



Ammoniacal nitrogen removal by *Eichhornia crassipes*-based phytoremediation: process optimization using response surface methodology

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Received: 27 November 2018 / Accepted: 18 February 2020 / Published online: 28 February 2020
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Abstract

Eutrophication is a serious environmental issue that needs urgent concern. There is necessity to treat wastewater with high ammoniacal nitrogen (AN) concentration to the permissible standard limit to protect the aquatic ecosystem. This study investigated the optimum condition for AN removal from wastewater using *Eichhornia crassipes*-based phytoremediation process. Face-centered central composite design (CCD) was employed as the experimental design, in which four operational variables including pH (4–10), retention time (2–14 days), macrophyte density (5–30 g/L) and salinity (0–5 g NaCl/L) were involved in the study, while five responses were investigated, namely AN removal efficiency (Y_1), fresh biomass growth (Y_2), COD (Y_3), BOD (Y_4) and TSS (Y_5). AN removal was the main focus in this study. Through numerical optimization, the highest AN removal efficiency of 77.48% (initial AN concentration = 40 mg/L) was obtained at the following optimum condition: pH 8.51, retention time of 8.47 days, macrophyte density of 21.39 g/L and salinity of 0 g NaCl/L. The values predicted from the models agreed satisfactorily with the experimental values, which implied that response surface methodology was reliable and practical for experimental design developed using optimization of the phytoremediation process. The validation experiment using real semiconductor effluent further supported the high potential of the *E. crassipes*-based phytoremediation system to remove AN and other organic pollutants in this industrial effluent under optimal condition.

Keywords Wastewater treatment · Water hyacinth · Phytoremediation · Optimization · Ammoniacal nitrogen

Introduction

Semiconductor industry is recognized as one of the fastest growing industries due to the high global demand of electronic products (Huang et al. 2017). Semiconductor manufacturing processes are complex which include silicon growth, oxidation, doping, photolithography, etching, stripping, dicing, metallization, planarization, cleaning (Wong et al. 2013). During semiconductor manufacturing processes, a vast amount of water is consumed in chemical

mechanical polishing (CMP) process for planarizing the surface of the silicon wafer, thus producing a huge quantity of wastewater containing both organic and inorganic pollutants (Nur Farehah et al. 2014). Ammoniacal nitrogen (AN) is one of the major pollutants present in semiconductor wastewater. High AN concentration in waterbodies will induce eutrophication, which subsequently contribute to oxygen-level reduction and aquatic species loss (Xiang et al. 2015). In Malaysia, AN concentration in industrial effluent is necessary to be treated to comply with standard discharge limit of 20 mg/L as stipulated by the Environmental Quality Regulations 2009. However, existing AN removal technologies are found to be inefficient and inadequate, thus contributing to high AN content in semiconductor effluent ranging from 40 to 250 mg AN/L (Aoudj et al. 2017). In order to overcome the aforementioned issue, there is an urge to look for an alternative solution which is accomplished with sustainable and cost-effective characteristics, especially in developing countries including Malaysia.

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s13201-020-1163-x>) contains supplementary material, which is available to authorized users.

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Phytoremediation technology is defined as a natural treatment method which makes use of plants (phyto) to treat (remediate) various pollutants present in soil, sediment, surface water and groundwater environments (Fox et al. 2008). In recent years, phytoremediation gained keen interest among researchers to remove contaminants mainly due to its advantages including environmentally friendly and cost-effective (Paz-Alberto and Sigua 2013). The high efficiency of phytoremediation to remove a wide range of pollutants, which include heavy metals, radioactive materials, petroleum hydrocarbon, nutrients, organic contaminants and suspended substances, had been reported by many researchers (Rezania et al. 2015; Rai and Singh 2016; Mishra and Maiti 2017; Nayanathara and Bindu 2017). In order to operate a successful phytoremediation system, the selection of the suitable vegetative is crucial. *Eichhornia crassipes*, commonly known as water hyacinth, is recommended as the AN phytoremediating candidate due to its characteristics such as fast growth rate, high nitrogen uptake capacity, easy to control and great adaptability to various wastewater environments (Ting et al. 2018). Besides, *E. crassipes* also showed superior nitrogen removal efficiency compared to other macrophytes, such as *Pistia stratiotes* L. (Shah et al. 2014; Qin et al. 2016), *Myriophyllum aquaticum* Verdc (Shah et al. 2014), *Ipomoea aquatica* (Loan et al. 2014), *Salvinia natans* (Kumari and Tripathi 2013). Apart from the efficiency in AN removal, floating species such as *E. crassipes* is more convenient and less expensive to be harvested compared to small plants (e.g., phytoplankton) or submerged plants (Valipour et al. 2015).

Other than vegetative selection, phytoremediation efficiency is also significantly influenced by the environmental factors, such as pH, temperature, salinity, climate, moisture and types of contaminants present in remediating medium (Lu et al. 2008, 2013; Zhang et al. 2010; Pedron and Petruzzelli 2011). In order to determine the highest treatment efficiency together with the reduced operation cost, optimization process is necessary. Response surface methodology (RSM) is a group of mathematical and statistical techniques which is helpful for modeling and problem analysis. Since RSM can be employed for process parameters modeling and optimization, it is widely applied in wastewater treatment process in order to achieve the desired goals especially for enhancement of pollutants removal efficiency and reduction of operating cost (Bashir et al. 2015). Numerous literatures have reported on the phytoremediation performance optimization using RSM, such as diesel-contaminated water (Al-Baldawi et al. 2014), heavy metal-contaminated soil or solution (Caraiman et al. 2012; Kumar et al. 2018; Titah et al. 2018), palm oil mill secondary effluent (POMSE) (Darajeh et al. 2016), petrochemical wastewater (Samimi and Moghadam 2018), tofu wastewater (Seroja et al. 2018) and polluted stormwater (Yahyapour et al. 2014). Even though

phytoremediation technology is widely applied in treating various types of wastewater, the study on phytoremediation of AN wastewater is rarely found. To the best of our knowledge, the application of RSM on AN phytoremediation process using *E. crassipes* has not been reported. Thus, the objective of this study is to perform RSM optimization to acquire the optimal condition which aims to enhance the AN removal efficiency through *E. crassipes*-based phytoremediation process. The optimization study would be beneficial for the design of phytoremediation process to remove AN effectively from the industrial effluent.

Materials and methods

Industrial effluent collection and characterization

The semiconductor effluent used in this study was obtained from a semiconductor factory located at Samajaya Free Industrial Zone, Sarawak, Malaysia. The effluent sample was collected from the final discharge point of the wastewater treatment plant, preserved at 4 °C, and was analyzed within a day in order to minimize the experimental error due to degradation of the sample. The parameters analyzed were pH, temperature, turbidity, BOD₅, COD, TSS, heavy metals (Cd, Cu, F, Fe, Pb, Zn) and AN. Effluent characterization was performed to determine the experimental matrix to be used in the process optimization design. The characteristics of the semiconductor effluent are shown in Table 1.

Phytoremediation setup and operation

Laboratory scale phytoremediation tanks were constructed with a dimension of 0.45 m length × 0.30 m width × 0.30 m height by using acrylic glass. The water capacity was

Table 1 Semiconductor effluent characteristics

| Parameters | Units | Values |
|------------------|-------|--------|
| pH | – | 6.54 |
| Temperature | °C | 26.5 |
| BOD ₅ | mg/L | 30 |
| COD | mg/L | 145 |
| TSS | mg/L | 6 |
| AN | mg/L | 36.40 |
| Turbidity | NTU | 1.9275 |
| Heavy metals | | |
| Cadmium (Cd) | mg/L | 0.0074 |
| Copper (Cu) | mg/L | 0.0131 |
| Fluoride (F) | mg/L | 0.4090 |
| Lead (Pb) | mg/L | 0.2244 |
| Iron (Fe) | mg/L | 0.0000 |
| Zinc (Zn) | mg/L | 0.0000 |

20.25 L with an effective depth of 15 cm. Native *Eichhornia crassipes* was collected and washed gently prior to the experimental use. Phytoremediation process was carried out in batch mode condition, in which each treatment system contained *E. crassipes* and these tanks were placed under the outdoor condition and arranged in such a way that light availability was maximum. Synthetic wastewater with AN concentration of 40 mg/L was prepared using ammonium chloride (NH₄Cl). pH adjustment was performed using 3 M hydrochloric acid (HCl) and 3 M sodium hydroxide (NaOH) solution. Tap water was added to the tank regularly to maintain constant water volume. Rainfall effect was prevented by shedding the experimental area with transparent polyethylene sheet. Fresh biomass weight of *E. crassipes* was measured before and after each phytoremediation process.

Wastewater analysis

For each wastewater sample, pH was measured on site using pH meter (Model pH 5+, Eutech Instruments). After each phytoremediation process, 500 mL of wastewater sample was collected and preserved at 4 °C before analysis to minimize experimental error due to sample degradation. The analysis of physiochemical parameters of the wastewater samples involved in AN, chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD₅) and total suspended solids (TSS). AN content in the wastewater sample was analyzed after each phytoremediation process according to salicylate method (Program 343N) using a multiparameter portable colorimeter (Model DR900, Hach). COD, BOD₅ and TSS analysis were conducted according to Standard Methods for Examination of Water and Wastewater (APHA 2005). For COD analysis, water sample solution was placed for digestion under 150 °C for 2 h in COD reactor block (Model DRB 200, Hach, USA) prior to titration using 0.1 M ferrous ammonium sulfate (FAS) solution. For BOD₅ analysis, water sample was incubated at 20 °C for 5 days with measurement of both initial and final dissolved oxygen (DO) level. For TSS analysis, filtration method was applied by using glass microfiber disks 47 mm, followed by drying process in oven at 103–105 °C for 1 h.

RSM optimization design

RSM optimization study was performed using Design Expert software version 7.1.6 (STAT-EASE Inc., Minneapolis, USA). Face-centered central composite design (CCD) was employed as the design of experiment (DoE), in which the design consisted of 30 runs, with 6 center points and 24 axial points, and $\alpha = 1$. Four variables including pH (A), retention time (B), macrophyte density (C) and salinity (D) were chosen as the independent variables. Preliminary studies were conducted to select the value range for

each input variable to be employed for optimization study, as shown in Table 2. Five responses (dependent variables) were investigated, namely AN removal efficiency (Y_1), fresh biomass growth (Y_2), COD (Y_3), BOD (Y_4) and TSS (Y_5). AN removal efficiency was the main focus in this study, whereas fresh biomass growth of the plants was another significant response to be considered since there was close and positive correlation between plants' growth and phytoremediation performance. Other physiochemical parameters (i.e., COD, BOD₅ and TSS) were considered as the monitoring responses to investigate the potential risk of extra pollutant load in the treated wastewater posed by *E. crassipes*-based phytoremediation system. All experiments were carried out in triplicate, and the mean values were reported. Models describing the relationship between each dependent variable and the independent variables were developed, and the fitness of the models developed was evaluated through analysis of variance (ANOVA) and diagnostics plots. Numerical optimization was performed to obtain the optimum conditions for achieving AN removal efficiency higher than 50% to meet the standard discharge limit of 20 mg/L with the lowest retention time and pollution load which included COD, BOD and TSS. To verify the optimization results, experiments of five replicates which simulated the predicted optimum conditions were conducted to compare the actual results with the predicted optimal values. Another set of validation experiment with three replicates was also conducted using real semiconductor wastewater to evaluate the efficiency of pollutant removal using *E. crassipes*-based phytoremediation system under optimal condition.

Results and discussion

Model fitting, regression analysis and diagnostics

As suggested by the software, five models in terms of coded factors describing the relationship between each dependent variable and the independent variables were obtained. Coded Eq. was useful for identifying the relative impact of the factors by comparing the factor coefficients. For response AN removal efficiency (Y_1), the two-factor interaction (2FI) model was selected, as shown in Eq. 1. Equations 2 and

Table 2 Independent variables and levels considered for the design of experiment (DoE)

| Independent variables | Units | - 1 Level | + 1 Level |
|------------------------|----------|-----------|-----------|
| pH (A) | – | 4 | 10 |
| Retention time (B) | days | 2 | 14 |
| Macrophyte density (C) | g/L | 5 | 30 |
| Salinity (D) | g NaCl/L | 0 | 5 |

3 on the other hand showed the selected quadratic models for responses of fresh biomass growth (Y_2) and COD (Y_3), respectively. For responses of BOD (Y_4) and TSS (Y_5), the linear models were selected, as described in Eqs. 4 and 5, respectively. The positive coefficient values indicated synergistic effect, while the negative coefficient values indicated antagonistic effect.

$$Y_1 = 58.28 + 28.22A + 15.62B + 4.75C - 5.79D + 0.44AB - 8.15AC + 4.50AD + 5.03BC - 4.09BD + 1.38CD \quad (1)$$

$$Y_2 = 170.32 - 19.67A + 42.24B + 13.36C - 61.98D - 5.56AB - 1.31AC - 16.15AD + 24.06BC - 26.85BD - 30.60CD - 73.01A^2 - 28.51B^2 - 37.43C^2 - 8.51D^2 \quad (2)$$

$$Y_3 = 19.18 + 26.44A + 12.22B + 14.17C + 15.06D + 17.69AB + 6.06AC + 6.44AD + 10.81BC + 0.19BD - 6.19CD + 25.77A^2 + 4.77B^2 + 2.27C^2 + 15.27D^2 \quad (3)$$

$$Y_4 = 3.04 + 0.14A + 1.73B + 0.50C + 0.76D \quad (4)$$

$$Y_5 = 6.15 + 0.14A + 0.34B + 0.18C + 0.50D \quad (5)$$

The fitness of the models developed was evaluated through both regression analysis and diagnostics plots. The model adequacy was justified through ANOVA. The

ANOVA of the model of response AN removal efficiency (Y_1) is shown in Table 3. The model F value of 19.77 implied that the model was significant. There was only 0.01% chance that an F value this large could occur due to noise. p values less than 0.0500 indicated that the model terms were significant. In this case, A , B , D , AC were significant model terms. In other words, factors pH (A), retention time (B) and salinity (D) played significant roles in affecting the AN removal efficiency. Values greater than 0.1000 indicated that the model terms were not significant. The lack of fit F value of 1.37 implied that the lack of fit was not significantly relative to the pure error. There was 44.78% chance that a lack of fit F value this large could occur due to noise (Al-Baldawi et al. 2014). According to fit statistics, the determination coefficient (R^2) obtained was 0.9208, which indicated that the model explained 92.08% of the response variability. The R^2 value also reflected a good fit of the model. The adjusted R^2 was 0.8742, which was considered moderately high to confirm the model significance. Adequate precision was the measurement of signal-to-noise ratio, and a ratio greater than 4 was desirable. The adequate precision was found to be 15.7214, which indicated an adequate signal and implied that the model could be used to navigate the design space (Al-Baldawi et al. 2014; Kumar et al. 2018).

The diagnostics of the model statistical properties are presented in Fig. 1, which included normal probability plot, predicted versus actual plot, leverage plot and externally studentized residuals plot. The normality assumption was satisfied since the residual plot approximated along a straight line, as shown in Fig. 1a. Figure 1b shows the predicted versus actual plot. The actual values were obtained from

Table 3 Analysis of variance (ANOVA) for response surface 2FI model for AN removal efficiency (Y_1)

| Source | Sum of squares | Degree of freedom (df) | Mean square | F value | p value |
|-------------|----------------|----------------------------|--------------------|-----------|-----------|
| Model | 21,828.75 | 10 | 2182.88 | 19.77 | <0.0001 |
| A | 14,333.50 | 1 | 14,333.50 | 129.80 | <0.0001 |
| B | 4394.22 | 1 | 4394.22 | 39.79 | <0.0001 |
| C | 405.37 | 1 | 405.37 | 3.67 | 0.0723 |
| D | 602.74 | 1 | 602.74 | 5.46 | 0.0320 |
| AB | 3.13 | 1 | 3.13 | 0.0284 | 0.8682 |
| AC | 1063.09 | 1 | 1063.09 | 9.63 | 0.0065 |
| AD | 324.54 | 1 | 324.54 | 2.94 | 0.1046 |
| BC | 404.21 | 1 | 404.21 | 3.66 | 0.0727 |
| BD | 267.49 | 1 | 267.49 | 2.42 | 0.1380 |
| CD | 30.47 | 1 | 30.47 | 0.2759 | 0.6062 |
| Residual | 1877.21 | 17 | 110.42 | | |
| Lack of fit | 1623.95 | 14 | 116.00 | 1.37 | 0.4478 |
| Pure error | 253.26 | 3 | 84.42 | | |
| SD | 10.51 | | R^2 | 0.9208 | |
| Mean | 58.28 | | Adjusted R^2 | 0.8742 | |
| C.V. % | 18.03 | | Adequate precision | 15.7214 | |

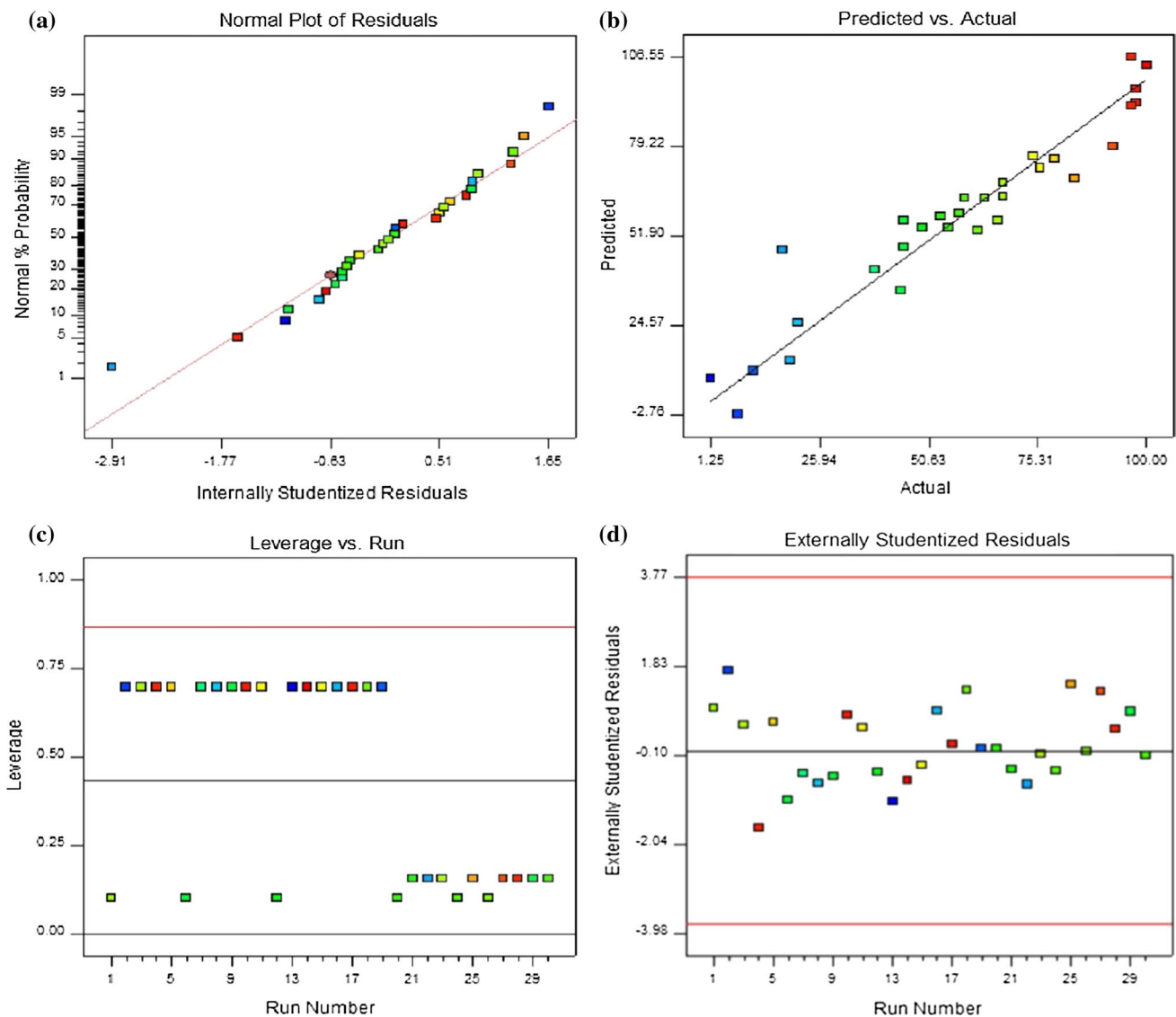
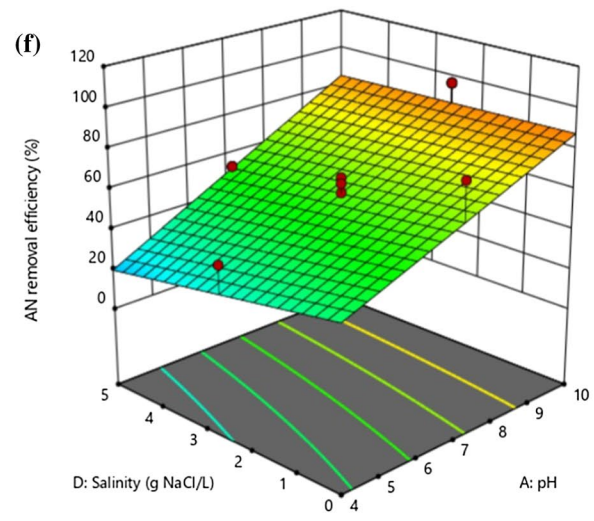
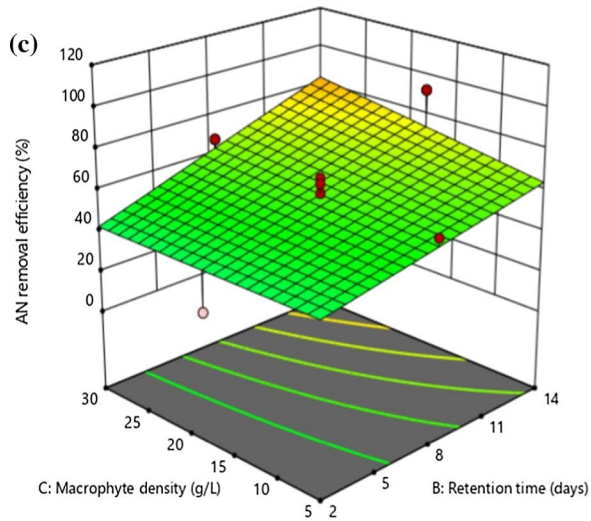
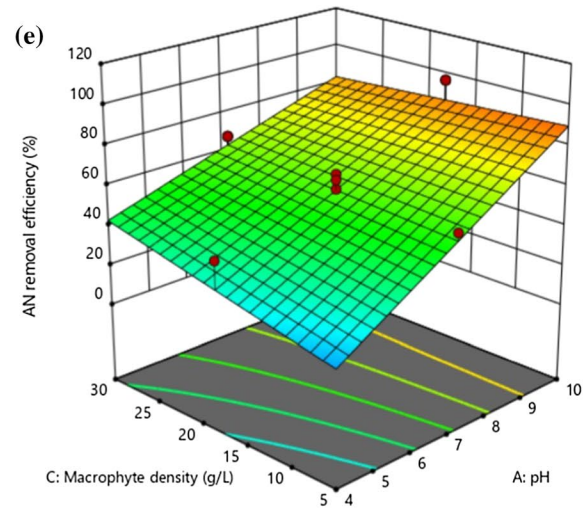
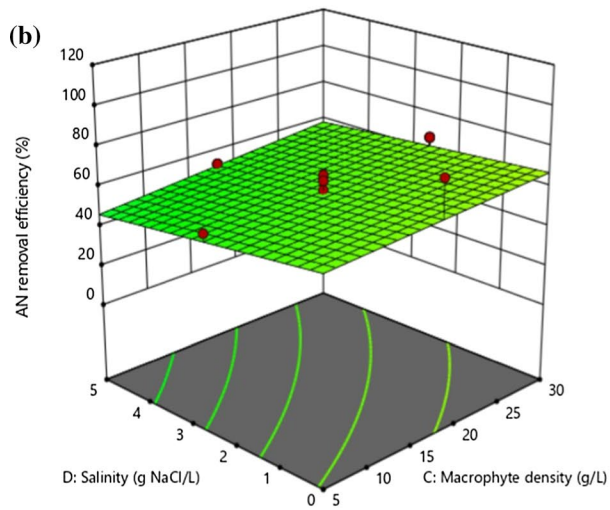
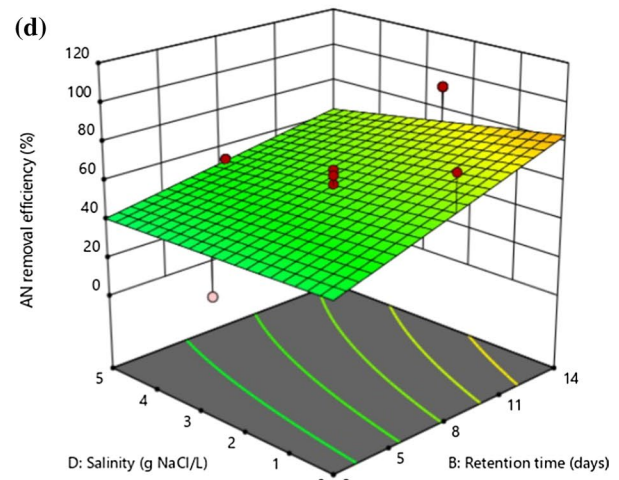
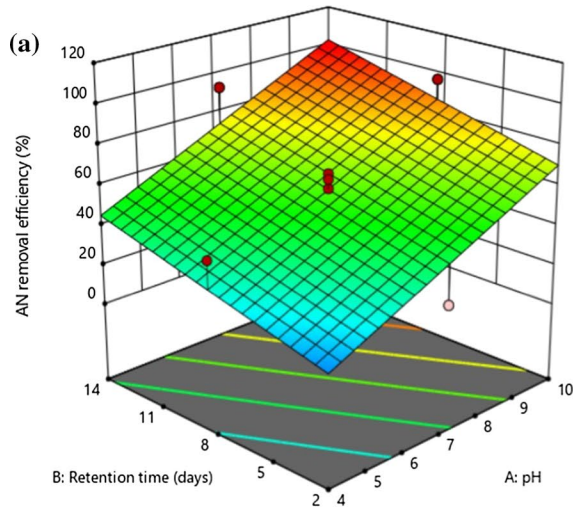


Fig. 1 Diagnostics of the model statistical properties for AN removal efficiency (Y_1)

the experiments, while the predicted values were obtained from the model fitting method. As shown in Fig., the predicted values fitted quite well with the actual values. The leverage plot is shown in Fig. 1c. The results portrayed that the leverage value was within 0–1 and no point fell above the threshold (twice the average leverage) for this statistic. Figure 1d shows the externally studentized residuals plot for outlier determination. All the results were within the range of externally studentized residuals, which indicated that there was no outlier detected.

According to the ANOVA of response fresh biomass growth (Y_2), the quadratic model F value of 7.39 implied that the model was significant. There was only 0.04% chance that an F value this large could occur due to noise. In this case, B, D, BD, CD, A^2 were significant model terms. The

R^2 obtained for Eq. 2 was 0.8884, which indicated that the model explained 88.84% of the response variability. The R^2 value also reflected a moderate fit of the model. The adjusted R^2 was 0.7682, which was considered moderately high to confirm the model significance. For the responses of COD (Y_3), BOD (Y_4) and TSS (Y_5), the R^2 obtained was 0.8252, 0.3824 and 0.0323, respectively. Even though the R^2 value of response COD (Y_3) reflected a moderate fit of the model, the low R^2 values obtained for responses BOD (Y_4) and TSS (Y_5) implied that the models were insignificant. This indicated that the input variables were poorly correlated with the output responses BOD (Y_4) and TSS (Y_5). Besides, this was probably due to the differed dirt condition of *E. crassipes* upon collection which contributed to the randomized increment values of contaminants in treated wastewater.



AN removal efficiency (%)

● Design Points

1.25 100

◀**Fig. 2** Interactive effect of multivariable (X_1 , X_2) on AN removal efficiency (Y_1): **a** pH and retention time; **b** macrophyte density and salinity; **c** retention time and macrophyte density; **d** retention time and salinity; **e** pH and macrophyte density; **f** pH and salinity

Interactive effects between variables

Interactive effect of pH (A) and retention time (B)

Figure 2a shows the interactive effect of pH (A) and retention time (B) on AN removal efficiency at actual factor conditions, at which macrophyte density was fixed at 17.5 g/L and salinity was fixed at 2.5 g/L. Suitable pH range of treatment medium is crucial to provide healthy vegetative growth for ensuring an effective phytoremediation process, at which the pH range for optimal growth of *E. crassipes* was reported as 5.8–7.5 by Edaigbini et al. (2015) and 6–8 by Rezanian et al. (2015). It is demonstrated in Fig. 2a that the increase in both pH value and retention time led to the increase in AN removal efficiency. At higher pH value, high AN removal (> 80%) was obtained with shorter retention time. This was because at higher pH condition, ammonia volatilization occurred at a faster rate (El-Gendy et al. 2004). The findings agreed with the study conducted by El-Gendy et al. (2004) which reported the increase in AN removal via volatilization at higher pH and it became more significant at pH > 8. Under low pH condition (pH = 4), the AN removal efficiency was relatively low for all levels of retention time. Low pH condition acted as inhibitor for healthy plant growth, and intolerance symptoms such as yellowing and withering of *E. crassipes* were observed during the experiment (Caicedo et al. 2000; Gupta et al. 2012).

Interactive effect of macrophyte density (C) and salinity (E)

Figure 2b shows the interactive effect of macrophyte density (C) and salinity (D) on AN removal efficiency. Under fixed conditions of pH 7 and retention time of 8 days, the response surface plot showed that the achievable AN removal efficiency was lower than 70%. It also indicated that AN removal efficiency tended to improve when higher macrophyte density and lower salinity were applied. A higher macrophyte density would form a tight root-biofilm network to maximize the contact between wastewater medium and root zone for microbial activity to degrade and assimilate pollutants, which served as filtration and entrapment media, and minimized the light penetration into water medium to inhibit algal growth (Nahlik and Mitsch 2006; Dixit et al. 2011; Mishra and Maiti 2017; Nayanathara and Bindu 2017). Salinity is another significant factor that affects phytoremediation efficiency, at which Neffati and Marzouk (2010) and Zhao et al. (2014) revealed that increasing salinity adversely affected plants' growth and AN removal efficiency, which

was probably due to reduced chlorophyll content caused by low osmotic potential of the medium. It was also found that the higher AN removal efficiency could be obtained at high salinity condition only when higher macrophyte density was employed. High macrophyte density could provide less stressful growth environment caused by the high salinity, consequently enhancing the AN removal performance (Zhao et al. 2014).

Interactive effect of retention time (B) and macrophyte density (C)

The interactive effect of retention time (B) and macrophyte density (C) is shown in Fig. 2c. The pH was fixed at 7, and salinity was fixed at 2.5 g/L. As shown in figure, the higher the retention time and macrophyte density, the higher the AN removal efficiency. Maximum macrophyte density was beneficial for enhancing AN removal efficiency by providing optimal microbial activity and plant assimilation for nutrients (Nahlik and Mitsch 2006). This agreed with the findings reported by Samimi and Moghadam (2018) that AN removal increased as both macrophyte density and retention time were increased. Another similar trend was also presented in the study, in which macrophyte density factor showed the insignificant effect on AN removal when there was a low level of retention time factor. As the macrophyte density was at its maximum value of 30 g/L, the AN concentration was reduced by more than 50% to achieve below 20 mg/L in less than 5 days of retention time. Without salinity effect (salinity = 0 g/L), only 4 days of retention time was required to reduce the AN concentration by half.

Interactive effect of retention time (B) and salinity (D)

The interactive effect of retention time (B) and salinity (D) is shown in Fig. 2d, at which pH was fixed at 7 and macrophyte density was fixed at 17.5 g/L. The response surface plot showed that longer retention time and lower salinity were preferable for achieving higher AN removal efficiency. However, the effect of retention time on AN removal efficiency was less significant as salinity was increased. The effect of salinity was shown to be more dominant as compared to retention time on the AN removal performance. Besides, *E. crassipes* in water medium containing salinity of 2.5 and 5 g NaCl/L exhibited toxic symptoms due to salinity stress after one day of phytoremediation process, which included twisted leaves and chlorotic leaf margin (Zeng et al. 2013). It was also observed that the twisted leaves became necrotic as retention time increased and the symptoms appeared on the older leaves first, followed by the younger foliage. For phytoremediation experiment which contained 2.5 g NaCl/L, the toxic symptoms ceased after four days of retention time, which showed that the *E. crassipes* adapted successfully

under these conditions. However, the toxic symptoms continued along the ten-day duration for phytoremediation set with salinity of 5 g NaCl/L. Although the results showed that the *E. crassipes* was still capable of tolerating salinity of 2.5 g NaCl/L, the attainment of negative biomass growth as well as observation of large amount of wilted and dead plants' parts at salinity of 5 g NaCl/L proved the unavailability of the *E. crassipes* for treating wastewater with extremely high salinity content.

Interactive effect of pH (A) and macrophyte density (C)

Figure 2e shows the interactive effect of pH (A) and macrophyte density (C), at which retention time was fixed at 8 days and salinity was fixed at 2.5 g/L. Apparently, the AN removal efficiency increased as pH was increased, and at the same time, the effect of macrophyte density was found to be insignificant. This was because the growth of macrophyte was highly dependent on the pH of the medium. As macrophyte was provided with the medium of extreme pH condition, the growth of the plants would exhibit retarded or even deteriorated behavior (Shah et al. 2014). Since plants' growth was closely related to AN removal efficiency, extremely low or high pH environment was unfavorable for proper plants' growth and thus would adversely affect the AN removal efficiency (Ting et al. 2018).

Interactive effect of pH (A) and salinity (D)

Figure 2f shows the interactive effect of pH (A) and salinity (D) on AN removal efficiency, at which retention time was fixed at 8 days and macrophyte density was fixed at 17.5 g/L. Under the acidic condition, the AN removal efficiency was found to be significantly influenced by the salinity variable. Phytoremediation system with wastewater medium containing both extreme salinity and pH conditions led to the highly stressful condition for plants' growth, and this finding was supported by the low biomass gain obtained after 8 days of phytoremediation process. De Casabianca et al. (1995) and Shah et al. (2014) reported on the zero biomass productivity of *E. crassipes* caused by stressful water medium, with pH

higher than 10 and salinity higher than 6 g NaCl/L, respectively. However, the response surface plot indicated that the effect of salinity became insignificant on the AN removal performance under alkaline condition. When salinity was increased from 1 to 5 g NaCl/L, the AN removal efficiency decreased from approximately 40 to 20% at pH 4, whereas at pH 10, the AN removal efficiency decreased slightly from 87.5 to 85%.

Numerical optimization and results validation

The optimum condition suggested by RSM was pH 8.51, retention time of 8.47 days, macrophyte density of 21.39 g/L and salinity of 0 g NaCl/L. Under this condition, optimum responses were predicted as the following: AN removal efficiency of 77.48%, fresh biomass growth of 218.95 g, COD of 45.48 mg/L, BOD of 2.64 mg/L and TSS of 5.80 mg/L. In order to validate the predicted results, five replicates of the experiments were carried out which simulated the given optimum condition. The experimental results are shown in Table 4. The comparison between the experimental and predicted results was made based on relative standard error (RSE), defined as the standard error referring to the fraction of the estimate and usually displayed as a percentage. The estimates with an $RSE \geq 25\%$ were considered as high sampling error and should be used with caution (Darajeh et al. 2016).

The validity of the model was further confirmed for two main responses, namely AN removal efficiency (%) and fresh biomass growth (g), with low mean RSE values of 5.79% and 10.11%, respectively. Low RSE value indicated that the experimental values were determined to be close to the predicted values, which implied that the empirical models derived from the RSM experimental design could be adequately used to describe the relationship between the independent variables and the responses (Darajeh et al. 2016). The experimental results showed that high RSE values were exhibited by the responses of COD, BOD and TSS, with mean RSE values of 48.55%, 28.83% and 22.74%, respectively. This indicated that the empirical models derived from RSM were inadequate to describe the relationship between

Table 4 Model validation results

| Replicate | AN removal efficiency (%) | RSE (%) | Fresh biomass growth (g) | RSE (%) | COD (mg/L) | RSE (%) | BOD (mg/L) | RSE (%) | TSS (mg/L) | RSE (%) |
|-----------|---------------------------|---------|--------------------------|---------|------------|---------|------------|---------|------------|---------|
| 1 | 72.50 | 6.42 | 203.94 | 6.86 | 17 | 62.62 | 1.77 | 33.06 | 6 | 3.43 |
| 2 | 80.00 | 3.26 | 257.89 | 17.78 | 35 | 23.04 | 1.55 | 41.38 | 8 | 37.91 |
| 3 | 70.00 | 9.65 | 185.25 | 15.39 | 19 | 58.22 | 2.52 | 4.69 | 6 | 3.43 |
| 4 | 75.00 | 3.20 | 227.39 | 3.85 | 24 | 47.23 | 2.01 | 23.98 | 9 | 55.15 |
| 5 | 72.50 | 6.42 | 233.51 | 6.65 | 22 | 51.62 | 3.73 | 41.07 | 5 | 13.81 |

Table 5 Model validation results using real semiconductor effluent

| Replicate | AN concentration (mg/L) | | AN removal efficiency (%) | Fresh biomass weight (g) | | Fresh biomass growth (g) | COD (mg/L) | BOD (mg/L) | TSS (mg/L) |
|-----------|-------------------------|-------|---------------------------|--------------------------|--------|--------------------------|------------|------------|------------|
| | Initial | Final | | Initial | Final | | | | |
| 1 | 24 | 10 | 58.33 | 204.34 | 284.72 | 80.38 | 37 | 1.7 | 2 |
| 2 | 24 | 9 | 62.50 | 219.94 | 305.04 | 85.10 | 34 | 2.5 | 1 |
| 3 | 24 | 10 | 58.33 | 209.29 | 302.44 | 93.15 | 31 | 2.1 | 2 |

the input and these three output responses. The high RSE values of these responses were also due to the amplified standard error due to the involvement of relatively small values. As compared to the contribution of COD values, the BOD and TSS values were quite insignificant. However, the overall results regarding pollution load were still considered satisfactory since significantly lower COD values were obtained from all the five replicates of the experiments as compared to the predicted COD values.

Another set of validation experiment with three replicates was conducted using real semiconductor wastewater which simulated the optimum condition. The COD, BOD and TSS of the real semiconductor effluent prior to the phytoremediation process were found to be 92 mg/L, 36.4 mg/L and 1 mg/L, respectively. Table 5 shows the model validation results for the treated semiconductor effluent. Under the simulated optimum condition, despite that lower AN removal efficiency was obtained for all three replicates as compared to the predicted AN removal efficiency, the goal to reduce the initial AN concentration by half had been achieved successfully. The achievement of lower AN removal efficiency was probably due to the lower biomass growth of *E. crassipes* in real semiconductor wastewater, as shown in Table 5. *E. crassipes* showed intolerant characteristic (i.e., yellowing of leaves) at the beginning of the experiment, possibly due to the stressful growth medium that contained high COD and BOD. However, the intolerant symptoms ceased after 3 days of retention time, and the plants exhibited healthy growth afterward. After the optimum retention time of 8.47 days, *E. crassipes*-based phytoremediation system was capable of reducing the COD and BOD contents significantly, with mean removal efficiency of 63.04% and 94.23%, respectively. Additionally, there was only negligible increment of TSS values (0–1 mg/L) for the treated semiconductor effluent. Overall, the results showed that *E. crassipes* was capable of removing AN content in semiconductor effluent effectively without contributing extra pollutant load (i.e., COD, BOD, TSS) to the treated wastewater. This further confirmed that the models developed in this study were reliable and accurate to relate the variables to the responses, and the optimum condition obtained was feasible to be applied to remove AN from real semiconductor wastewater.

Conclusions

Face-centered central composite design was employed to optimize the AN removal efficiency through *E. crassipes*-based phytoremediation system. The two-factor interaction (2FI) model was successfully developed for the response of AN removal efficiency. The model adequacy was evaluated through ANOVA, at which the model significance was confirmed by attainment of high R^2 value of 0.9208 and model F value of 19.77. Through numerical optimization, the highest AN removal efficiency of 77.48% was obtained at the following optimum condition: pH 8.51, retention time of 8.47 days, macrophyte density of 21.39 g/L and salinity of 0 g NaCl/L. Based on the experimental results, low mean RSE values of 5.79% were obtained for the response of AN removal efficiency, which confirmed the validity of the empirical model developed and implied that the RSM method was practical to be employed for the process optimization. The validation experiment using real semiconductor effluent further provided evidence on the efficiency of *E. crassipes* to remove AN, COD and BOD in the effluent. Overall, phytoremediation using *E. crassipes* has been shown to be promising for AN removal in wastewater.

Acknowledgements The authors acknowledge the research grants provided by Universiti Malaysia Sarawak under Fundamental Research Grant Scheme FRGS/TK02(05)/1305/2015(22) from Ministry of Higher Education Malaysia.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflicts of interest regarding the publication of this paper.

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