Pollution, 5(3): 623-636, Summer 2019
DOI: 10.22059/poll.2019.271649.552
Print ISSN: 2383-451X Online ISSN: 2383-4501
Web Page: https://jpoll.ut.ac.ir, Email: jpoll@ut.ac.ir

Modeling and Optimization of the Coagulation–Flocculation Process in Turbidity Removal from Aqueous Solutions Using Rice Starch

Usefi, S. and Asadi-Ghalhari, M.[*]

Research Center for Environmental Pollutants, Qom University of Medical Sciences, Qom, Iran

Received: 16.12.2018 Accepted: 29.03.2019

ABSTRACT: Natural coagulants have received much attention for turbidity removal, thanks to their environmental friendliness. The present study investigates potential application of rice starch for removal of turbidity from aqueous solutions. It considers the effects of four main factors, namely settling time (40-140 min), pH (2-8), slow stirring speed (20-60 rpm), and rice starch dosage (0-200 mg/L), each at five levels, by means of central composite design. Results show that a quadratic model can adequately describe turbidity removal in case of non-autoclaved rice starch with statistics of R^2= 0.95, $R^2_{adj.}$= 0.91, $R^2_{pred.}$= 0.77, AP = 23.75, and CV = 4.77. It has also been found that the performance of non-autoclaved rice starch is superior to the autoclaved variety, in terms of removal efficiency and floc size. In the optimal point, predicted by the model, a removal efficiency equal to 98.4% can be attained, using non-autoclaved rice starch, which is higher than that of the autoclaved rice starch (71.29%). The significant effective parameters have proven to be settling time along with pH. Overall, rice starch can be considered a promising high potential coagulant for removal of turbidity from water or wastewater.

Keywords: Rice starch, high turbidity aqueous, response surface methodology.

INTRODUCTION

In addition to the aesthetic problems, turbidity can carry and/or protect water polluting agents such as microorganisms and heavy metals, thus it plays a significant role in overall pollution of water bodies and environmental risks. That is why it has received a great deal of interest to remove these stable material from drinking waters (Jafari Dastanaie et al., 2007; Nasrabadi et al., 2018; Nasrabadi, Ruegner, Sirdari, Schwientek, & Grathwohl, 2016). Coagulation-flocculation is a critical step in water and industrial wastewater treatment processes, applied for removal of turbidity from suspended particles and colloidal material (M. G. Antov, M. B. Šćiban, & N. J. Petrović, 2010). This process is accomplished most commonly via addition of conventional chemical or mineral-based coagulants such as alum, poly aluminum chloride, ferric chloride, and synthetic organic polymers. Although the effectiveness of these chemicals as coagulants is well-recognized, there are some major drawbacks related to their application, especially when used to supply drinking water, e.g., ineffectiveness at low-temperature conditions, relatively high procurement costs, production of large

---

[*] Corresponding Author Email: Mehdi.asady@gmail.com

sludge volumes, significant impact on pH of treated water, and detrimental effects on human health and environment. To counteract the mentioned drawbacks, it is desirable to replace these chemical coagulants with plant-based ones (Antov, Šćiban, & Prodanović, 2012; Dhivya, Ramesh, Gandhimathi, & Nidheesh, 2017). Nowadays, the degradable coagulant or flocculants, based on recycled materials, are an appropriate alternative to prevent the secondary damages of chemical coagulants on humans and the environment (S. Y. Choy, Prasad, Wu, Raghunandan, & Ramanan, 2014; Genest, Petzold, & Schwarz, 2015). Therefore, recent years have witnessed much attention paid to the feasibility of using natural and eco-friendly flocculating agents to reduce toxicity and treatment costs (Khiari, Dridi-Dhaouadi, Aguir, & Mhenni, 2010).

Natural coagulants have attracted more attention, thanks to their inherent advantages like broad availability, low cost, non-corrosiveness, environmental compatibility and degradability, high reactivity, and low sludge production (Huang, Liu, Li, & Yang, 2017; Huang et al., 2016a; Oladoja, 2015; Subramonian, Wu, & Chai, 2014; Wu, Liu, Yang, & Li, 2016; Zia, Zia, Zuber, Kamal, & Aslam, 2015). Cellulose, chitosan, and starch are three main reported natural coagulants used in coagulation processed, either as coagulant or flocculent. The high cost of chitosan and low water solubility of cellulose limit their usage in the treatment process (Du, Wei, Li, & Yang, 2017; Z. Liu, Huang, Li, & Yang, 2017). Starch is an abundant and inexpensive natural polymer in the world, the application of which as a coagulant has received a great deal of interest in turbidity removal from industrial wastewater. Its crystalline structure is disrupted when contacting hot water, which causes irreversible swelling of granules, followed by an increase in the viscosity. This is considered a potential favorite feature in the process of coagulation and flocculation of highly turbid effluents of industries (S. Y. Choy, K. N. Prasad, T. Y. Wu, M. E. Raghunandan, & R. N. Ramanan, 2016a). On the other hand, rice starch has more advantages than other starches due to its high stability, high acid resistance, and wide range of amylase to amylopectin ratios.

In recent years, many studies have reported the feasibility of applying natural coagulants for turbidity removal; however, the focus in most of these has been on investigation with one-variable-at-a-time (OVAT) methodology (Kukić, Šćiban, Prodanović, Tepić, & Vasić, 2015; Wu et al., 2016), in which the effect of main influential parameters are presented individually with the combined effects of two or more factors not getting investigated at all (Jiang, Joens, Dionysiou, & O'Shea, 2013). For these reasons, multivariate statistical strategies are more preferable to their traditional counterparts, as it identifies a combination of factors as well as the interactions among them, not to mention the cost- and time-effectiveness of such approaches. Moreover, it introduces a mathematical model to forecast the response, check the model adequacy, and determine the optimal settings for a specified response (Bingöl, Hercan, Elevli, & Kılıç, 2012; Foroughi et al., 2017; Shokoohi et al., 2017). Central Composite Design (CCD) may be considered the most appropriate subgroup of RSM. This strategy is able to estimate the parameters of quadratic model, construct sequential designs, recognize lack of fit, and use the blocks (Samarghandi, Khiadani, Foroughi, & Nasab, 2016). Thus, it has received a wide application for assessment of critical experimental conditions even in water and wastewater treatment (Folens, Huysman, Van Hulle, & Du Laing, 2017; Mourabet et al., 2012).

Consequently, this study aims at investigating the effect of rice starch on highly turbid aqueous solutions. For this, rice starch has been employed in two forms (non-autoclaved and autoclaved) for coagulation of highly turbid water. Afterwards, the governed behavior of the process, contributing to the main effective parameters has been modeled and optimized via CCD approach.

MATERIAL AND METHODS

All the chemicals used in this work were of analytical grade. Kaolin powder (Sigma-Aldrich, USA) was employed to simulate turbidity in the studied samples, with rice starch (Sigma Aldrich, USA) utilized as the natural coagulant in both autoclaved and non-autoclaved forms. The pH of samples was adjusted at 1 M HCl or NaOH solutions (Merck, Germany) and monitored with a SevenEasy pH meter (Mettler Toledo, Germany). Turbidity of the samples was measured, using a turbidimeter (AL250T-IR, Aqualytic, Germany). Scanning electron microscopy (FE-SEM, Hitachi S-4160, Japan) was employed to achieve detailed information on rice starch morphology before and after treatment of the turbidity-containing solution.

To evaluate the effect of gelatinization, starch was used in non-autoclaved and autoclaved forms so that the coagulant solutions could be obtained at a concentration of 3%. Non-autoclaved starch solution (NSS) was used directly (without any pre-processing) at the mentioned concentration. Autoclaved starch solution (ASS) was prepared by starch sterilization at 121 °C and 21.7 bar for 15 min. In order to prevent the solutions' hydration along with any other adverse interventions in the results, they were prepared freshly for each set of experimentations.

Turbidity-containing wastewater was prepared using kaolin powder (Sigma-Aldrich) as stated in detail elsewhere (Foroughi, Chavoshi, Bagheri, Yetilmezsoy, and Samadi, 2018). To put it briefly, 10 g of the powder was dehydrated at 105ºC over a 3-hour period, then to get dissolved in 50 mL of deionized water and stay at room temperature for 24 h. The suspension volume then reached 1 L, got completely agitated for 20 min, and was allowed to settle for an additional 4 h. Ultimately, almost 1 L of the supernatant was decanted as turbidity stock solution, stored in refrigerator for further experiments.

The study then examined the impacts of main effective parameters on removal of turbidity from aqueous solutions, using rice starch as a natural coagulant. Flocculation-coagulation process was modeled and optimized by considering four main effective parameters, i.e. rice starch dosage (mg/L), pH, time (min), and speed (rpm), each measured at five levels, using a central composite design (CCD). In general, CCD contains three main points, including a two-level factorial design as lower and upper bounds (coded ± 1), axial or star points (coded ± α), and several replications of the central point (coded 0) (Witek-Krowiak, Chojnacka, Podstawczyk, Dawiec, & Pokomeda, 2014). The α-value is the radius of the circumscribed sphere, which depends on the number of factors. In this study, it was 2, as calculated by Equation 1. The central points helped estimating the pure error as well as checking the model adequacy (Dong, Bortner, & Roman, 2016; Nair & Ahammed, 2015). The number of experiments in CCD approach got calculated according to Equation 2:

$$\alpha = \left(N_f\right)^{\frac{1}{4}} \quad (1)$$

$$\mathrm{N} = 2^{\mathrm{f}} + 2\mathrm{f} + \mathrm{C}_0 \quad (2)$$

where N_f indicates on the number of factors, and k and C_0 stand for the factorial and replicate number of the central point, respectively, (Said & Amin, 2016).

According to Equation 2, there were thirty-three experimental runs in order to investigate the effect of starch on turbidity removal, with Design-Expert software (version 8.1, Stat-Ease, Inc., Minneapolis, USA) used to design of the experiments and analyze the data. Table. 1 gives the variables and their levels in both coded and actual terms. The quadratic polynomial model (Equation. 3) was employed to correlate the response and operational factors.

$$\mathrm{Y} = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta b_i X_i X_j + \varepsilon \qquad (3)$$

where *Y* is the predicted response from the model (turbidity removal (%)); X_i and X_j, the independent parameters; b_0, the constant coefficient; and b_i, b_ii, and b_ij; the linear, quadratic, and interactions coefficients of the model, respectively. Also ε refers to the prediction error and *k* indicates the number of factors.

Models' adequacy and input parameters' effect on the responses was checked through analysis of variance (ANOVA) via statistical evaluation of *p*-value and *F*-value of the regression coefficients at 95 % confidence interval. Moreover, the fitness quality of the developed model was assessed by the coefficient of determination (R^2), adjusted coefficient of determination (R^2_{adj}), adequate precision (*AP*), and coefficient variation (*CV*). The interaction between independent factors and their respective effect on the response was visualized by three-dimensional response surface plots.

Table 1. Coded and actual values of numeric factors for NSS and ASS

Original factors	Coded levels				
	- α	**-1**	**0**	**+1**	**+α**
(A) Time, min	40	45	90	95	140
(B) pH	2	3.5	5	6.5	8
(C) Speed, rpm	20	30	40	50	60
(D) Starch dosage, mg/L	0	50	100	150	200

The coagulation and flocculation experiments were carried out, using a six-beaker jar-test apparatus (Aqualytic). For all jar-test studies, the procedure sequence was comprised of 60 s for rapid mixing at 120 rpm, 120 s for slow mixing at various speeds (viz. 20, 30, 40, 50, and 60 rpm), and different settling periods (viz. 40, 45, 90, 95, and 140 min) with no disturbance. In different tests, rice starch dosage (mg/L), pH, time (min), and speed (rpm) varied at different levels with Table 1 listing the values. Thirty-three tests were performed, based on CCD matrix for either autoclaved or non-autoclaved starch coagulants. For each experiment, as much as 500 mL of wastewater with a fixed turbidity of 170 NTU was introduced to each beaker, adjusted for pH, then to get mixed rapidly once a desired dosage of rice starch was added to it, so that it could be flocculated at a given time. After each test, about 20 mL of the supernatant was taken from 5 cm below the sample surface and measured for final turbidity concentration without more preparation process (e.g., filtration or centrifugation). The performance of each run was described by removal efficiency, calculated via Equation 4 (Rahmani, Foroughi, Noorimotlagh, and Adabi, 2016). All the experiments were conducted at the laboratory temperature.

$$RE\,(\%) = \left[1 - \left(\frac{\mathrm{Tur_f}}{\mathrm{Tur_i}}\right)\right] \times 100 \qquad (4)$$

where, RE is the removal efficiency (%) and $\mathrm{Tur_i}$ and $\mathrm{Tur_f}$ are the initial and final turbidity concentrations (NTU), respectively.

RESULTS AND DISCUSSION

The relation between the four independent variables (namely, rice starch dosage, flocculation speed, pH, and time) on one hand and the response (i.e., turbidity removal) on the other, were investigated through a CCD-generated experimental matrix. The obtained results were then adjusted to develop mathematical models for NSS and ASS, as presented in Equations 5 and 6, respectively. Table 2 shows the obtained and predicted responses for turbidity removal with ASS and NSS.

Table 2. CCD matrix and observed and predicted responses for NSS and ASS

Run no.	Time (min)	pH	Speed (rpm)	Dose (mg/L)	ASS		NSS	
					Observed values (%)	Predict values (%)	Observed values (%)	Predict values (%)
1	115	3.5	30	150	69.27	70.17	77.72	78.70
2	65	6.5	30	150	57	57.20	48.1	50.85
3	90	5	40	100	68.39	69.10	72.17	72.23
4	65	3.5	30	50	68.39	68.05	78.14	77.14
5	90	8	40	100	61.88	63.56	56.27	54.33
6	65	6.5	50	50	70.37	67.89	53.74	54.82
7	90	5	40	0	63.29	65.83	62.27	67.87
8	90	5	40	100	69.47	69.10	68.37	72.23
9	115	6.5	30	150	65.27	65.54	55.64	56.83
10	90	5	40	100	71.29	69.10	71.52	72.23
11	65	6.5	30	50	61.43	61.72	65.15	61.74
12	90	5	60	100	69.29	71.46	67.37	68.90
13	90	5	40	100	69.39	69.10	73.62	72.23
13	90	5	40	100	68.62	69.10	70.37	72.23
14	40	5	40	100	64.9	65.20	59.61	61.05
15	90	5	40	100	69.92	69.10	75.8	72.23
16	65	3.5	50	50	71.23	71.03	78.45	76.49
17	90	5	40	200	63.52	62.76	68.86	65.58
18	115	6.5	30	50	69.02	67.26	60.68	64.96
19	115	6.5	50	50	69.85	69.83	71.37	69.17
20	90	5	40	100	67.25	69.10	68.62	72.23
21	90	5	40	100	67.31	69.10	70.24	72.23
22	115	3.5	30	50	68.9	68.84	73.61	70.89
23	65	3.5	50	150	69.51	69.68	84.58	82.34
24	115	3.5	50	150	69.9	69.67	87.35	89.97
25	90	5	20	100	66.21	65.80	63.84	64.54
26	90	5	40	100	69.88	69.10	74.41	72.23
27	115	6.5	50	150	69.47	68.22	58.8	61.84
28	90	2	40	100	71.25	71.34	93.7	97.87
30	65	3.5	30	150	66.49	66.58	80.76	82.20
31	65	6.5	50	150	63.37	63.48	42.8	44.73
32	140	5	40	100	69.25	70.74	70.78	71.90
33	115	3.5	50	50	70	68.22	82.05	81.37

$$Y_{NSS} = +71.68 + 4.82\ A -21.77\ B +2.20\ C - 1.19\ D +9.47\ AB + 11.12\ AC + 2.76\ AD - 6.26\ BC -15.94\ BD +0.82\ CD -5.92\ A^2 + 3.87\ B^2 - 5.51\ C^2 - 5.55\ D^2 \tag{5}$$

$$Y_{ASS} = + 69.06 + 2.72\ A - 3.89\ B + 2.84\ C - 1.54\ D + 4.75\ AB - 3.60\ AC + 2.80\ AD + 3.19\ BC - 3.05\ BD + 0.13\ CD - 1.14\ A^2 - 1.65\ B^2 - 0.46\ C^2 - 4.81\ D^2 \tag{6}$$

Table 3 summarizes the results of ANOVA test for the two coagulants. The F-test and *p*-value were applied in order to measure the significance of the regression coefficients of each model and their corresponding terms were considered more significant in larger absolute F-value and smaller *p*-value. With a Fisher's F-value equal to 24.49 and 8.66 for NSS and ASS, respectively, along with *p*-value < 0.0001 for both, the models found to be significant. Besides, Lack of fit (LOF) was used to determine whether a developed model adequately described the functional relation between the experimental parameters and the response variable. LOF is based on comparison of residual to pure error from the replicated experimental design points (i.e., center points) and should be insignificant (Foroughi, Chavoshi, et al., 2018). The ANOVA results showed *p*-values of 0.14 and 0.19 for LOF of NNS and ANS models, respectively.

The models' prediction efficiency was evaluated by the correlation coefficient (R^2) that were fairly high (0.95 and 0.87 for NSS and ASS, respectively) to ensure a good correlation between the models' predicted and obtained values. On the one hand, close agreement of R^2 with $R^2_{adj.}$ values (0.91 and 0.77, for NSS and ASS, respectively) indicated little chance of including insignificant terms in the models. On the other hand, $R^2_{pred.}$ was in reasonable agreement with $R^2_{adj.}$ only for NSS model (0.77) but not for ASS one (0.42). Adequate Precision (AP) indicates range of the forecasted values to their average standard deviation and in an appropriate model should stay above 4 (Foroughi, Chavoshi, et al., 2018). AP values of 23.75 and 13.25 for NSS and ASS, respectively, ensured that the models could be employed for navigation within the design space. Precision and repeatability of the models were checked by the coefficient of variance (CV), which as a matter of fact represents the ratio of the standard deviation to the average (Nair & Ahammed, 2015). For a reproducible model, the CV should be below 10%. Here, CV values were 4.77 and 2.37 for NSS and ASS models, respectively, indicative of their reproducibility.

The models' adequacy was also evaluated by means of residuals-based diagnostic plots. In fact, residuals are different between the observed and forecasted responses and should be applied to navigate a model adequacy along with ANOVA (Foroughi, Rahmani, et al., 2018). Accordingly, distribution of the data was evaluated by normal probability plots (Fig. 1a), which in a minor deviation of the data from the straight line indicated their normality. The residuals versus predicted response plots (Fig. 1b) showed that the points experienced neither an ascending nor a descending trend, which supports the assumption of constant variance. The plots of internally studentized residuals versus experimental runs demonstrated independency of the residuals from experimental run order (Fig. 1c). All the presented plots in Fig. 1, revealed that both models were adequate to describe the turbidity removal through response surface methodology.

Table 3. ANOVA results of regression coefficients for turbidity removal by NSS and ASS

Source	Sum of Squares		df		Mean Square		F Value		*p*-value Prob > F		Status
	NSS	ASS	NSS	ASS	NSS	ASS	NSS	ASS	NSS	ASS	
Model	3742.45	309.14	14	14	267.32	22.08	24.49	8.66	< 0.0001	< 0.0001	significant
A-Time	139.39	44.25	1	1	139.39	44.25	12.77	17.35	0.0022	0.0006	
B-pH	2843.60	90.68	1	1	2843.60	90.68	260.55	35.56	< 0.0001	< 0.0001	
C-Speed	29.04	48.42	1	1	29.04	48.42	2.66	18.99	0.1202	0.0004	
D-Dose	8.47	14.18	1	1	8.47	14.18	0.78	5.56	0.3899	0.0299	
AB	89.78	22.54	1	1	89.78	22.54	8.23	8.84	0.0102	0.0082	
AC	123.77	12.98	1	1	123.77	12.98	11.34	5.09	0.0034	0.0368	
AD	7.62	7.83	1	1	7.62	7.83	0.70	3.07	0.4144	0.0968	
BC	39.25	10.16	1	1	39.25	10.16	3.60	3.98	0.0741	0.0613	
BD	254.08	9.32	1	1	254.08	9.32	23.28	3.65	0.0001	0.0720	
CD	0.67	0.02	1	1	0.67	0.02	0.06	0.01	0.8068	0.9372	
A^2	66.42	2.45	1	1	66.42	2.45	6.09	0.96	0.0239	0.3399	
B^2	28.37	5.14	1	1	28.37	5.14	2.60	2.02	0.1243	0.1727	
C^2	57.54	0.41	1	1	57.54	0.41	5.27	0.16	0.0339	0.6949	
D^2	58.38	43.79	1	1	58.38	43.79	5.35	17.17	0.0328	0.0006	
Residual	196.45	45.90	18	18	10.91	2.55					
Lack of Fit	143.88	32.26	10	10	14.39	3.23	2.19	1.89	0.1396	0.1891	not significant
Pure Error	52.57	13.64	8	8	6.57	1.71					
Cor Total	3938.90	355.04	32	32							

$R^2 = 0.95; 0.87$, $R^2_{adjusted} = 0.91; 0.77$, $R^2_{predicted} = 0.77; 0.43$, AP = 23.75; 13.25, CV = 4.77; 2.37, for NSS and ASS, respectively.

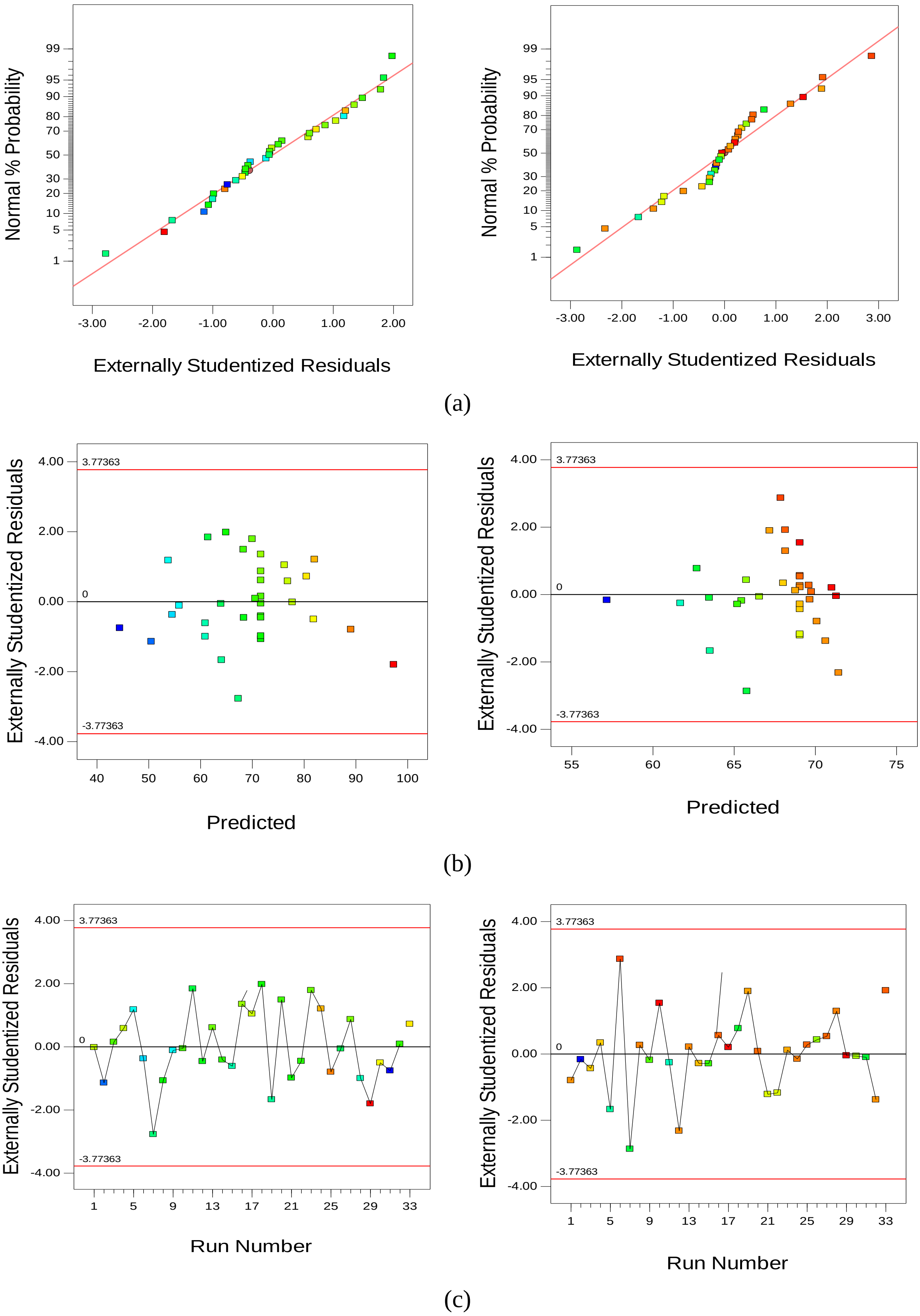


Fig. 1. Residual plots: a) normal probability, b) residuals versus predicted, and c) residuals versus runs for removal of turbidity using NSS (left) and ASS (right)

Fig. 2 illustrates SEM photographs of ASS and NSS stocks. Figs. 2a and 2b show that autoclaved starch molecules swelled as a result of water absorption, leading to an increase in their viscosity. In contrast, NSS showed a smooth, non-porous surface. As evident in Fig. 2c, the non-autoclaved starch was insoluble in water; its particles, getting deposited after a while.

Fig. 3 demonstrates the settled flocs of NSS and ASS. Comparison of two coagulants types in terms of floc formation shows that although the performance of both was excellent at similar conditions, the flocs of NSS were larger and better than ASS, supporting better efficiency of NSS for removal of the initial turbidity from wastewater (Fig. 3b). This uniformity and larger surface area of the flocs led to more collisions with turbidity particles and, therefore, better performance of NSS. SEM images did not show any significant change in the structure of either non-autoclaved or autoclaved starch solutions; only the latter was slightly crystallized due to water absorption. It seems that the adhesive properties of starch were much more important to eliminate the initial turbidity than its crystallization (S. Y. Choy et al., 2016a).

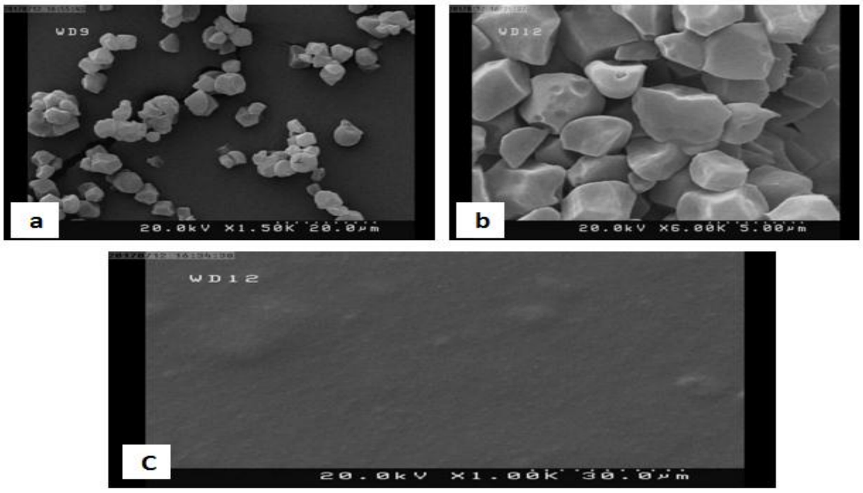


Fig. 2. SEM images of (a and b) ASS and (c) NSS

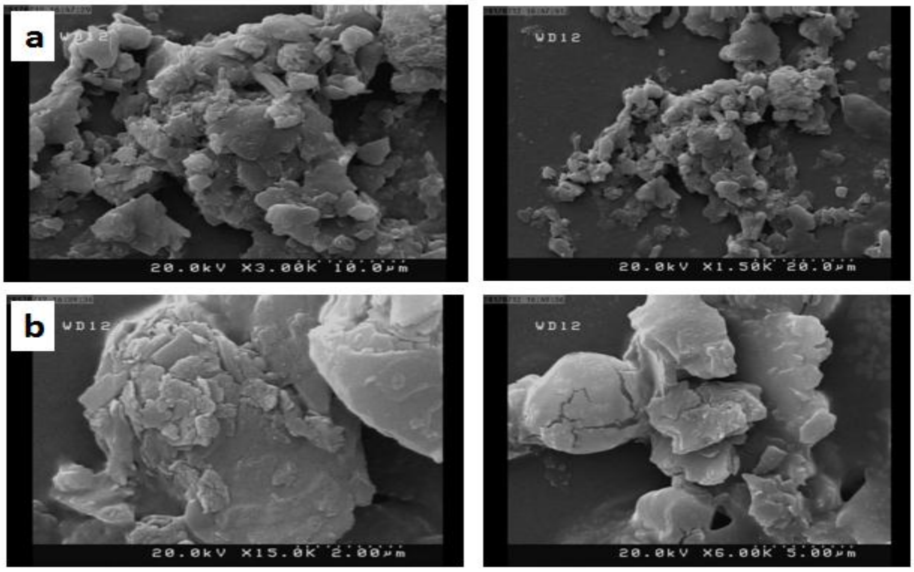


Fig. 3. SEM images for settled flocs after application of (a) ASS and (b) NSS

Figure 4 shows the relation between the studied variables and turbidity removal by NSS and ASS. As can be seen from this figure, turbidity removal got improved by decreasing pH, and increasing time, speed, and the coagulant dose for both forms of the used coagulants. It should be noted that more satisfied statistics and no need for pre-processing of the coagulant, turned NSS to an interesting option, compared to ASS. Therefore, the rest of this paper will discuss the results of NSS coagulant.

In general, coagulation is a highly pH-dependent process among different units employed in water/wastewater treatment. In this study, the use of rice starch as coagulant at low pHs resulted in maximum turbidity reduction (Fig. 4a), which can be contributed to pH effect on surface charges of both coagulant and pollutant. It seems that neutralization of the negatively-charged turbidity particles improved significantly at acidic pHs, leading to improvement of their destabilization and flocculation. On the other hand, negatively-charged groups on the coagulant were also protonated and neutralized in acidic pHs (Shamsnejati, Chaibakhsh, Pendashteh, & Hayeripour, 2015).

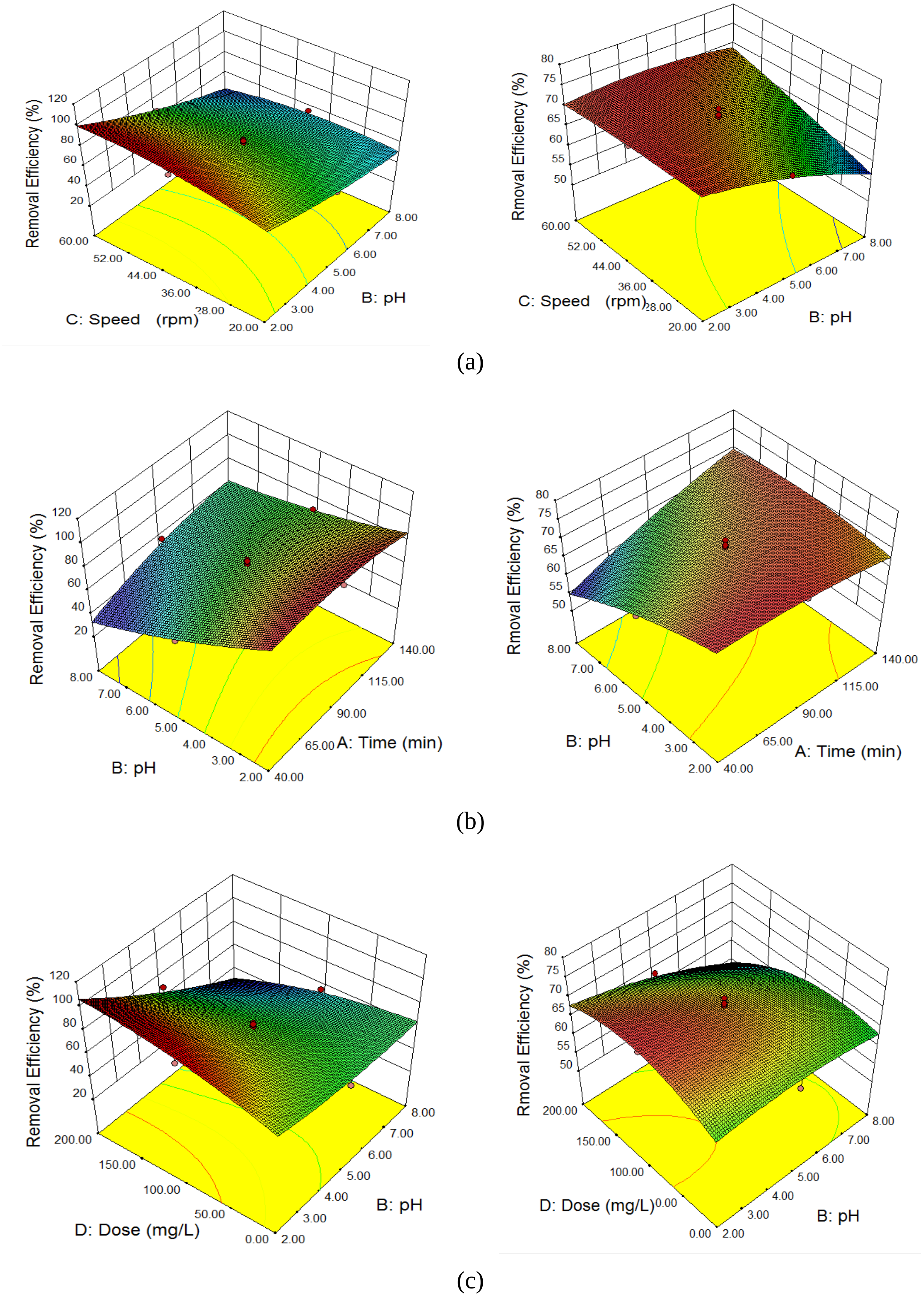
Depending on the type of coagulant, an effective coagulation can result from one of the following mechanisms or their combination: charge neutralization, adsorption, entrapment/sweep flocculation, and/or bridging. The latter plays the main role in coagulation when natural polymers and organic colloids are used as coagulant or coagulant aid, specifically in acidic environments. In fact, an inter-particle bridging mechanism is expected through the adsorption of polymer onto surface sites on the particle via hydrogen bonding. In this welcomed phenomenon, bridges also entrap bind multiple colloids together. The high molecular weight of polymers and their long chain length is favorite for bridging or attachment to a greater number of particles. Therefore, an effective polymer bridging can ensure a high efficiency of turbidity removal (S. Choy, Prasad, Wu, & Ramanan, 2015; Shak & Wu, 2014; Yang, Li, Huang, Yang, & Li, 2016). However, the success of bridging flocculation is mainly influenced by zeta potential of the coagulant. It is reported that zeta potential of rice starch declined when pH rose from 2 to 12, regardless of its protein content. Generally, in acidic conditions, the protonation of a nitrogen pair of amino groups in protein converts it to a positively-charged ($–NH_3^+$) species, while carboxyl group of protein remains as zwitterion form (–COOH) (Teh, Wu, & Juan, 2014). With negative zeta potential of turbidity, lower pH could accelerate the adsorption process of the particles into NSS polymer chain, resulting in higher turbidity removal. On the other hand, at high pHs, carboxyl groups of the proteins turn into negatively-charged ($–COO^-$) species while some amino groups become neutral ($–NH_3$). These phenomena cause repulsion between the particles and the polymer chain, which could discourage the bridging flocculation process (Teh et al., 2014). Hence, lower pH was desirable in the present study when NSS was used as a primary coagulant in treatment of wastewater-containing turbidity. As it is clear from Table. 2, another significant effective factor on turbidity removal by rice starch is sedimentation time (*p*-value = 0.0022 for NSS), due to the fact that by increasing the time, the fine firstly-developed flocs have more opportunity to grow and/or settle (Cho, Lee, & Lee, 2006). In fact, the fine flocs have more chance to aggregate and form large flocs, capable of settling down, in longer times (Xiao, Simcik, & Gulliver, 2013). Coagulant dosage turned out to have an insignificant positive effect on the process, which is not in agreement with the study of Liu et. al. (T. Liu, Chen, Yu, Shen, & Gregory, 2011), who reported that removal efficiency of humic acid probably depended on overall coagulant dose instead of coagulation condition. This would be due to a constant turbidity value in this study. Since bridging mechanism can be improved at high concentrations of turbidity (Association & Edzwald, 2010), while in fixed values the reactions cannot show any dramatic change. No significant effect of slow mixing rate (*p*-value = 0.12) indicates that the process can be performed at lower levels of the speed range that is important from operational, economic, and retention time perspectives.

- By defining all parameters within their studied ranges as well as turbidity removal (%) at the maximum value, the optimum condition for NSS was introduced, using desirability function (DF) approach as follows: settling time = 60 min, pH = 2.37, slow stirring speed = 37 rpm, and dosage = 113 (mg/L). At that optimal point, turbidity removal was predicted 94.8%, being much higher than the turbidity removal efficiency of 50% reported by Yan Choy et. al. (S. Y. Choy et al., 2016a) who used autoclaved rice starch with the conventional method. However, in real situations where the natural pH values are dramatically far from the one, introduced above (pH of 2.37), this may not be applicable. That is why the optimal points were redefined while considering pH at the normal range of 5-8. Hence, the optimum conditions were found to be as follow: settling time = 130 min, pH = 5.00, slow stirring speed = 56 rpm, and dosage = 110 mg/L with a desirability of about 0.8, which can achieve a removal efficiency of 70.17%.

Table 4. Comparison of the obtined results and other plant-based reported coagulants on turbidity removal from water [*]

Plant-based coagulants	Operating conditions	Coagulant dose	Initial turbidity concentration	Removal efficiency (%)	Reference
Rice, wheat, corn, and potato starches	pH = 4 – 10, 2 min for coagulation process at 100 rpm, 20 min for flocculation at 40 rpm, and 30 min for sedimentation	0 – 600 mg/L	165 ± 5 NTU	86.07	)S. Y. Choy, K. N. Prasad, T. Y. Wu, M. E. Raghunandan, & R. N. J. E. E. Ramanan, 2016b)
Dual-function starch-based flocculants	pH = 2 – 11 , 5 min for coagulation process at 200 rpm, 15 min for flocculation at 50 rpm, and 60 min for sedimentation	0 – 8 mg/L (optimum value = 5 mg/L)	given as kaolin (0.1 wt%)	99.1	)Huang et al., 2016b)
seed extracts horse chestnut and common oak acorn	pH = 3 – 10, 1 min for coagulation process at 200 rpm, 30 min for flocculation at 80 rpm, and 1 h for sedimentation	0 – 3 mL/L	17.5 – 70 NTU	70 and 80	)Šćiban, Klašnja, Antov, & Škrbić, 2009)
common bean: *Phaseolus vulgaris*	pH = 7 – 9, 2 min for coagulation process at 200 rpm, 30 min for flocculation at 80 rpm, and 1 h for sedimentation	0.5 – 2 mL/L	35 NTU	72.3	)M. G. Antov, M. B. Šćiban, & N. J. J. B. t. Petrović, 2010)
Non-autoclaved starch	pH = 2 – 8, 1 min for coagulation process at 120 rpm, 20 min for flocculation at 20-60 rpm, and 40-140 min for sedimentation.	0-200 mg/L	170 NTU	94.8 for pH =2.37, 70.17 for pH =5	This study

[*] All the experiments were conducted at laboratory temperature (ranging between 20 and 25 °C), with simulated turbidity solutions by kaolin.



(a)

(b)

(c)

Fig. 4. 3D-surface plots on relation between contributed factors and turbidity removal by (a) NNS (left side) and (b) ASS (right side)

CONCLUSION

The present study dealt with the performance of autoclaved and non-autoclaved forms of rice starch as coagulant for highly turbid solutions. The Central Composite Design (CCD) was applied to evaluate the effect of the coagulants' dosage, pH, settling time, and slow mixing speed on the effectiveness of coagulation and flocculation process. The main conclusions of this study can be categorized as follow:

- Non-autoclaved rice starch could effectively coagulate highly turbid waters. In optimum conditions (i.e., settling time = 60 min, pH = 2.37, slow stirring speed = 37 rpm, and dosage = 113 mg/L), more than 94% of turbidity could be removed. By adjusting pH within the range of 5-8 (as the normal range in water bodies) at the optimization process of the model, the values will be as follows: settling time = 130 min, pH = 5.00, slow stirring speed = 56 rpm, and dosage = 110 mg/L, with a desirability of about 0.8, which can achieve a removal efficiency of 70.17%.
- The used coagulant does not need to get pre-processed, meaning no more cost, time, and energy consumption. Non-autoclaved form of rice starch showed a similar pattern of effectiveness and even better performance, compared with its autoclaved counterpart in terms of efficiency, statistics, floc size, and consistency;
- The behavior of the process when NSS was applied fit well with the quadratic model, the statistics of which was R^2= 0.95, $R^2_{adj.}$= 0.91, $R^2_{pred.}$= 0.77, AP = 23.75, and CV = 4.77, showing that the response surface method can successfully be used to model and optimize the coagulation and flocculation process by means of rice starch as a coagulant.

All in all, rice starch can be take into account as an environmentally friend, cost effective, natural, and accessible material for (waste)water treatment purposes, especially when applied in coagulation. However, more studies are needed to pay on the real turbidity-containing samples, at both low and high concentrations, the latter being mainly imposed by seasonal overflows. Moreover, the effect of some crucial parameters such as natural organic matters (in forms of humic and fulvic acids), which pose very controversial challenges to water treatment plants especially in fall seasons, should be investigated before scaling up the results. The process also needs to be analyzed economically and compared with the traditional coagulants (e.g. PAC, Alum, etc.) from cost-effectiveness perspective in addition to technical points.

ACKNOWLEDGEMENT

This work was financially supported by Qom University of Medical Sciences (Grant No. 96824).

REFERENCE

Antov, M. G., Šćiban, M. B. and Petrović, N. J. J. B. t. (2010). Proteins from common bean (Phaseolus vulgaris) seed as a natural coagulant for potential application in water turbidity removal. 101(7), 2167-2172.

Antov, M. G., Šćiban, M. B. and Prodanović, J. M. (2012). Evaluation of the efficiency of natural coagulant obtained by ultrafiltration of common bean seed extract in water turbidity removal. Ecological Engineering, 49, 48-52.

Association, A. W. W. and Edzwald, J. K. (2010). Water Quality & Treatment: A Handbook on Drinking Water: McGraw-Hill Education.

Bingöl, D., Hercan, M., Elevli, S. and Kılıç, E. (2012). Comparison of the results of response surface methodology and artificial neural network for the biosorption of lead using black cumin. Bioresource Technology, 112, 111-115.

Cho, M.-H., Lee, C.-H. and Lee, S. (2006). Effect of flocculation conditions on membrane permeability in coagulation–microfiltration. Desalination, 191(1), 386-396.

Choy, S., Prasad, K., Wu, T. and Ramanan, R. (2015). A review on common vegetables and legumes as promising plant-based natural coagulants in water clarification. International Journal of Environmental Science and Technology, 12(1), 367-390.

Choy, S. Y., Prasad, K. M. N., Wu, T. Y., Raghunandan, M. E. and Ramanan, R. N. (2014). Utilization of plant-based natural coagulants as future alternatives towards sustainable water clarification. Journal of environmental sciences, 26(11), 2178-2189.

Choy, S. Y., Prasad, K. N., Wu, T. Y., Raghunandan, M. E. and Ramanan, R. N. (2016). Performance of conventional starches as natural coagulants for turbidity removal. Ecological Engineering, 94, 352-364.

Dhivya, S., Ramesh, S. T., Gandhimathi, R and Nidheesh, P. V. (2017). Performance of Natural Coagulant Extracted from Plantago ovata Seed for the Treatment of Turbid Water. Water, Air, & Soil Pollution, 228(11), 423.

Dong, S., Bortner, M. J and Roman, M. (2016). Analysis of the sulfuric acid hydrolysis of wood pulp for cellulose nanocrystal production: A central composite design study. Industrial Crops and Products, 93, 76-87.

Du, Q., Wei, H., Li, A and Yang, H. (2017). Evaluation of the starch-based flocculants on flocculation of hairwork wastewater. The Science of the total environment, 601, 1628.

Folens, K., Huysman, S., Van Hulle, S and Du Laing, G. (2017). Chemical and economic optimization of the coagulation-flocculation process for silver removal and recovery from industrial wastewater. Separation and Purification Technology, 179, 145-151.

Foroughi, M., Arezoomand, H. R. S., Rahmani, A. R., Asgari, G., Nematollahi, D., Yetilmezsoy, K. and Samarghandi, M. R. (2017). Electrodegradation of tetracycline using stainless steel net electrodes: Screening of main effective parameters and interactions by means of a two-level factorial design. Korean Journal of Chemical Engineering, 34(11), 2999-3008.

Foroughi, M., Chavoshi, S., Bagheri, M., Yetilmezsoy, K. and Samadi, M. T. (2018). Alum-based sludge (AbS) recycling for turbidity removal in drinking water treatment: an insight into statistical, technical and health-related standpoints. Journal of Material Cycles and Waste Management, 1-19.

Foroughi, M., Rahmani, A. R., Asgari, G., Nematollahi, D., Yetilmezsoy, K. and Samarghandi, M. R. (2018). Optimization of a three-dimensional electrochemical system for tetracycline degradation using box-behnken design. FRESENIUS ENVIRONMENTAL BULLETIN, 27(3), 1914-1922.

Genest, S., Petzold, G. and Schwarz, S. (2015). Removal of micro-stickies from model wastewaters of the paper industry by amphiphilic starch derivatives. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 484, 231-241.

Huang, M., Liu, Z., Li, A. and Yang, H. (2017). Dual functionality of a graft starch flocculant: Flocculation and antibacterial performance. Journal of Environmental Management, 196, 63-71.

Huang, M., Wang, Y., Cai, J., Bai, J., Yang, H. and Li, A. (2016a). Preparation of dual-function starch-based flocculants for the simultaneous removal of turbidity and inhibition of Escherichia coli in water. Water research, 98, 128-137.

Huang, M., Wang, Y., Cai, J., Bai, J., Yang, H. and Li, A. J. W. r. (2016b). Preparation of dual-function starch-based flocculants for the simultaneous removal of turbidity and inhibition of Escherichia coli in water. 98, 128-137.

Jafari Dastanaie, A., Nabi Bidhendi, G. R., Nasrabadi, T., Habibi, R., Hoveidi, H. J. I. J. o. E. S. and Technology. (2007). Use of horizontal flow roughing filtration in drinking water treatment. 4(3), 379-382.

Jiang, W., Joens, J. A., Dionysiou, D. D. and O'Shea, K. E. (2013). Optimization of photocatalytic performance of TiO2 coated glass microspheres using response surface methodology and the application for degradation of dimethyl phthalate. Journal of Photochemistry and Photobiology A: Chemistry, 262, 7-13.

Khiari, R., Dridi-Dhaouadi, S., Aguir, C. and Mhenni, M. F. (2010). Experimental evaluation of eco-friendly flocculants prepared from date palm rachis. Journal of environmental sciences, 22(10), 1539-1543.

Kukić, D. V., Šćiban, M. B., Prodanović, J. M., Tepić, A. N. and Vasić, M. A. (2015). Extracts of fava bean (Vicia faba L.) seeds as natural coagulants. Ecological Engineering, 84, 229-232.

Liu, T., Chen, Z.-l., Yu, W.-z., Shen, J.-m. and Gregory, J. (2011). Effect of two-stage coagulant addition on coagulation-ultrafiltration process for treatment of humic-rich water. Water research, 45(14), 4260-4268.

Liu, Z., Huang, M., Li, A. and Yang, H. (2017). Flocculation and antimicrobial properties of a cationized starch. Water research, 119, 57-66.

Mourabet, M., El Rhilassi, A., El Boujaady, H., Bennani-Ziatni, M., El Hamri, R. and Taitai, A.

(2012). Removal of fluoride from aqueous solution by adsorption on Apatitic tricalcium phosphate using Box–Behnken design and desirability function. Applied Surface Science, 258(10), 4402-4410.

Nair, A. T. and Ahammed, M. M. (2015). The reuse of water treatment sludge as a coagulant for post-treatment of UASB reactor treating urban wastewater. Journal of Cleaner Production, 96, 272-281.

Nasrabadi, T., Ruegner, H., Schwientek, M., Bennett, J., Valipour, S. F. and Grathwohl, P. J. P. o. (2018). Bulk metal concentrations versus total suspended solids in rivers: Time-invariant & catchment-specific relationships. 13(1), e0191314.

Nasrabadi, T., Ruegner, H., Sirdari, Z. Z., Schwientek, M. and Grathwohl, P. J. A. G. (2016). Using total suspended solids (TSS) and turbidity as proxies for evaluation of metal transport in river water. 68, 1-9.

Oladoja, N. A. (2015). Headway on natural polymeric coagulants in water and wastewater treatment operations. Journal of Water Process Engineering, 6, 174-192.

Rahmani, A. R., Foroughi, M., Noorimotlagh, Z. and Adabi, S. (2016). Hexavalent Chromium Adsorption onto Fire Clay. Avicenna Journal of Environmental Health Engineering, 3(1).

Said, K. A. M. and Amin, M. A. M. (2016). Overview on the Response Surface Methodology (RSM) in Extraction Processes. Journal of Applied Science & Process Engineering, 2(1).

Samarghandi, M. R., Khiadani, M., Foroughi, M. and Nasab, H. Z. (2016). Defluoridation of water using activated alumina in presence of natural organic matter via response surface methodology. Environmental Science and Pollution Research, 23(1), 887-897.

Šćiban, M., Klašnja, M., Antov, M. and Škrbić, B. J. B. T. (2009). Removal of water turbidity by natural coagulants obtained from chestnut and acorn. 100(24), 6639-6643.

Shak, K. P. Y. and Wu, T. Y. (2014). Coagulation–flocculation treatment of high-strength agro-industrial wastewater using natural Cassia obtusifolia seed gum: treatment efficiencies and flocs characterization. Chemical Engineering Journal, 256, 293-305.

Shamsnejati, S., Chaibakhsh, N., Pendashteh, A. R. and Hayeripour, S. (2015). Mucilaginous seed of Ocimum basilicum as a natural coagulant for textile wastewater treatment. Industrial Crops and Products, 69, 40-47.

Shokoohi, R., Asgari, G., Leili, M., Khiadani, M., Foroughi, M. and Hemmat, M. S. (2017). Modelling of moving bed biofilm reactor (MBBR) efficiency on hospital wastewater (HW) treatment: a comprehensive analysis on BOD and COD removal. International Journal of Environmental Science and Technology, 14(4), 841-852.

Subramonian, W., Wu, T. Y. and Chai, S.-P. (2014). A comprehensive study on coagulant performance and floc characterization of natural Cassia obtusifolia seed gum in treatment of raw pulp and paper mill effluent. Industrial Crops and Products, 61, 317-324.

Teh, C. Y., Wu, T. Y. and Juan, J. C. (2014). Optimization of agro-industrial wastewater treatment using unmodified rice starch as a natural coagulant. Industrial Crops and Products, 56, 17-26.

Witek-Krowiak, A., Chojnacka, K., Podstawczyk, D., Dawiec, A. and Pokomeda, K. (2014). Application of response surface methodology and artificial neural network methods in modelling and optimization of biosorption process. Bioresource Technology, 160, 150-160.

Wu, H., Liu, Z., Yang, H. and Li, A. (2016). Evaluation of chain architectures and charge properties of various starch-based flocculants for flocculation of humic acid from water. Water research, 96, 126-135.

Xiao, F., Simcik, M. F. and Gulliver, J. S. (2013). Mechanisms for removal of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) from drinking water by conventional and enhanced coagulation. Water research, 47(1), 49-56.

Yang, R., Li, H., Huang, M., Yang, H. and Li, A. (2016). A review on chitosan-based flocculants and their applications in water treatment. Water research, 95, 59-89.

Zia, F., Zia, K. M., Zuber, M., Kamal, S. and Aslam, N. (2015). Starch based polyurethanes: a critical review updating recent literature. Carbohydrate polymers, 134, 784-798.