pH 6, the equilibrium time of 4 hrs and the pH 6 were found to be sufficient for isotherm studies.

3.3. Acidic Dye Adsorption. Although the basic dye sorption on woody biomass is mainly a chemisorption process, the acidic dye adsorption is more or less physical process [22]. Due to the negatively charged characteristics of cellulose materials in aqueous medium [29], the lignocellulosic adsorbents have been found to have low adsorption capacities to anionic dyes.

In this study, we aimed to enhance the adsorption capacity of lignocellulosic adsorbents by modification and to study their adsorption behavior toward acidic dye (a cationic dye), comparatively. There is limited study on modification of lignocellulosic materials to enhance their anionic dye adsorption capacity. It has been shown that treatment of

Posidonia oceanica (L.) leaf sheaths with H_3PO_4 and HNO_3 solutions increased the adsorption efficiency up to 80% for a reactive textile dye [20]. On the other hand, the treatment of wood shavings with HCl increased the sorption ability for Egacid Orange (acid dye) to some extent [22]. The improving of the dye adsorption capacity through chemical treatment of the biomass was also reported by other authors [13, 21, 30].

The effect of pH on the amount of Acid Red 111 removal was analyzed over the pH range from 2 to 5 and for different contact times. Figure 7 shows the effect of pH and agitation time on dye removal by PC. As expected, the pH significantly affected the extent of adsorption of dye over both the adsorbents, and a reduction in the amount adsorbed with increasing pH was observed in both cases. This trend is in agreement with earlier report on anionic dye adsorption [6]. This behavior can be explained on the basis of change in surface charge of the lignocellulosic materials. By increasing the pH, the surface of adsorbents get more negatively charged (Figure 3), which does not favor the adsorption of dye anions due to the electrostatic repulsion. The maximum biosorption capacity reached was at pH 2. The equilibrium time was found to be 8 and 4 h for PC and OC, respectively. Although surface negativity of both sorbents was similar, the uptake of dye by OC occurred faster than PC. This may show that the covalent coordination bonds between dye molecules and surface functional groups is also important in adsorption as well as electrostatic forces.

In the case of modified pine cone and modified oak cups pulp, maximum dye uptake was obtained at pH 2, as in the case of native biosorbents. The contact times of 6 and 4 hrs for PC-N and OC-N were found to be sufficient to attain equilibrium. As in the case of basic dye, the uptake of acidic dye by PC-N occurred faster than PC due to its less negative surface. In addition, it was noted that sorption of Acid Red 111 onto modified PC was more influenced by pH than that onto PC. The dye uptake drastically decreased above pH 3 (Figure 8).

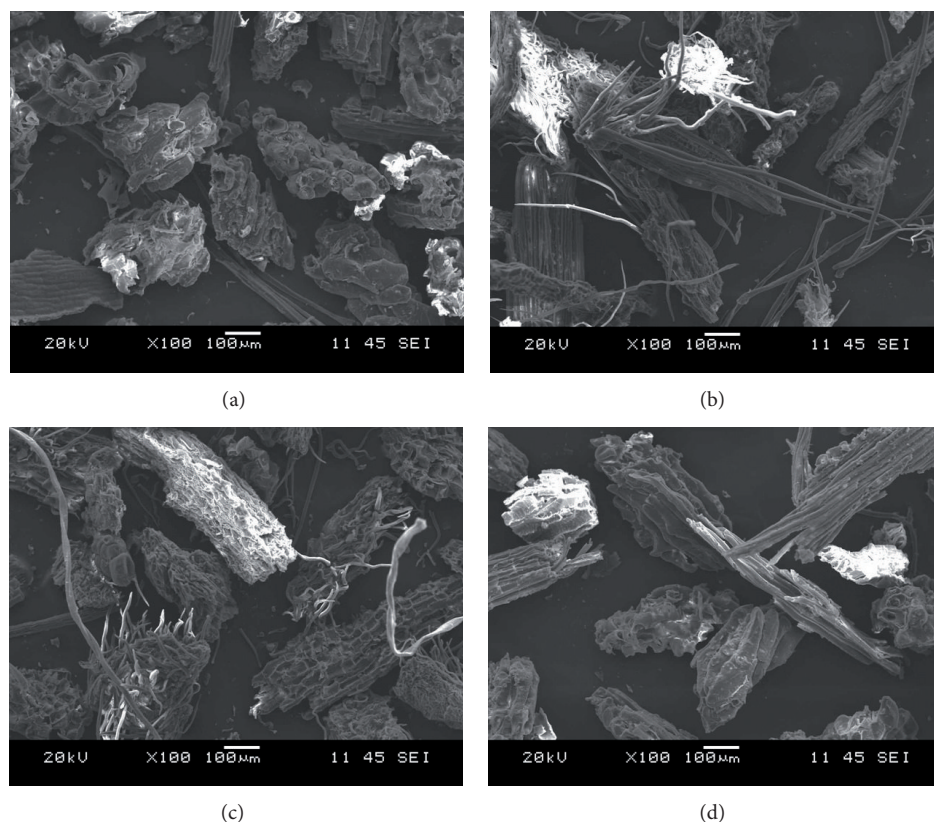


FIGURE 4: Micrograph of PC (a), PC-N (b), OC (c), and OC-N (d) (magnification: X100).

TABLE 4: Reported basic dye adsorption capacities for agricultural wastes.

Adsorbent	Adsorbate	S_M (mg g ⁻¹)	Reference
Beach sawdust	Methylene blue	10.9	[3]
Wood shavings	Methylene blue	17.9	[22]
Tea wates	Methylene blue	156.0	[8]
Beech sawdust	Methylene blue	9.8	[4]
Palm kernel fibre	Methylene blue	671.8	[11]
Rice straw	Malachite green	94.3	[23]
Modified rice straw	Malachite green	256.41	[23]
Hen feather	Malachite green	9.4	[36]
Luffa cylindrica	Malachite green	29.4	[28]
Sunflower seed hull	Methyl violet	92.6	[10]
Banana peel	Methyl violet	12.2	[5]
Orange peel	Methyl violet	11.5	[5]
Coir pith	Rhodamine B	203.2	[12]
Canola hul	Basic Blue 41	67.6	[18]
Canola hull	Basic Red 46	49.0	[18]
Canola hull	Basic Violet 16	25.0	[18]

3.4. Cr (VI) Adsorption. Several lignocellulosic wastes have been investigated for chromium removal. Mohan and Pittman, have reviewed the sorption capacities of lignocellulosic sorbents for chromium remediation [31]. In the adsorption of Cr (VI) on lignocellulosic material, two mechanism, namely, adsorption and reduction to trivalent chromium, can

simultaneously occur [14]. Some researchers have claimed that Cr (VI) was removed from the aqueous phase by binding of anionic Cr (VI) ion species to the positively charged groups of biosorbent [32]. But several authors reported that organic substances, such as lignocellulosic materials, have the capacity to reduce Cr (VI) to Cr (III) at acidic pHs

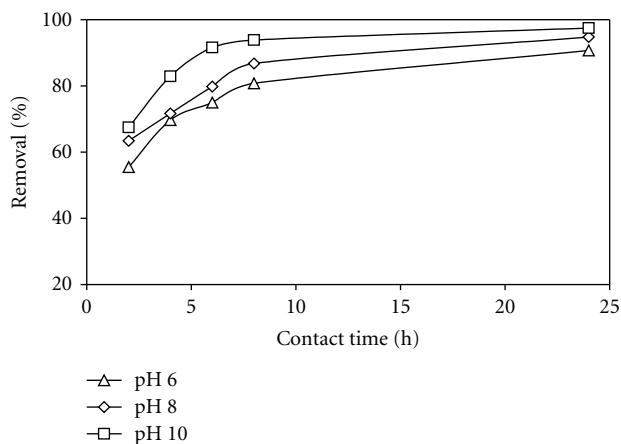


FIGURE 5: Effect of pH and contact time on basic dye removal by PC (adsorbent dosage, 500 mg per 100 mL; dye concentrations, 50 mg L⁻¹).

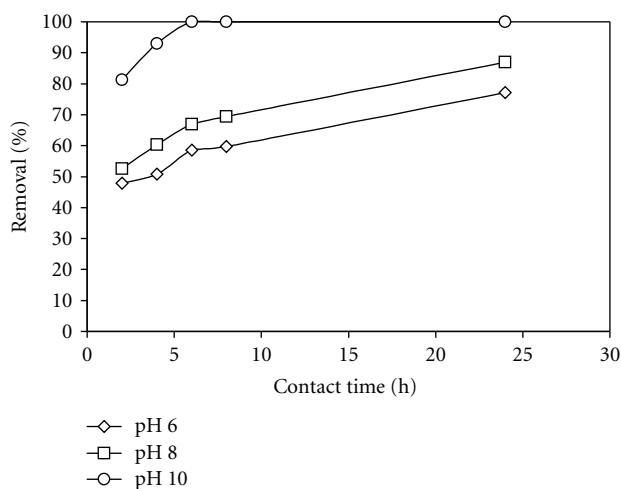


FIGURE 6: Basic dye adsorption capacity of PC-N as a function of contact time (adsorbent dosage, 500 mg per 100 mL; dye concentrations, 50 mg L⁻¹).

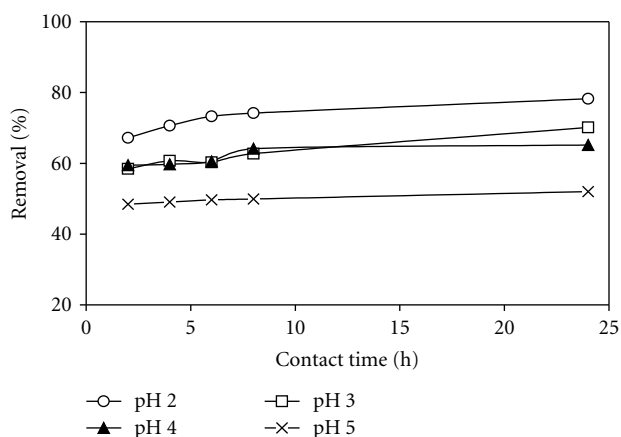


FIGURE 7: Acidic dye adsorption capacity of PC as a function of pH and contact time (adsorbent dosage, 500 mg per 100 mL; dye concentrations, 50 mg L⁻¹).

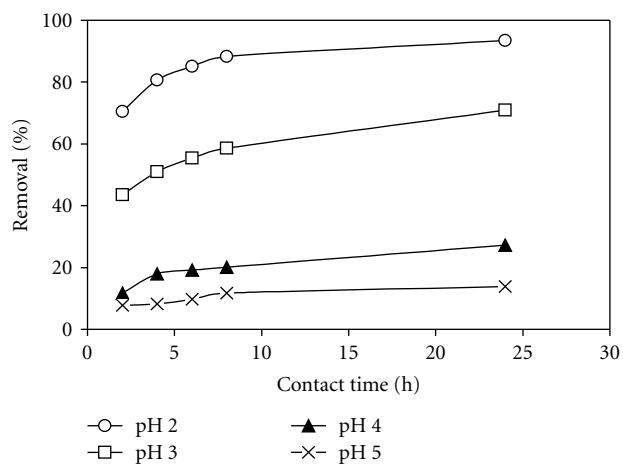
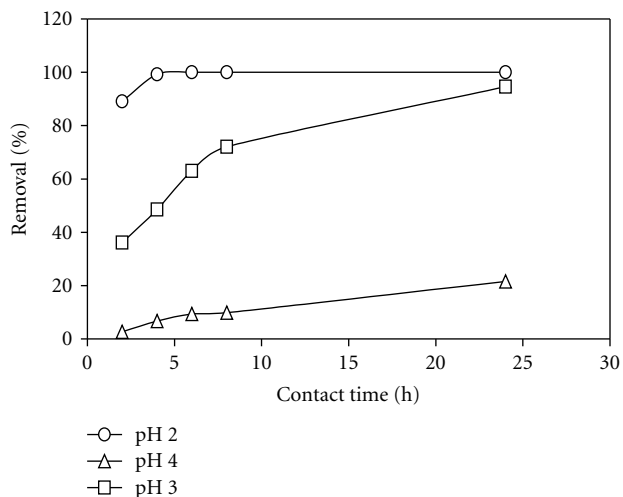
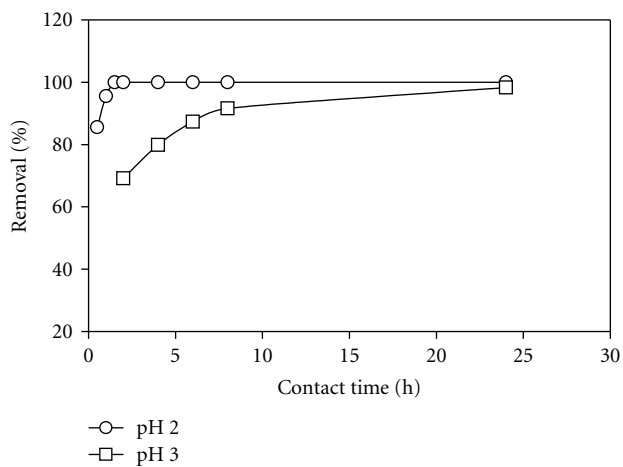


FIGURE 8: Acidic dye adsorption capacity of PC-N as a function of pH (adsorbent dosage, 500 mg per 100 mL dye concentrations, 50 mg L⁻¹).



(a)



(b)

FIGURE 9: Cr(VI) adsorption capacity of PC (a) and OC (b) as a function of pH (Adsorbent dosage, 2500 mg per 100 mL; Cr(VI) concentration, 10 mg L⁻¹).

[14, 15, 33]. Fiol et al. [14] proposed that Cr (VI) sorption process involves two different mechanisms: adsorption of the HCrO_4^- anion and reduction of Cr (VI) to Cr (III) releasing into the solution totally or partially the formed trivalent chromium. They observed the adsorption of both trivalent and hexavalent chromium on grape stalks by XPS analysis in their study on Cr (VI) sorption.

As well known, the pH value of the solution is an important controlling parameter in the Cr (VI) adsorption process. The uptake of Cr (VI) increased with a decrease in the solution pH. The pH dependence of the metal uptake is mainly related to the functional groups on the adsorbent and also on the metal solution chemistry. From pH 1 to pH 6, most chromium species exist in solution in the form HCrO_4^- , while from pH 6 to pH 10, the CrO_4^{2-} species become predominant in solution. As expected, the adsorption capacity of chromium onto both lignocellulosic materials decreases with increasing pH (Figure 9). Similar behavior has also been reported for yohimbe bark [14], soya cake [15], and lignocellulosic substrate derived from wheat bran [33]. This phenomenon can be attributed to the fact that a lower pH decreases the negatively charged groups on the surface of sorbents (Figure 3), which leads to higher Cr (VI) uptake. In addition, by considering the above explanations, one can also say that reduction of Cr (VI) to Cr (III) may also lead to a decrease in concentration of Cr (VI) in solution. It is seen that pH 2.0 is the optimal pH for the Cr (VI) uptake for both adsorbents. But, the Cr (VI) uptake by OC occurred faster than that by PC. Almost 100% of adsorption was achieved for the contact times 1 h and 4 hrs at pH 2 for OC and PC, respectively. Although surface negativity of both sorbents was similar, there is a significant difference between optimum contact times of OC and PC. This shows that the complex formation and/or chelation between chromium ions and surface functional groups [17] is also important in adsorption as well as electrostatic forces at acidic condition. It must be remarked that for longer contact time (24 hrs), the removal efficiency of both PC and OC at pH 3 was similar within the case of pH 2.

For modified pine cone and modified oak cups pulp, maximum chromium uptake was obtained at pH 2. The uptake of Cr (VI) by PC-N occurred faster than PC, corresponding to 93.3% removal at an equilibrium time of 3 h. The reason might be the increase in available adsorption sites area by the modification of PC with HNO_3 treatment. In the case of OC-N, almost 100% of adsorption was obtained for the contact time 1 h at pH 2, as in the case of OC.

3.5. Biosorption Equilibrium. The adsorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the adsorbent when the biosorption process reaches an equilibrium state. For practical operation, correlation of the isotherms using a theoretical or empirical equation is desired. In this study, two common isotherms were used for describing the experimental results, namely, the Freundlich isotherm and the Langmuir isotherm. The parameters in Freundlich and Langmuir equations are very useful for predicting adsorption capacities and also for incorporating

into mass transfer relationships in the design of contacting equipment.

The Freundlich model is considered to be suitable for highly heterogeneous surfaces and indicates that significant adsorption takes place at low concentrations, but the increase in the amount adsorbed with concentration becomes less significant at higher concentration. Although the used adsorbents were natural adsorbent exhibiting the chemical heterogeneity [34], the experimental results for all tested adsorbates fitted best to Langmuir model.

The Langmuir equation describes adsorption on strongly homogeneous surfaces, which is not the case of natural adsorbents exhibiting first of all a chemical heterogeneity represented by the different functional groups. Langmuir model is based on the assumption of monolayer adsorption onto a surface containing finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the pores of the adsorbent surface [35]. The linear form of Langmuir isotherm is given by the following equation:

$$\frac{Ce}{qe} = \frac{1}{K_L S_M} + \frac{Ce}{S_M}, \quad (1)$$

where, S_M (mg g^{-1}) is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface, qe (mg g^{-1}) is the amount of dye, K_L (l g^{-1}) is the Langmuir constant, and Ce is the equilibrium liquid phase concentrations of dye solution.

The isotherm parameters obtained for dyes and Cr (VI) are reported in Table 3. Both PC-N and OC adsorbed the Basic Red 18 in a greater degree in comparison with the other adsorbents within this study. Although, the FT-IR spectrum of adsorbents did not differ significantly from each other, suggesting that the treatment process did not change the lignocellulose structure substantially; however, the adsorption capacities of modified sorbents for basic dye are different from that of natural sorbents. For example, modification of oak cups pulp led to decrease its basic dye adsorption capacity. The reason may be higher negative surface charge of OC than that of OC-N, which favors adsorption between the positively charged dye ion and the surface of OC by electrostatic interaction. On the other hand, the adsorption capacity of PC-N is higher than that of PC; even C-N has lesser surface negativity than PC. It may be due to the fact that HNO_3 treatment affected the accessibility of some functional groups on the surface of adsorbent, which may lead to changes in its adsorption behavior. The basic dye adsorption capacity of the adsorbents tested in this study can be compared with the other agricultural solid wastes (Table 4).

On the other hand, all the tested adsorbents showed low adsorption capacity for Acid Red 111 because the negative surface charge on the adsorbent does not favor the adsorption of dye anions due to the electrostatic repulsion. The similar aspect took place for other adsorbents in the literature. The adsorption capacities of all adsorbents for Acid Red 111 were ranged in $7.54\text{--}9.95 \text{ mg g}^{-1}$ adsorbent. These values are quite comparable with the sorption capacities of natural

materials as listed in the review of Crini [36]. The S_M values reported in this paper are in the ranges 5.92–20 mg/g for acidic dyes. However, the adsorption capacities of soy meal hull for C.I. Direct red 80, C.I. Direct red 81, C.I. Acid blue 92, and C.I. Acid red 14 were found to be 178.57, 120.48, 114.94, and 109.89 mg g⁻¹ of adsorbent, respectively [16].

In addition, Mahmoodi et al. obtained the maximum adsorption capacities for Acid Black 26, Acid Green 25 and Acid Blue 7 onto Pine Cone (PC) as 62.89, 43.29 and 37.45 g g⁻¹, respectively [37]. The differences in adsorption capacities found in the literature might be not only attributed to surface characteristics of adsorbent, it might be also attributed to the size and shape of the dye molecule.

It was evident from the present study that both pine cone and oak cups pulp showed similar Cr (VI) adsorption capacity, and modification of native sorbents could not enhance their adsorption capacities. The adsorption capacities for Cr (VI) were ranged in 4.19–8.36 mg g⁻¹ adsorbent. It must be noted that the used adsorbents in this study had lower Cr (VI) adsorption capacities than some of the lignocellulosic based adsorbents found in the literature. Mohan and Pittman reviewed the remediation of tri- and hexavalent chromium from water by activated carbons and low-cost adsorbents [31]. The S_M values reported in this review are in the range of 0.2–103 mg g⁻¹ for lignocelluloses based adsorbents.

4. Conclusions

This study demonstrated that the raw and acid-treated oak cups pulp and pine cone could be used as efficient biosorbent for the treatment of basic dyes containing aqueous solutions. The chemical modification of pine cone with nitric acid enhanced the basic dye adsorption capacity due to the increase number of available adsorption sites. In contrast, chemical modification of oak cups pulp decreased its dye adsorption capacity due to the less negative surface charge of modified biosorbent. It has been concluded that the use of oak cups pulp is more economic than pine cone because it does not require an additional pretreatment step, and the adsorption can be done at a wide range pH between 6 and 10. On the other hand, both two biosorbents were not much effective for acidic dye and chromium removal. Modification of biosorbents could not enhance their acidic dye and Cr (VI) uptake capacities.

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References

- [1] M. M. Nassar and M. S. El-Geundi, "Comparative cost of colour removal from textile effluents using natural adsorbents," *Journal of Chemical Technology and Biotechnology*, vol. 50, no. 2, pp. 257–264, 1991.
- [2] R. Y. L. Yeh and A. Thomas, "Color difference measurement and color removal from dye wastewaters using different adsorbents," *Journal of Chemical Technology and Biotechnology*, vol. 63, no. 1, pp. 55–59, 1995.
- [3] F. A. Batzias and D. K. Sidiras, "Simulation of dye adsorption by beech sawdust as affected by pH," *Journal of Hazardous Materials*, vol. 141, no. 3, pp. 668–679, 2007.
- [4] F. A. Batzias and D. K. Sidiras, "Dye adsorption by prehydrolysed beech sawdust in batch and fixed-bed systems," *Bioresource Technology*, vol. 98, no. 6, pp. 1208–1217, 2007.
- [5] G. Annadurai, R. S. Juang, and D. J. Lee, "Use of cellulose-based wastes for adsorption of dyes from aqueous solutions," *Journal of Hazardous Materials*, vol. 92, no. 3, pp. 263–274, 2002.
- [6] M. Arami, N. Y. Limaee, N. M. Mahmoodi, and N. S. Tabrizi, "Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies," *Journal of Colloid and Interface Science*, vol. 288, no. 2, pp. 371–376, 2005.
- [7] B. C. Qi and C. Aldrich, "Biosorption of heavy metals from aqueous solutions with tobacco dust," *Bioresource Technology*, vol. 99, no. 13, pp. 5595–5601, 2008.
- [8] N. Nasuha, B. H. Hameed, and A. T. M. Din, "Rejected tea as a potential low-cost adsorbent for the removal of methylene blue," *Journal of Hazardous Materials*, vol. 175, no. 1–3, pp. 126–132, 2010.
- [9] A. Mittal, "Adsorption kinetics of removal of a toxic dye, malachite green, from wastewater by using hen feathers," *Journal of Hazardous Materials*, vol. 133, no. 1–3, pp. 196–202, 2006.
- [10] B. H. Hameed, "Equilibrium and kinetic studies of methyl violet sorption by agricultural waste," *Journal of Hazardous Materials*, vol. 154, no. 1–3, pp. 204–212, 2008.
- [11] A. E. Ofomaja, "Kinetics and mechanism of methylene blue sorption onto palm kernel fibre," *Process Biochemistry*, vol. 42, no. 1, pp. 16–24, 2007.
- [12] C. Namasivayam, M. Dinesh Kumar, K. Selvi, R. Ashruffunnisa Begum, T. Vanathi, and R. T. Yamuna, "'Waste' coir pith—a potential biomass for the treatment of dyeing wastewaters," *Biomass and Bioenergy*, vol. 21, no. 6, pp. 477–483, 2001.
- [13] R. Gong, Y. Ding, C. Yang, M. Li, H. Liu, and Y. Sun, "Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution," *Dyes and Pigments*, vol. 64, no. 3, pp. 187–192, 2005.
- [14] N. Fiol, C. Escudero, and I. Villaescusa, "Chromium sorption and Cr(VI) reduction to Cr(III) by grape stalks and yohimbe bark," *Bioresource Technology*, vol. 99, no. 11, pp. 5030–5036, 2008.
- [15] N. Daneshvar, D. Salari, and S. Aber, "Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake," *Journal of Hazardous Materials*, vol. 94, no. 1, pp. 49–61, 2002.
- [16] M. Arami, N. Y. Limaee, N. M. Mahmoodi, and N. S. Tabrizi, "Equilibrium and kinetics studies for the adsorption of direct and acid dyes from aqueous solution by soy meal hull," *Journal of Hazardous Materials*, vol. 135, no. 1–3, pp. 171–179, 2006.
- [17] Z. Aksu and I. A. Isoglu, "Use of dried sugar beet pulp for binary biosorption of Gemazol Turquoise Blue-G reactive dye and copper(II) ions: equilibrium modeling," *Chemical Engineering Journal*, vol. 127, no. 1–3, pp. 177–188, 2007.
- [18] N. M. Mahmoodi, M. Arami, H. Bahrami, and S. Khorramfar, "Novel biosorbent (Canola hull): surface characterization and dye removal ability at different cationic dye concentrations," *Desalination*, vol. 264, no. 1–2, pp. 134–142, 2010.
- [19] V. K. Gupta and A. Rastogi, "Biosorption of hexavalent chromium by raw and acid-treated green alga *Oedogonium*

- hatei from aqueous solutions,” *Journal of Hazardous Materials*, vol. 163, no. 1, pp. 396–402, 2009.
- [20] M. C. Ncibi, B. Mahjoub, and M. Seffen, “Adsorptive removal of textile reactive dye using *Posidonia oceanica* (L.) fibrous biomass,” *International Journal of Environmental Science and Technology*, vol. 4, no. 4, pp. 433–440, 2007.
- [21] D. Inthorn, S. Singtho, P. Thiravetyan, and E. Khan, “Decolorization of basic, direct and reactive dyes by pre-treated narrow-leaved cattail (*Typha angustifolia* Linn.),” *Bioresource Technology*, vol. 94, no. 3, pp. 299–306, 2004.
- [22] P. Janoš, S. Coskun, V. Pilařová, and J. Rejnek, “Removal of basic (Methylene Blue) and acid (Egacid Orange) dyes from waters by sorption on chemically treated wood shavings,” *Bioresource Technology*, vol. 100, no. 3, pp. 1450–1453, 2009.
- [23] R. Gong, Y. Jin, F. Chen, J. Chen, and Z. Liu, “Enhanced malachite green removal from aqueous solution by citric acid modified rice straw,” *Journal of Hazardous Materials*, vol. 137, no. 2, pp. 865–870, 2006.
- [24] E. E. Saka and C. Güler, “The effects of electrolyte concentration, ion species and pH on the zeta potential and electrokinetic charge density of montmorillonite,” *Clay Minerals*, vol. 41, no. 4, pp. 853–861, 2006.
- [25] F. Suárez-García, A. Martínez-Alonso, and J. M. D. Tascón, “A comparative study of the thermal decomposition of apple pulp in the absence and presence of phosphoric acid,” *Polymer Degradation and Stability*, vol. 75, no. 2, pp. 375–383, 2002.
- [26] K. Stana-Kleinschek and V. Ribitsch, “Electrokinetic properties of processed cellulose fibers,” *Colloids and Surfaces A*, vol. 140, no. 1–3, pp. 127–138, 1998.
- [27] C. Bellmann, A. Caspari, V. Albrecht et al., “Electrokinetic properties of natural fibres,” *Colloids and Surfaces A*, vol. 267, no. 1–3, pp. 19–23, 2005.
- [28] A. Altınışık, E. Gür, and Y. Seki, “A natural sorbent, *Luffa cylindrica* for the removal of a model basic dye,” *Journal of Hazardous Materials*, vol. 179, no. 1–3, pp. 658–664, 2010.
- [29] R. Sanghi and B. Bhattacharya, “Review on decolorisation of aqueous dye solutions by low cost adsorbents,” *Coloration Technology*, vol. 118, no. 5, pp. 256–269, 2002.
- [30] Y. Fu and T. Viraraghavan, “Removal of Congo Red from an aqueous solution by fungus *Aspergillus niger*,” *Advances in Environmental Research*, vol. 7, no. 1, pp. 239–247, 2002.
- [31] D. Mohan and C. U. Pittman, “Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water,” *Journal of Hazardous Materials*, vol. 137, no. 2, pp. 762–811, 2006.
- [32] E. Malkoç and Y. Nuhoglu, “The removal of chromium(VI) from synthetic wastewater by *Ulothrix zonata*,” *Fresenius Environmental Bulletin*, vol. 12, no. 4, pp. 376–381, 2003.
- [33] L. Dupont and E. Guillon, “Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran,” *Environmental Science and Technology*, vol. 37, no. 18, pp. 4235–4241, 2003.
- [34] M. M. Dávila-Jiménez, M. P. Elizalde-González, and A. A. Peláez-Cid, “Adsorption interaction between natural adsorbents and textile dyes in aqueous solution,” *Colloids and Surfaces A*, vol. 254, no. 1–3, pp. 107–114, 2005.
- [35] G. Duman, Y. Onal, C. Okutucu, S. Onenc, and J. Yanik, “Production of activated carbon from pine cone and evaluation of its physical, chemical, and adsorption properties,” *Energy and Fuels*, vol. 23, no. 4, pp. 2197–2204, 2009.
- [36] G. Crini, “Non-conventional low-cost adsorbents for dye removal: a review,” *Bioresource Technology*, vol. 97, no. 9, pp. 1061–1085, 2006.
- [37] N. M. Mahmoodi, B. Hayati, M. Arami, and C. Lan, “Adsorption of textile dyes on Pine Cone from colored wastewater: kinetic, equilibrium and thermodynamic studies,” *Desalination*, vol. 268, no. 1–3, pp. 117–125, 2011.

