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## Treatment of egg processing industry effluent using chitosan as an adsorbent

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**Abstract:** The objective of the present study was to investigate the efficiency of chitosan as an adsorbent for the treatment of wastewater from the egg processing industry. Parameters affecting the effluent treatment process, such as pH, chitosan dosage, settling time and initial chemical oxygen demand (*COD*) on the reduction percentage of turbidity, *COD* and biochemical oxygen demand (*BOD*) were studied. The optimum conditions were found to be pH 4, chitosan dosage of 1.1 g L<sup>-1</sup> and a settling time of 40 min. The maximum reduction percentage of turbidity, *COD* and *BOD* were found to be 94, 88 and 83 %, respectively. The effective adsorption process was confirmed by FT-IR spectral analysis. The experimental data were analyzed by different isotherm and kinetic models. The Langmuir isotherm type I model satisfactorily described the adsorption mechanism. The rate of *COD* reduction followed a pseudo-first-order kinetic model. A four factor, three levels Box–Behnken response surface design was employed to develop second order polynomial mathematical models from the experimental data.

**Keywords:** egg wastewater; chitosan; adsorption; isotherms; kinetics; experimental design.

### INTRODUCTION

Water is a scarce resource of the world and only 0.03 % is available for human activities.<sup>1</sup> Domestic and industrial sources have made the use of waters unwholesome and have produced great amounts of wastewater. The release of raw wastewater into the environment causes aesthetic problems and has a negative impact on environmental bodies and human living resources. A few decades, there were no stringent laws guiding environmental pollution and hence, many industries discharged untreated or inadequately treated wastewater into the environment.<sup>2</sup> Recently, pollution control boards made stringent regulation to adopt

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zero discharge methods in order to protect the ecological system. Therefore, nowadays, effluent treatment is one of the most important targets for various industries.<sup>3</sup> Different type of industries discharge huge amount of wastewaters, of which the egg processing industry generates more than 9.5 billion liters of wastewater annually. The discharge of untreated egg processing industrial wastewater creates many environmental problems due to its high concentrations of organic matter.<sup>4</sup>

Numerous effluent treatment methods, such as anaerobic,<sup>5</sup> aerobic,<sup>6</sup> advanced oxidation processes,<sup>7</sup> ozonation,<sup>8</sup> electro-oxidation,<sup>9</sup> photochemical oxidation using UV/H<sub>2</sub>O<sub>2</sub>,<sup>10</sup> electrochemical techniques,<sup>11</sup> coagulation–flocculation,<sup>12</sup> ion exchange,<sup>13</sup> membrane processes<sup>14</sup> and biosorption,<sup>15</sup> have been used to treat the various industrial effluents. Among these methods, chemical coagulation is a widely used method for the treatment of industrial effluent, due to its superior removal efficiency of toxic substances.<sup>16</sup> In chemical coagulation processes, aluminum and iron salts are widely used as coagulants that destabilize the colloidal materials and cause the small particles to agglomerate into larger settleable flocs; thus, effectively reducing the content of organic matter.<sup>17,18</sup> However, the chemical coagulation method has some disadvantages, such as large chemical addition, sludge generation,<sup>19</sup> economic viability and secondary pollution may arise.<sup>20</sup> Hence, there is critical need to identify an environmental friendly material that has the capability to treat industrial wastewaters efficiently without having any negative impact on the receiving environmental bodies.

Chitosan, which is derived from the de-acetylation of chitin, is one of the most predominantly employed polymeric materials for use as an adsorbent to treat different wastewaters, such as seafood processing wastewater,<sup>21</sup> milk processing wastewater,<sup>22</sup> brewery wastewater,<sup>23</sup> textile wastewater,<sup>24</sup> pulp and paper mill wastewater,<sup>25</sup> olive oil industry wastewater<sup>26</sup> and metal industry wastewater,<sup>27</sup> because of its biodegradability, biocompatibility, adsorption properties and possibilities of regeneration.<sup>28</sup> Moreover, the sludge produced from the chitosan can be efficiently degraded by micro-organisms<sup>29</sup> without causing any harmful effects on ecological systems. An extensive literature survey showed that no research reports are available for the treatment of egg processing industrial wastewater using chitosan as an adsorbent. Hence, the objective of the present study was to investigate and optimize the effects of the operating parameters, such as pH, chitosan dose, settling time and initial concentration on reduction percentage of turbidity, *COD* and *BOD*, on the treatment of wastewater from the egg processing industry. Different isotherms and kinetics models were employed to describe the obtained results. Finally, from the experimental data, second order polynomial models were developed for the responses (turbidity, *COD* and *BOD* reduction) using a four-factor, three-level Box–Behnken response surface design (BBD). BBD is a spherical, revolving response surface methodol-

ogy (RSM) design that consists of a central point and the middle points of the edges of a cube circumscribed on a sphere, which is useful for developing and understanding the performance of complex systems.<sup>30</sup>

## EXPERIMENTAL

### Wastewater sample

Egg wastewater samples were collected from an egg processing industry located in Erode, Tamilnadu, India. The samples were stored at  $\leq 5$  °C in order to avoid changes in the physico-chemical characteristics of the effluent. Chitosan (fine white powder), hydrochloric acid (98.5 % of purity) and sodium hydroxide (98 % of purity) were obtained from Merck Chemicals, Chennai, Tamilnadu, India. The characteristics of effluent used in the present study are given in Table I.

TABLE I. Characteristics of the egg processing industry wastewater

Characteristic	Value
Turbidity, NTU	306–832
<i>COD</i> / mg L <sup>-1</sup>	1574–4000
<i>BOD</i> / mg L <sup>-1</sup>	894–2185
pH	6.9–7.5
Conductivity, mS cm <sup>-1</sup>	0.588–0.724
Total dissolved solids, mg L <sup>-1</sup>	3120–3876

### Experimental procedure

Conventional batch studies were performed with different dosages of chitosan (0.7–1.3 g L<sup>-1</sup>) in 100 mL of composite wastewater of pH values in the range 2–7. The pH of the effluent was measured and adjusted with 0.1M HCl or NaOH solutions. Then the samples were agitated (1 min at 100 rpm followed by 3 min at 40 rpm) in a combined incubator and shaker (GeNei™ OS-250, India) and then allowed to settled down. The clear supernatant effluent was centrifuged (Remi R-24 Centrifuge, India) and filtered through a 0.45 µm filters. The *COD* and *BOD* content of the filtered effluent were analyzed by the procedures suggested by the American Public Health Association (APHA) standard method of examination of water and wastewater.<sup>31</sup> The turbidity of samples was determined using a turbidity meter (Elico CL52D, India). All the adsorption experiments were performed in triplicate to check the reproducibility of the results. The value of  $q_e$  was calculated using the following equation:<sup>32</sup>

$$q_e = \left( \frac{c_0 - c_e}{w} \right) V \quad (1)$$

The value of  $q_t$  was calculated using the following equation:<sup>32</sup>

$$q_t = \left( \frac{c_0 - c_t}{w} \right) V \quad (2)$$

where,  $c_0$  is initial *COD* concentration and  $c_t$  is concentration of *COD* at time  $t$ ,  $V$  is the volume of the wastewater sample (L), and  $w$  is the weight of the chitosan used (g). The reduction efficiency (*RE*) was calculated by the following equation:<sup>33</sup>

$$RE = \left( \frac{c_0 - c_e}{c_0} \right) \times 100 \quad (3)$$

where,  $c_0$  and  $c_e$  are the initial and after treatment concentrations, respectively, of *COD* or *BOD*, or the turbidity.

#### Fourier-transform infrared red (FT-IR) spectroscopic analysis

The FT-IR spectra of chitosan (raw and after adsorption process) were recorded on an FT-IR spectrometer (Instrument model RX<sub>1</sub>, India) in the range of 4000–400 cm<sup>-1</sup> using potassium bromide (KBr) pellets.

#### Statistical analysis

Different statistical parameters such as standard absolute errors (*SAE*),<sup>34</sup> the Marquardt percent standard deviation (*MPSD*) and average relative error (*ARE*)<sup>35</sup> were used to analyze the various isotherms and kinetic models. The following equations were used to evaluate the different statistical parameters

$$SAE = \sum_{i=1}^n |q_{e,cal} - q_{e,exp}|_i \quad (4)$$

$$MPSD = 100 \sqrt{\frac{\sum_{i=1}^n \left( \frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right)^2}{n - p}} \quad (5)$$

$$ARE = \frac{100}{n} \sum_{i=1}^n \left| \frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right|_i \quad (6)$$

where,  $p$  is the number of parameters in the isotherm equation and  $n$  is the number of data points.

#### Box–Behnken (BBD) design

Response surface methodology (RSM) is an empirical statistical modeling technique employed for multiple regression analysis using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously.<sup>36</sup> In the present study, a three-level, four-factor BBD was employed to study the effect of process variables such as the initial *COD* concentration, pH, adsorbent dose and settling time on the reduction efficiency of turbidity, *COD* and *BOD*. The process variables were coded at three levels (low, middle and high, *i.e.*, -1, 0 and +1, respectively) for statistical calculations and the design is given in Table II. The coding of the process variables were realized according to the following equation:<sup>37</sup>

$$x_i = \frac{X_i - X_{cp}}{\nabla X_i} \quad (7)$$

where  $x_i$  is a dimensionless value of an independent variable;  $X_i$  is the real value of an independent variable;  $X_{cp}$ , is the real value of an independent variable at the center point and  $\nabla X_i$  is the step change of the real value of variable  $i$ , corresponding to a variation of a unit for the dimensionless value of the variable  $i$ .

A total number of 29 experiments were performed in a randomized order. A second order polynomial model was used to fit the experimental data in order to develop mathematical

models to represent the predicted experimental data using a statistical software package (Stat ease design expert 8.0.7.1). The generalized second order polynomial equation is given below:<sup>37</sup>

$$Y = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum_{i < j=2}^k \beta_{ij} x_i x_j + e_i \quad (8)$$

where  $Y$  is the response;  $x_i$  and  $x_j$  are variables ( $i$  and  $j$  ranged from 1 to  $k$ );  $\beta_0$  is the model intercept coefficient;  $\beta_j$ ,  $\beta_{jj}$  and  $\beta_{ij}$  are interaction coefficients of linear, quadratic and the second-order terms, respectively;  $k$  is the number of independent parameters ( $k = 4$  in this study); and  $e_i$  is the error.

TABLE II. Ranges of the independent variables and their levels

Variable	Factor $X$	Level		
		-1	0	1
Initial $COD$ concentration, $mg\ L^{-1}$	$X_1$	1574	2786	4000
pH	$X_2$	3	4	5
Chitosan dosage, $g\ L^{-1}$	$X_3$	0.9	1.1	1.3
Settling time, min	$X_4$	10	30	50

## RESULTS AND DISCUSSION

### Effects of pH

The effects of different pH values in the range 2–7 on the reductions of turbidity,  $COD$  and  $BOD$  were examined. It was observed (Fig. 1) that the reduction percentages of turbidity,  $COD$  and  $BOD$  all increased with increasing pH up to 4. In acidic pH, chitosan forms  $-NH_3^+$  groups that attract the negatively charged organic matter in the wastewater,<sup>38</sup> which increased the reduction percentage of turbidity,  $COD$  and  $BOD$  (88, 80 and 76 %, respectively). Above pH of 4, the positive charge on the chitosan surface decreased<sup>39</sup> and it became insoluble,<sup>40</sup> which negatively affected the treatment process and decreased the reduction percentage of turbidity,  $COD$  and  $BOD$ .

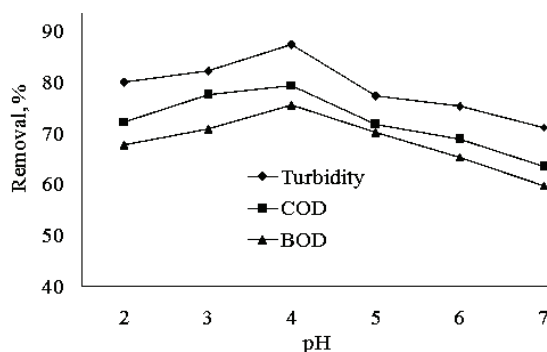


Fig. 1. Effect of pH on the reduction percentage of turbidity,  $COD$  and  $BOD$  (chitosan dosage =  $0.9\ g\ L^{-1}$  and settling time = 50 min).

### Effects of chitosan dosage

The effects of chitosan dosage on the treatment process were evaluated at different levels (0.7–1.3 g L<sup>-1</sup>). As shown in Fig. 2, the reduction percentage of turbidity, *COD* and *BOD* increased with increasing chitosan dosage up to 1.1 g L<sup>-1</sup> and the maximum percentage reductions were found to be: turbidity, 94 %; *COD*, 88 % and *BOD*, 83 %. This is mainly because higher dosages of chitosan increase the number of exchangeable reaction sites<sup>41</sup> available for an effective reduction process of organic matters in the effluent, which could increase the reduction percentage. Beyond a chitosan dosage of 1.1 g L<sup>-1</sup>, no significant effect on the reduction percentage of turbidity, *COD* and *BOD* were observed.

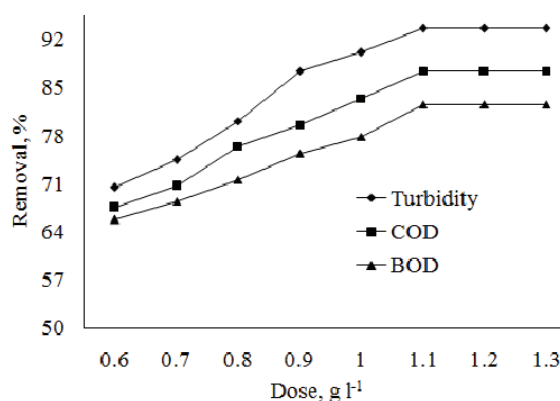


Fig. 2. Effect of the adsorbent dose on the reduction percentage of turbidity, *COD* and *BOD* (pH 4 and settling time = 50 min).

### Effect of settling time

To study the effective settling time on the treatment process, studies were performed at different settling times in the range from 10–60 min. The bridging flocculation mechanism of chitosan enhances the compact nature and strength of flocs,<sup>42</sup> which could affect the treatment process significantly. The reduction percentage of turbidity, *COD* and *BOD* increased with settling time up to 40 min resulting in values of 94, 88 and 83 %, respectively (Fig. 3). Thereafter, no significant changes were observed in the reduction percentage of turbidity, *COD* and *BOD*.

### Effects of initial concentration

The effects of the initial concentration on the reduction percentage of turbidity, *COD* and *BOD* are shown in Fig. 4, from which it was found that reduction percentages of turbidity were 96, 95 and 94 % for initial values of 306, 416 and 832 NTU, respectively (Fig. 4A). Moreover, the *COD* reduction was found to be 91, 90 and 88 % for initial concentrations of 1574, 2786 and 4000 mg L<sup>-1</sup>,

respectively (Fig. 4B) and *BOD* reduction was found to be 85, 84 and 83 % for initial concentrations of 894, 1324 and 2185 mg L<sup>-1</sup>, respectively (Fig. 4C) under treatment process conditions of pH 4 and a chitosan dosage of 1.1 g L<sup>-1</sup>. From the results, it was observed that longer settling times are required to enhance the reduction percentage of turbidity, *COD* and *BOD* when their values are higher.<sup>43</sup>

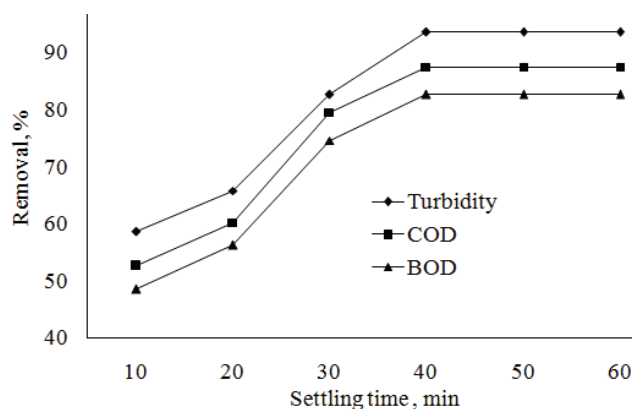


Fig. 3. Effect of settling time on the percentage removal of turbidity, *COD* and *BOD* (pH 4 and chitosan dosage = 1.1 g L<sup>-1</sup>).

#### FT-IR analysis

FT-IR spectrophotometric measurements were used to study the mechanism of the treatment process and it is shown in Fig. 5. Curve A shows that, the broad band at 3402 cm<sup>-1</sup> (N–H stretching) and the peaks at 1604 and 1415 cm<sup>-1</sup> (N–H bending vibration and N–H deformation) indicating the presence of –NH<sub>2</sub> groups on raw chitosan and the band at 1371 cm<sup>-1</sup> exhibited the presence of O–H group. Both of these functional groups on raw chitosan can serve as reaction sites for the present treatment process.<sup>44</sup> From Fig. 5, it was found that, transmittance shifted from 3402 cm<sup>-1</sup> (curve A) to lower wave number 3287 cm<sup>-1</sup> (curve B) shows the interaction between chitosan and organic matters and also disappearance of the peak at 1604 cm<sup>-1</sup> (curve A) and the formation of a new peak at 1640 cm<sup>-1</sup> (curve B) was related to consumption of –NH<sub>2</sub> groups.<sup>45</sup> It could be concluded that, both –NH<sub>2</sub> and –OH groups were involved in this treatment process.

#### Isotherms

In this study, various isotherm equations, *i.e.*, the Langmuir (type I–IV), Freundlich, Tempkin, and Dubinin–Radushkevich (D–R) models<sup>35</sup> were used to describe the present treatment process. The isotherm parameters and statistical error values for the models are given in Table III. The separation factor ( $R_L$ ) in Langmuir isotherm models can be used to verify whether the adsorption process is favorable ( $0 < R_L < 1$ ), irreversible ( $R_L = 0$ ), linear ( $R_L = 1$ ) or unfavorable

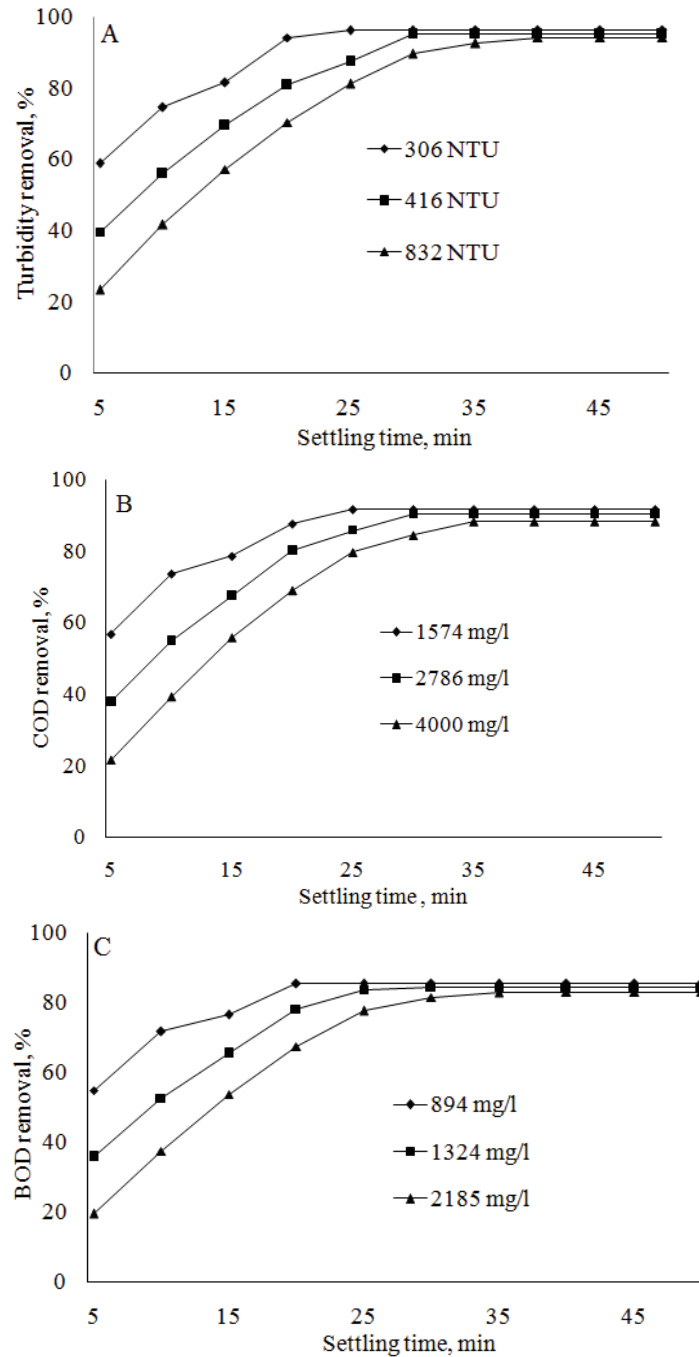


Fig. 4. The effect of initial concentration on reduction percentage of turbidity (A), COD (B) and BOD (C) (pH 4 and chitosan dosage = 1.1 g L<sup>-1</sup>).



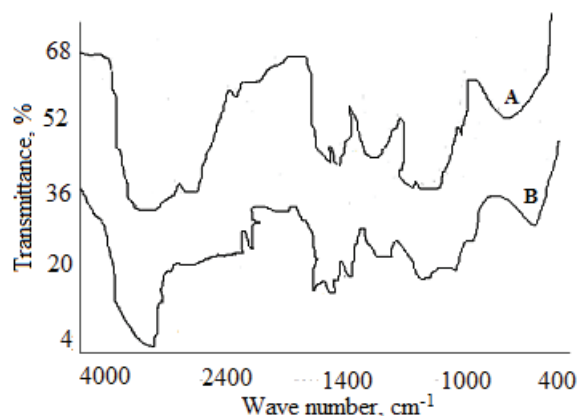


Fig. 5. FT-IR spectra of raw chitosan (A) and after treatment (B).

TABLE III. Isotherm parameters and error analysis values for *COD* reduction; conditions: pH 4; wastewater, 100 mL; adsorbent dose, 1.1 g L<sup>-1</sup>; *SAE*, sum of absolute errors; *MPSD*, Marquardt percent standard deviation; *ARE*, average relative error

Parameter	Langmuir I	Langmuir II	Langmuir III	Langmuir IV	Freundlich	Tempkin	Dubinin–Radushkevich
$q_m$	735.73	781.58	743.04	0.008	$K_F$ 1.85	$q_T$ 149.56	$q_{D-R}$ 785.88
$K_L$	0.001	655.49	743.04	149.56	$n$ 1.40	$K_T$ 0.01	$\beta$ 0.0026
$R_L$	0.27	0.00	0.00	0.00	$1/n$ 0.71	$B_T$ 16.84	$E$ 0.11
Statistical error analysis							
Parameter	Langmuir I	Langmuir II	Langmuir III	Langmuir IV	Freundlich	Tempkin	Dubinin–Radushkevich
<i>SAE</i>	1.70	650.53	612.00	131.03	1673.12	116.56	951.70
<i>MPSD</i>	1.30	496.44	467.03	99.99	1276.80	88.95	726.27
<i>ARE</i>	1.28	83.23	82.36	<1000	92.74	804.97	87.89

( $R_L > 1$ ).<sup>46</sup> In this study, the  $R_L$  values ranged from 0 to 0.27, which indicate the Langmuir isotherm model can hardly describe the studied system. In the case of the Freundlich isotherm, the  $K_F$  parameter (heterogeneity factor) can be used to indicate whether the process is linear ( $K_F = 1$ ) or whether a chemical process ( $K_F < 1$ ) or physical process ( $K_F > 1$ ) is favorable. The value of  $K_F$  obtained in this study was 1.85, which indicates that a physical process was favorable for the studied system. In the Tempkin isotherm model, the positive value of the  $B_T$  constant (16.84) showed that the studied system was exothermic in nature. From the Table III, the estimated values of the D–R constants do not represent the experimental data for the reduction of *COD* satisfactorily. The best fitting of the Langmuir (type I–IV), Freundlich, Tempkin, and Dubinin–Radushkevich (D–R) models were analyzed by three different error functions, *i.e.*, *SAE*, *MPSD* and *ARE*, and it was found (Table III) that the Langmuir type I isotherm was the best

model (lowest statistical error value) to describe the present treatment process adequately.

### Kinetics

Two kinetic models, *i.e.*, pseudo-first-order and pseudo-second-order (type I–IV), were employed to evaluate the present study and the results are given in Table IV. From the Table IV, it could be seen that the  $q_e$  values calculated using the pseudo-second-order kinetic models did not fit the experimental  $q_e$  values as well as those calculated using the pseudo-first-order kinetic model. The statistical error analysis results also indicated that the pseudo-first-order kinetic model fitted well the obtained experimental data (Table IV). From these results, it was confirmed that the present system followed pseudo-first-order kinetics.

TABLE IV. Kinetic parameters and error analysis values for COD reduction; conditions: pH 4; wastewater, 100 mL; adsorbent dose, 1.1 g L<sup>-1</sup>

Kinetic model	COD Concentration mg L <sup>-1</sup>	$q_{e,exp}$ mg g <sup>-1</sup>	$q_{e,cal}$ mg g <sup>-1</sup>	SAE	MPSD	ARE
Pseudo-first-order model						
Lagergren	1574	131.04	120.38	10.66	8.13	8.86
	2786	229.16	221.86	7.30	3.19	3.29
	4000	320.87	386.71	65.84	20.52	17.03
Pseudo-second-order model						
Type I	1574	131.04	155.47	24.43	18.64	15.71
Type II		131.04	0.01	131.03	99.99	< 1500
Type III		131.04	151.52	20.48	15.63	13.52
Type IV		131.04	152.99	21.95	16.75	14.35
Type I	2786	229.16	333.37	104.21	45.47	31.26
Type II		229.16	0.00	229.16	100.00	< 1500
Type III		229.16	308.12	78.96	34.46	25.63
Type IV		229.16	319.23	90.07	39.30	28.21
Type I	4000	320.87	912.53	591.66	184.39	64.84
Type II		320.87	0.00	320.87	100.00	<1500
Type III		320.87	913.09	592.22	184.57	64.86
Type IV		320.87	920.21	599.34	186.79	65.13

### BBD analysis

The BBD consisted of 29 experimental runs with 5 center points and the experiments were performed according to the experimental design, and the results are listed in Table V. The statistical analysis was performed using Design Expert Statistical software package 8.0.7.1 (Stat Ease Inc., Minneapolis, USA). The adequacy of the models was justified by Pareto analysis of variance (ANOVA).

TABLE V. Box–Behnken experimental design and the obtained results

Run	COD Concentration mg L <sup>-1</sup>	pH	Chitosan dosage g L <sup>-1</sup>	Settling time min	Turbidity reduction %	COD Reduction %	BOD Reduction %
1	2786	3	1.3	30	30.58	28.76	25.67
2	2786	3	1.1	10	9.564	8.46	5.12
3	1574	3	1.1	30	45.85	43.54	40.25
4	1574	5	1.1	30	55.64	53.48	50.84
5	1574	4	1.1	10	65.45	63.47	60.54
6	4000	5	1.1	30	66.34	64.58	61.78
7	2786	5	1.3	30	66.247	64.28	61.72
8	2786	4	0.9	10	45.28	43.58	40.28
9	4000	4	1.3	30	92.54	90.28	87.58
10	2786	4	1.1	30	94.53	90.38	87.54
11	2786	5	0.9	30	64.28	63.54	60.24
12	2786	3	1.1	50	44.78	43.58	40.54
13	2786	4	1.3	10	55.64	54.28	51.42
14	2786	4	1.1	30	94.53	90.38	87.54
15	4000	4	1.1	50	94.28	90.28	87.32
16	2786	4	1.1	30	94.53	90.38	87.54
17	4000	4	0.9	30	85.24	83.56	80.46
18	2786	4	1.3	50	94.28	89.64	86.48
19	2786	4	1.1	30	94.53	90.38	87.54
20	2786	5	1.1	10	30.86	29.34	26.68
21	1574	4	0.9	30	88.64	86.42	83.54
22	4000	3	1.1	30	31.54	30.87	27.84
23	4000	4	1.1	10	34.58	32.84	29.64
24	2786	3	0.9	30	50.84	52.84	49.62
25	2786	5	1.1	50	64.58	63.48	60.48
26	2786	4	0.9	50	84.28	86.94	83.24
27	1574	4	1.1	50	94.25	90.28	87.48
28	2786	4	1.1	30	94.53	90.38	87.54
29	1574	4	1.3	30	94.28	90.78	87.54

#### *Development of mathematical equation and validation*

A second order polynomial equation (quadratic) with interaction terms was fitted to the experimental data obtained on the basis of BBD and the final equation obtained in terms of coded factors are given below:

$$\begin{aligned}
 Y_1 = & 94.53 - 3.30X_1 + 11.24X_2 + 1.25X_3 + 19.59X_4 + 6.25X_1X_2 + \\
 & + 0.42X_1X_3 + 7.73X_1X_4 + 5.56X_2X_3 - 0.37X_2X_4 - 0.09X_3X_4 - \quad (9) \\
 & - 3.26X_1^2 - 39.20X_2^2 - 2.83X_3^2 - 19.61X_4^2
 \end{aligned}$$

$$Y_2 = 90.38 - 2.96X_1 + 10.89X_2 + 0.09X_3 + 19.36X_4 + 5.94X_1X_2 + \\ + 0.59X_1X_3 + 7.66X_1X_4 + 6.21X_2X_3 - 0.25X_2X_4 - 2.00X_3X_4 - (10) \\ - 3.02X_1^2 - 37.23X_2^2 - 1.21X_3^2 - 18.55X_4^2$$

$$Y_3 = 87.54 - 2.96X_1 + 11.06X_2 + 0.25X_3 + 19.33X_4 + 5.84X_1X_2 + \\ + 0.78X_1X_3 + 7.69X_1X_4 + 6.36X_2X_3 - 0.41X_2X_4 - 1.97X_3X_4 - (11) \\ - 3.01X_1^2 - 37.27X_2^2 - 1.39X_3^2 - 18.71X_4^2$$

where,  $Y_1$ ,  $Y_2$  and  $Y_3$  are the predicted reduction percentages of the turbidity, *COD* and *BOD*, respectively, and  $X_1$ ,  $X_2$ ,  $X_3$  and  $X_4$  are the initial concentration, pH, adsorbent dose and settling time, respectively. The adequacy and fitness of the models were tested by analysis of the variance (ANOVA) and the results are listed in Table VI. Analysis of the variance followed by the Fisher statistical test (*F*-test) was applied to evaluate the significance of each variable. The high Fisher *F*-values of 89.34, 84.81 and 83.83 for turbidity, and *COD* and *BOD* reduction, respectively, imply that the developed model was statistically significant. The values of  $R^2$  were calculated to be 0.9760, 0.9753 and 0.9750 for turbidity, and *COD* and *BOD* reduction, respectively, which indicated that 97 % of experimental data was compatible. The values of adjusted- $R^2$  (0.8617 for turbidity, 0.8577 for *COD* and 0.8562 for *BOD*) were also high and showed a high corre-

TABLE VI. ANOVA table of the responses

Source	Turbidity reduction		<i>COD</i> Reduction		<i>BOD</i> Reduction	
	<i>RC</i>	<i>P</i> value	<i>RC</i>	<i>P</i> value	<i>RC</i>	<i>P</i> value
Model	94.5273	< 0.0001	90.3776	< 0.0001	17086.7	< 0.0001
$X_1$	-3.2992	0.0631	-2.9633	0.0856	105.435	0.0876
$X_2$	11.2362	< 0.0001	10.8908	< 0.0001	1468.29	< 0.0001
$X_3$	1.25081	0.4568	0.09533	0.9534	0.76768	0.8777
$X_4$	19.5939	< 0.0001	19.3567	< 0.0001	4481.88	< 0.0001
$X_{12}$	6.25243	0.0444	5.94252	0.0503	136.308	0.0555
$X_{13}$	0.4166	0.8851	0.59221	0.8341	2.44662	0.7837
$X_{14}$	7.72709	0.0163	7.65891	0.0153	236.33	0.0157
$X_{23}$	5.55675	0.0698	6.205	0.0421	161.671	0.0392
$X_{24}$	-0.374	0.8968	-0.245	0.9309	0.6561	0.8869
$X_{34}$	-0.09	0.9751	-2.00	0.4829	15.6025	0.4914
$X_1^2$	-3.2602	0.1646	-3.0192	0.1875	58.8518	0.1916
$X_2^2$	-39.204	< 0.0001	-37.225	< 0.0001	9009.27	< 0.0001
$X_3^2$	-2.8258	0.2244	-1.2067	0.5885	12.5701	0.5362
$X_4^2$	-19.614	< 0.0001	-18.548	< 0.0001	2271.5	< 0.0001
<i>CV</i> / %	8.37		8.47		8.94	
<i>AP</i>	22.39		22.23		22.16	
$R^2$	0.976		0.9753		0.975	
Adj- $R^2$	0.952		0.9506		0.9501	

lation between the observed and the predicted values. The low values of the correlation of variance (8.37, 8.47 and 8.94 for turbidity, *COD* and *BOD* reduction, respectively) clearly represent the high degree of precision and good reliability of the conducted experiments. An adequate precision measures the signal-to-noise ratio and compares the range of the predicted values at the design points to the average prediction error. A value of this ratio greater than 4 is desirable<sup>47</sup> and indicates adequate model discrimination. In the present study, the ratio was found to be >22.15 for all the responses, which indicates an adequate signal. Therefore, the quadratic model was used to navigate the design space. The validation of quadratic model was confirmed by diagnostic plots, such as the predicted vs. the experimental values (Fig. 6A, B and C). The data points on this plot lie reasonably close to a straight line and indicate an adequate agreement between the real data and the data obtained from the models.<sup>48</sup>

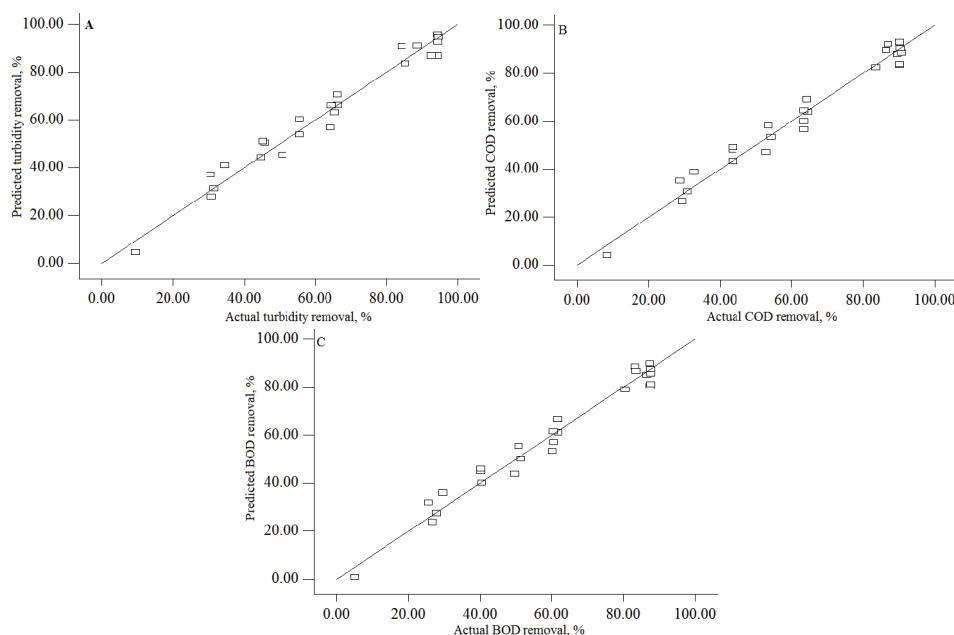


Fig. 6. Experiments vs. predicted plot for the reduction of turbidity (A), *COD* (B) and *BOD* (C).

#### CONCLUSION

The present investigation revealed that chitosan could be used to reduce the turbidity, *COD* and *BOD* from the wastewater from the egg processing industry. Under the optimum conditions of pH 4, a chitosan dosage of 1.1 g L<sup>-1</sup> and a settling time 40 min, the maximum reductions of turbidity, *COD* and *BOD* of 94, 88 and 83 %, respectively, were attained for initial values of 832 NTU, 4000 and

2185 mg L<sup>-1</sup>, respectively. The effective adsorption process was confirmed by FT-IR spectroscopy. Various isotherm and kinetic models were fitted to the experimental COD reduction data. Among the various isotherm models, the Langmuir isotherm Type I described the process adequately. From the kinetic studies, it was found that, the reduction rate of COD followed the pseudo-first-order kinetic model. The developed mathematical models using BBD provided a very high degree of correlation with the experimental data and showed all the independent variables have a significant effect on the responses.

## ИЗВОД

ТРЕТИРАЊЕ ЕФЛУЕНТА У ИНДУСТИЈИ ПЕРЕРАДЕ ЈАЈА КОРИШЋЕЊЕМ ХИТОСАНА  
КАО АДСОРБЕНТА

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Циљ ове студије је био да се испита ефикасност хитосана као адсорбента за третман отпадних вода из индустрије прераде јаја. Одређивани су параметри који утичу на процес адсорпције, као што су рН, доза адсорбента, време деловања и почетна концентрација хемијске потрошње кисеоника (BOD) на проценат умањења замућености, НРК и биохемијске потрошње кисеоника (COD). Нађено је да су оптимални услови рН 4; доза хитосана 1,1 g L<sup>-1</sup> и време деловања 40 min. Максимално смањење замућености, BOD и COD били су 94, 88 и 83 %. Ефективни процес адсорпције био је потврђен FTIR спектралном анализом. Експериментални резултати су били анализирани коришћењем различитих изотерми и кинетичких модела. Лангмирова (*Langmuir*) изотерма типа I на задовољавајући начин је описала адсорпциони механизам, а брзина опадања НРК пратила је кинетички модел псеудо-првог реда. На основу експерименталних података развијени су математички модели са полиномима другог реда коришћењем методе Бокс–Бенкенове (*Box–Behnken*) повшине са три нивоа.

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## REFERENCES

1. C. Allegre, M. Maisseu, F. Charbit, *J. Hazard. Mater.* **116** (2004) 57
2. B. Sarkar, P. P. Chakrabarti, A. Vijaykumar, V. Kale, *Desalination* **195** (2006) 141
3. S. Lacorte, A. Latorre, D. Barceló, A. Rigol, A. Malmqvist, T. Welander, *Trends Anal. Chem.* **725** (2003) 22
4. R. E. Carawan, J. V. Ahambers, R. R. Zall, *The North Carolina Agricultural Extension Service, Raleigh. NC.* **81** (1979) 785
5. J. P. Guyot, H. Macarie, A. Noyola, *Appl. Biochem. Biotechnol.* **25** (1990) 579
6. G. R. Pophali, R. Khan, R. S. Dhodapkar, T. Nandy, S. Devotta, *J. Environ. Manage.* **85** (2007) 1024
7. E. Neyens, J. Baeyens, *J. Hazard Mater.* **98** (2003) 33
8. V. Fontanier, V. Farines, J. Albet, S. Baig, J. Molinier, *Water Res.* **40** (2006) 303
9. E. Brillas, J. C. Calpe, J. Casado, *Water Res.* **34** (2000) 2253
10. Y. Yang, D. T. Wyatt, M. Bahorsky, *Text. Chem. Color.* **30** (1998) 27
11. G. Chen, *Sep. Purif. Technol.* **38** (2004) 11
12. A. A. Tatsi, A. I. Zouboulis, K. A. Matis, P. Samaras, *Chemosphere* **53** (2003) 737

13. A. H. Elshazly, A. H. Konsowa, *Desalination* **158** (2003) 189
14. C. Bhattacharjee, P. K. Bhattacharya, *Sep. Purif. Technol.* **49** (2006) 281
15. P. Lodeiro, R. Herrero, M. E. Sastre de Vicente, *Environ. Chem.* **3** (2006) 400
16. F. M. Menezes, R. Amal, D. Luketina, *Powder Technol.* **88** (1996) 27
17. J. Xu, B. W. Sheldon, R. E. Carawan, D. K. Larick, A. C. Chao, *Poult. Sci.* **80** (2001) 57
18. R. J. Stephenson, S. J. B. Duff, *Water Res.* **30** (1996) 781
19. A. A. Tatsi, A. I. Zouboulis, K. A. Matis, P. Samaras, *Chemosphere* **53** (2003) 737
20. F. W. Pontius, *J. Am. Waterworks Assoc.* **92** (2000) 18
21. W. A. Bough, *Process Biochem.* **11** (1976) 13
22. F. H. Chi, W. P. Cheng, *J. Polym Environ.* **14** (2006) 411
23. W. P. Cheng, F. H. Chi, R. F. Yu, Y. C. Lee, *J. Polym. Environ.* **13** (2005) 383
24. E. Guibal, J. Roussy, *React. Funct. Polym.* **67** (2007) 33
25. A. C. Rodrigues, M. Boroski, N. S. Shimada, J. C. Garcia, J. Nozaki, N. Hioka, *J. Photochem. Photobiol., A* **194** (2008) 1
26. B. Meyssami, A. B. Kasaeian, *Bioresour Technol.* **96** (2005) 303
27. A. Gamage, F. Shahidi, *Food Chem.* **104** (2007) 989
28. N. V. Ravi Kumar, *React. Funct. Polym.* **46** (2000) 1
29. F. H. Chi, W. P. Cheng, *J. Polym. Environ.* **14** (2006) 411
30. J. Prakash Maran, V. Sivakumar, R. Sridhar, V. Prince Immanuel, *Ind. Crop. Prod.* **42** (2013) 159
31. L. S. Clesceri, A. E. Greenberg, A. D. Eaton, *Standard Methods for Examination of Water & Wastewater*, 21<sup>st</sup> ed., American Public Health Association (APHA), American Water Works Association (AWWA) & Water Environment Federation (WEF), Washington DC, 2005, pp. 5210–5520B
32. J. Zhu, H. Zhao, J. Ni, *Sep. Purif. Technol.* **56** (2007) 184
33. B. Krajewska, *Sep. Purif. Technol.* **41** (2005) 305
34. I. D. Mall, V. C. Srivastava, N. K. Agarwal, I. M. Mishra, *Colloids Surfaces, A* **264** (2005) 17
35. B. Kayranli, *Chem. Eng. J.* **173** (2011) 782
36. J. P. Maran, V. Sivakumar, R. Sridhar, K. Thirugnanasambandham, *Carbohydr. Polym.* **92** (2013) 1335
37. R. Sridhar, V. Sivakumar, V. Prince Immanuel, J. Prakash Maran, *Environ. Prog. Sustain. Energy* **31** (2012) 558
38. R. P. Jill, H. S. C. Chihpin, C. C. Ying, *Colloids Surfaces, A* **147** (1999) 359
39. A. L. Ahmad, S. Sumathi, B. H. Hameed, *Water Res.* **39** (2005) 2483
40. M. A. A. Hassan, T. P. Li and Z. Z. Noor, *J. Chem. Nat. Res. Eng.* **4** (2009) 43.
41. K. Thirugnanasambandham, V. Sivakumar, J. Prakash Maran, *Carbohydr. Polym.* **97** (2014) 451
42. A. L. Ahmad, S. Sumathi, B. H. Hameed, *Chem. Eng. J.* **118** (2006) 99
43. D. Asandei, L. Bulgariu, E. Bobu, *Cell. Chem. Technol.* **43** (2009) 211
44. T. S. Anirudhan, S. Rijith, *Colloids Surfaces, A* **351** (2009) 52
45. A. Pawlak, M. Mucha, *Thermochim. Acta* **396** (2003) 153
46. V. Vimonses, L. Shaomin, J. Bo, C. W. K. Chow, S. Chris, *Chem. Eng. J.* **148** (2009) 354
47. J. Prakash Maran, S. Manikandan, K. Thirugnanasambandham, C. V. Nivetha, R. Dinesh, *Carbohydr. Polym.* **92** (2013) 604
48. P. M. Jeganathan, S. Venkatachalam, T. Karichappan, S. Ramasamy, *Prep. Biochem. Biotech.* **44** (2014) 56.