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Removal of COD from real textile effluents using agro-industrial wastes

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ABSTRACT

In this work, the biosorption potential of agro-industrial wastes was assessed for the removal of chemical oxygen demand (COD) from real textile effluents. The screening test conducted indicated that corncobs biomass has maximum potential among five agricultural waste materials (sugarcane bagasse, peanut husk, corncobs, cotton sticks, and sunflower) to remove COD from both textile effluents. The effect of important operating parameters like biosorbent dose, agitation time, agitation speed, and temperature was evaluated during the study. The maximum COD removal (80.8 and 72.4% for Effluents 1 and 2, respectively) was achieved at 0.5 g biosorbent dose and 140 rpm agitation speed. The biosorption process was found to be exothermic in nature. The data were also subjected to different kinetic and equilibrium models and the results depicted the fitness of pseudo-second-order kinetic model and Langmuir adsorption isotherm on the experimental data. The physicochemical characteristics (pH, electrical conductivity, COD, total dissolved solids, and TDS) of textile effluents were also evaluated before and after the treatment. The FT-IR spectrum of corncobs biomass indicates the involvement of carboxylic, carbonyl, and hydroxyl group in the adsorption process. The results indicated that corncobs biomass is a potential and cost-effective biomass for the treatment of real textile effluents.

Keywords: Real textile effluents; COD; Kinetic modeling; Equilibrium modeling; Physicochemical characteristics

1. Introduction

The exponential increase in population has resulted in concomitant growth in water demand which is being needed for agriculture, running industries, and domestic use. The growing industrialization has intensified the water shortage problems [1]. This insufficiency of water is majorly due to the mismanagement of water usage and pollution of natural water reservoirs [2]. Among the different factors that are responsible for the deterioration of natural water resources, the textile effluents are of major concern [3].

The textile effluents are responsible for accelerating the water pollution problems [4]. Different processes are being carried out in textile industries. These processes result in the release of effluents-containing dyes, detergents, oils, and other different chemicals which contribute to high suspended solids, chemical

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oxygen demand (COD), biochemical oxygen demand (BOD), heat, color, acidity, basicity, and other soluble substances [5]. COD is considered as the major contaminant in the industrial effluents and different technologies have been used to reduce the COD and color from the textile industrial wastewaters. These processes include ion exchange, filtration, coagulation/flocculation, reverse osmosis, and electrodialysis [6]. Biological treatment process are also used frequently to treat the textile effluents and these methods are efficient to reduce BOD, but are found to be inefficient for the treatment of dissolved non-biodegradable complex organic dyes [7]. Adsorption process has been proved effective for the reduction of COD from different effluents [8–10] and it becomes more attractive if low-cost materials are used as adsorbent.

In the past few decades, the agricultural waste materials are receiving stern consideration for the treatment of textile effluents [11–16]. The use of agricultural waste materials for wastewater treatment has been increased because of their good adsorption potential due to presence of carboxyl, hydroxyl, and amino groups over their surfaces [17]. Their easy availability, low-cost, and good adsorption potential make the process more attractive [18].

Pakistan is an agricultural country and agricultural waste products are abundantly available in Pakistan. The agricultural waste materials are randomly discarded or burnt in the fields, which lead to the increase in environmental pollution. The textile sector of Pakistan is also playing a very important role in the economy of country. Faisalabad is an industrial city of Pakistan with a large number of textile industries. The present study was designed to check out the efficiency of adsorption process for the reduction of COD from two local textile industries of Faisalabad, Pakistan by using agricultural waste materials.

2. Materials and methods

2.1. Textile wastewater

The raw textile wastewater samples were collected from two different local textile industries of Faisalabad, Pakistan (Kamal Textile Industry, Faisalabad and Arzo Textile Dying and Printing Industry Faisalabad). Samples were collected in sampling bottles and placed in an icebox to preserve for analysis. The effluents from Kamal Textile Industry, Faisalabad and Arzo Textile Dying and Printing Industry Faisalabad were labeled as Effluents 1 and 2, respectively. The physicochemical parameters such as pH, electrical conductivity (EC), COD, total dissolved solids (TDS), and total suspended solids (TSS) were estimated before and after the biosorption process, according to the methods prescribed in APHA [19].

2.2. Preparation of biosorbents

The agricultural waste materials (sugarcane bagasse, peanut husk, corn cobs, cotton sticks, and sunflower) were collected from different areas of Pakistan. These waste materials were washed with distilled water in order to remove dust. They were then dried in sunlight and then oven-dried for 24 h at 60˚C. The washed and dried biosorbents were ground with a food processor (Moulinex, France) and sieved using an Octagon sieve (OCT-DIGITAL 4527-01) to a 300 μm mesh size and stored in air tight bottles.

2.3. Batch experimental program

The optimization of important process parameters (biosorbent dose, contact time, shaking speed, and temperature) for the maximum removal of COD from textile effluents was carried out using classical approach. The 250 mL conical flasks containing 50 mL of dye containing effluents with known biosorbent dose were shaken in an orbital shaking incubator (PA250/25H). Blank solutions were run under same conditions except the addition of biosorbent. All the experiments were performed in triplicate and the results are reported as mean value. After certain time, the samples were taken out and their COD was recorded.

The percentage of COD removal from each sample was calculated by using the following relationship:

$$\% \text{ Removal} = (\text{COD}_{\text{Ini}} - \text{COD}_{\text{Final}})\,100/\text{COD}_{\text{Ini}} \tag{1}$$

2.4. Biosorption kinetics

Biosorption kinetics data were analyzed using two commonly used kinetic models viz. pseudo-first-order [20] and pseudo-second-order [21] kinetic models.

2.5. Biosorption equilibrium

Then, most commonly employed biosorption isotherm models (Langmuir [22], Freundlich [23], and Temkin and Pyzhev [24]) were applied in the present investigation on the experimental results obtained from biosorbent dose data.

3 Results and discussion

3.1. Screening study

Five different agricultural waste materials (sugarcane bagasse, peanut husk, corncobs, cotton sticks, and sunflower) were used for the screening study to select one biosorbent having maximum capacity for the reduction of COD from the textile effluents. The results of screening study are presented in Fig. 1. The results indicated that for both effluents, corncobs showed maximum capacity to reduce COD. Initial COD of Effluent 1 was recorded as 287 mg/L while for Effluent 2 initial COD was found to be 189 mg/L. By using corncobs, 18.64 and 15.56% reduction in COD was observed for Effluents 1 and 2, respectively. Corncobs biomass was selected for further study.

3.2. Effect of biosorbent dose

Effect of biosorbent dose was determined by varying the amount of corncobs biomass from 0.1 to 0.6 g/50 mL effluent solution and results are presented in Fig. 2. The results indicated that with the increase in biosorbent dose, there is an increase in percent removal of COD from textile effluents. A sharp increase in the percent removal of COD was observed with the increase in biosorbent dose up to 0.5 g while further increase in biosorbent dose has not shown any remarkable change in the COD reduction. So, 0.5 g biosorbent dose 50 mL effluent solution was selected for further study. Almost, 75 and 69% reduction in COD was observed for Effluents 1 and 2, respectively. Higher COD reduction at higher biosorbent doses was due to the availability of more surface area which facilitates the adsorption of COD from the effluent [25]. Patel and Vashi [10] also worked on the treatment of real textile effluents through adsorption and while investigating the effect of biosorbent dose, they found similar trend of increasing COD reduction by increasing adsorbent dose.

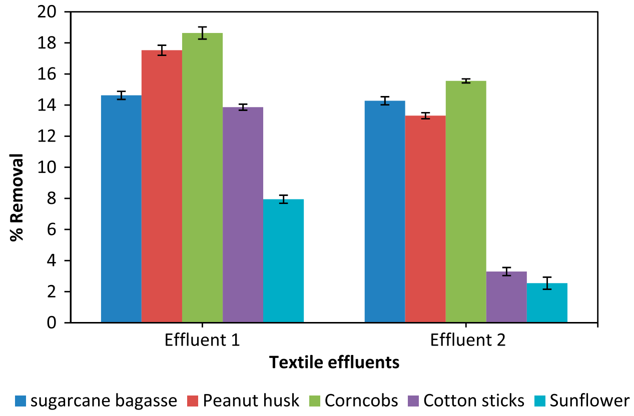

Fig. 1. Screening of different agricultural waste materials for the reduction of COD from real textile effluents.

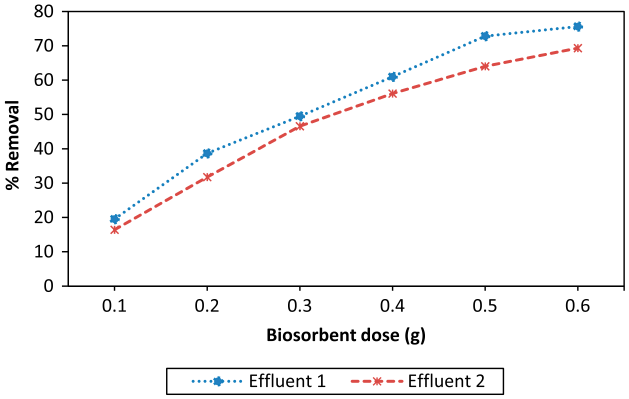

Fig. 2. Effect of biosorbent dose on the removal of COD from real textile effluents.

3.3. Effect of contact time

The effect of contact time on the removal of COD from real textile effluents was explored by varying the contact time from 0 to 120 min and results are presented in Fig. 3. The results clearly indicated that in the initial 30 min, the percent removal of COD was very high, which later began slowing down with the passage of time. No remarkable change in the reduction of COD was observed after 60 min for Effluents 1 and 2. Contact time of 60 min was found to be sufficient to attain equilibrium. In the start, the rapid reduction in COD might be attributed to the presence of a large number of binding sites on the surface of biomass, which results in the quick attachment of

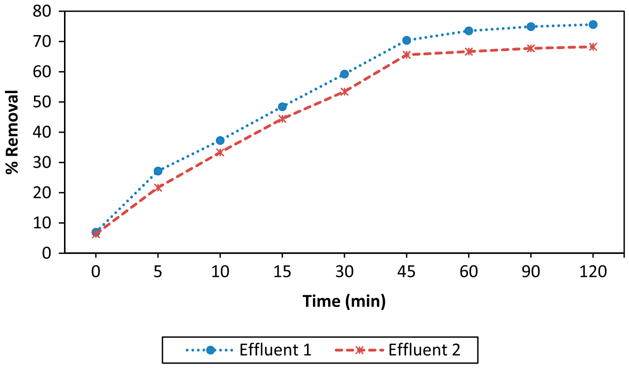

Fig. 3. Effect of contact time on the removal of COD from real textile effluents.

solute to the biosorbent surface. After some time, the biosorption began to slow down due to slow movement of solute molecules into the interior of bulk of the biosorbent [26]. This can also be explained in the way that after some period of contact time, the saturation of the available binding sites on the biosorbent surface leads to the slowdown of biosorption process. El-Naas et al. [6] worked on the treatment of refinery effluent by using date pit waste biomass for the reduction in COD and found similar results for the effect of contact time [6]. They varied the contact time from 0 to 120 min and observed increase in the percentage of COD reduction with the increase in contact time up to 30 min.

3.4. Effect of agitation speed

To check out the effect of agitation speed on the removal of COD from textile effluents, the agitation speed was varied from 60 to 140 rpm and results are depicted in Fig. 4. The results indicate that with the increase in agitation speed, the percent removal of COD also increased. With increasing agitation speed, the rate of diffusion of solute molecules from bulk liquid to the liquid boundary layer surrounding the particle becomes higher because of an enhancement of turbulence and a decrease of thickness of the liquid boundary layer [27]. Almost, 80.4 and 72.4% reduction in COD was observed at the agitation speed of 140 rpm for Effluents 1 and 2, respectively.

3.5. Effect of temperature

Mostly, the textile effluents are released at higher temperatures so that temperature can be an important process parameter which affects the biosorption process. To investigate the effect of temperature on the removal of COD from textile effluents, the temperature range was selected from 30 to 70°C and results are shown in Fig. 5. The results showed that by increasing the temperature from 30 to 70°C, there was a pronounced decrease in the percent removal of COD. The removal of COD decreased from 80.8 to 34.8% for Effluent 1 and from 67.7 to 30.1% for Effluent 2 with the increase in temperature from 30 to 70°C. This can be explained by the fact that at higher temperatures, the biosorption capacity of biosorbent decreased due to the weakening of bonds between the dye molecules and binding sites of biosorbent [28].

3.6. Kinetic studies

The biosorption mechanism and potential rate controlling steps are important aspects to study for design purposes during the wastewater treatment. Several kinetic models are available to describe the sorption kinetics. Mostly used models, including the pseudo-first-order and pseudo-second-order, were applied to the experimental data to evaluate the kinetic behavior of adsorption of COD from textile effluents onto corncobs biomass. The applicability of these kinetic models was determined by measuring the correlation coefficients (R^2).

The integral form of the pseudo-first-order model generally expressed as:

$$\log(q_e - q_t) = \log q_e - K_1 \cdot \frac{t}{2.303} \tag{2}$$

where q_e and q_t are the biosorption capacity (mg/g) at equilibrium and time t, respectively; K_1 is the rate constant (L/min); and t is the contact time (min). The

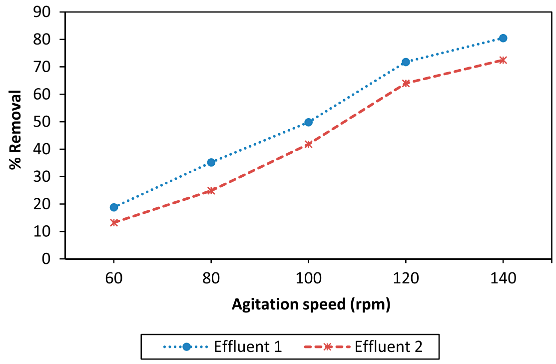

Fig. 4. Effect of agitation speed on the removal of COD from real textile effluents.

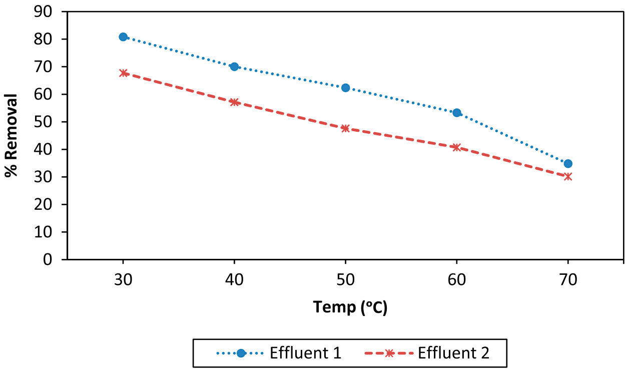

Fig. 5. Effect of temperature on the removal of COD from real textile effluents.

values of rate constant K_1, q_e calculated, q_e experimental, and R^2 for the remoal of COD from two textile effluents are presented in Table 1. By Lagergren pseudo-first-order model, a plot of $\log(q_e - q_t)$ vs. t gives a straight line with very poor correlation coefficient (R^2). Pseudo-first-order kinetic model predicted significantly lower biosorption capacity (q_e) as compared with the experimental biosorption capacity. So, results indicate inapplicability of pseudo-first-order kinetic model to the kinetic data.

The pseudo-second-order kinetic model can be presented as:

$$\left(\frac{t}{q_t}\right) = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where K_2 (g/mg min) is the second-order rate constant of biosorption process. A plot between t/q_t vs. t gives the value of the constants K_2 (g/mg min) and q_e (mg/g) can also be calculated. The second-order parameters K_2, q_e calculated, q_e experimental, and R^2 for the removal of COD from textile effluents are shown in Table 1. Results indicated that the values calculated and experimental q_e values are closer to each other for both the effluent samples. The higher values of correlation coefficient (R^2) showed that the pseudo-second-order kinetic model is well fitted to experimental data. The results showed that the pseudo-second-order kinetic model is more appropriate and effective than pseudo-first-order kinetic model.

3.7. Adsorption isotherms

Three different adsorption isotherm models (Langmuir, Freundlich, and Temkin adsorption isotherm models) have been applied on the experimental data obtained at different biosorbent doses for the removal of COD and results of application of these isotherms are presented in Table 2.

Table 1
Kinetic modeling of data for the removal of COD from textile effluents using corncobs biomass

Kinetic models	Effluent 1	Effluent 2
Pseudo-first-order		
K_1 (L/min)	0.033	0.031
q_e Experimental (mg/g)	21.7	12.9
q_e Calculated (mg/g)	11.93	6.308
R^2	0.742	0.603
Pseudo-second-order		
K_2 (g/mg min)	0.005	0.009
q_e Experimental (mg/g)	21.7	12.9
q_e Calculated (mg/g)	23.2	13.88
R^2	0.993	0.991

The Langmuir adsorption isotherm model is valid for the biosorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of binding sites [22]. The linear form of Langmuir can be written as:

$$\frac{C_e}{q_e} = \frac{1}{q_m^b} + \frac{C_e}{q_m} \tag{4}$$

The Langmuir constants, q_m (maximum biosorption capacity) (mg/g) and b (values for Langmuir constant related to the energy of biosorption (L/mg)), are predicted from the plot between C_e/q_e and C_e. The results are presented in Table 2.

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor for equilibrium parameter, R_L [29], which can be calculated as:

$$R_L = \frac{1}{1 + bC_o} \tag{5}$$

where C_o is the initial dye concentration and b is the Langmuir constant. The values of R_L indicate the type of isotherm to be favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), irreversible ($R_L = 0$), or linear ($R_L = 1$). The values of R^2 and Langmuir constant for the reduction of COD from textile effluents are presented in Table 2. Higher values of R^2 suggest the good fitness of Langmuir isotherm on the experimental data.

Table 2
Equilibrium modeling of data for the removal of COD from textile effluents using corncobs biomass

Isotherm models	Effluent 1	Effluent 2
Langmuir		
q_m Calculated (mg/g)	36.49	20.24
b	0.013	0.022
R_L	0.192	0.195
R^2	0.98	0.99
Freundlich		
K_F	4.29	2.81
N	2.86	2.89
R^2	0.92	0.917
Temkin		
A	0.146	0.208
B	311.6	550.9
R^2	0.922	0.936

The Freundlich isotherm model is valid for multilayer biosorption and is derived by assuming a heterogeneous surface with interaction between adsorbed molecules with a non-uniform distribution of heat of sorption over the surface [23]. Mathematically, it can be expressed as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{6}$$

where q_e is the amount of dye adsorbed per unit of adsorbent at equilibrium time (mg/g); C_e is equilibrium concentration of dye in solution (mg/L); and K_F and n are isotherm constants where K_F indicate the biosorption capacity, and n is a measure of deviation from linearity of the biosorption and used to verify types of biosorption [30]. It is suggested that if n is equal to unity, the biosorption is linear; n below unity indicates that biosorption is a chemical process whereas n above unity is associated with a favorable biosorption [31]. The values of R^2, K_F, and n are presented in Table 2.

The Temkin isotherm model [24] suggests an equal distribution of binding energies over the number of the exchanging sites on the surface. The distribution of these energies depends on the number of functional groups on the dye molecule and the biosorbent surface.

The linear form of Temkin isotherm can be written as:

$$q_e = B \ln A + B \ln C_e \tag{7}$$

where $B = RT/b$, T is the absolute temperature in Kelvin, b is Temkin constant, and R is the universal gas constant (8.314 J mol^{-1} K^{-1}). A is the equilibrium binding constant and B is corresponding to the heat of sorption. These constants and R^2 values can be calculated by plotting graph between q_e and ln C_e. The values of R^2 and Temkin isotherm constants for the removal of COD from textile effluents are presented in Table 2.

3.8. Characterization of real textile effluents

The physicochemical characteristics of textile effluents were analyzed before and after the treatment of textile effluents and results are presented in Table 3. These results are also compared with National Environmental Quality Standards (NEQS) fixed by the Ministry of Environment, Government of Pakistan. The Standards are also given in Table 3. The water quality may be evaluated by measuring its pH. Generally, the pH less than 6.5 is considered acidic and pH more than 8.5 is considered alkaline and both of these are non-desirable [32]. The suitability of water can also be evaluated on the basis of EC. It is a good measure of salinity hazard to crops as it reflects the soluble salts in the water [33]. TDS is also an important parameter that can be used to judge the quality of water. TDS refers to any minerals, salts, metals cation, or anion dissolved in water [34]. The results indicate a decrease in COD, TDS, and TSS after the treatment of textile effluents through biosorption which shows that biosorption process is effective for the treatment of textile effluents.

3.9. FT-IR study

The FT-IR spectrum indicates the exchanging sites and functional groups involved during biosorption. The FT-IR spectrum of corncobs biomass is presented in Fig. 6. The presence of sharp peak at 3,550 cm^{-1} region is due to the OH stretching vibrations of carboxylic group. The presence of peaks in the region of 2,370 cm^{-1} might be due to presence of C≡C bonds. The presence of peak at 1,634 cm^{-1} is due to the presence of C=O stretching vibrations of amide group. The peak at 1,384 cm^{-1} is OH in-plane vibrations of alcohols.

4. Conclusion

The study focused on the utilization of agricultural waste materials for the reduction of COD from real

Table 3
Physicochemical characteristics of real effluents

		Effluent 1		Effluent 2		
Parameters	Units	Before treatment	After treatment	Before treatment	After treatment	NEQS [35] limits
pH	–	6.94	6.80	6.86	7.12	6–9
EC	mS/cm	3.65	1.49	4.69	1.38	–
COD	mg/L	287	55	189	61	150
TDS	mg/L	1,923	977	1,834	909	3,500
TSS	mg/L	376	189	119	59	200

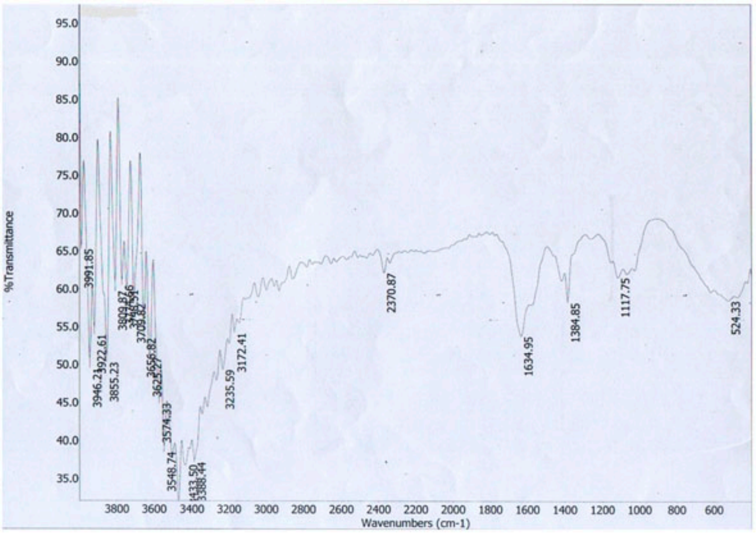

Fig. 6. FT-IR of corncobs biomass.

textile effluents. The batch experiments were conducted for the optimization of important process parameters. The results indicated the fitness of pseudo-second-order kinetic model on the experimental results. Langmuir adsorption isotherm model was found the most suitable equilibrium model on the experimental data. The corncobs biomass depicted great potential for the treatment of textile effluents.

Acknowledgements

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