Korean J. Chem. Eng., 39(10), 2702-2712 (2022)
DOI: 10.1007/s11814-022-1149-5

pISSN: 0256-1115
eISSN: 1975-7220

Bioremediation of imidacloprid using *Azospirillium* biofertilizer and *Rhizobium* biofertilizer

Kavita Kulkarni*,†, Aishwarya Chawan*, Anand Kulkarni*, and Sandip Gharat**

*Department of Chemical Engineering, Bharati Vidyapeeth (Deemed To Be University), College of Engineering, Pune
**Department of Chemical Engineering, Gharda Institute of Technology Lavel, Khed, Ratnagiri

(*Received 19 January 2022 • Revised 19 April 2022 • Accepted 19 April 2022*)

Abstract−Imidacloprid is a pesticide used for agricultural purposes. Residue of pesticide in water and soil will affect the water and soil quality. Seepage out of imidacloprid to the ecological system could affect aquatic life as well as human. The toxic pollutants would affect the quality of agriculture run off, in turn contaminating water bodies acting as sink for these runoffs. Hence, there is need for reparation of these pollutants. *Azospirillium* biofertilizer and *Rhizobium* biofertilizer were used as adsorbent for the removal of imidacloprid. These biofertilizers have capability to reduce the harmful component as well as be useful for plant growth. *Azospirillium* bacteria and *Rhizobium* bacteria are competent for the removal of organic pollutant from wastewater. These biofertilizers maintain biological activity without any adverse effect. The adsorptive removal of imidacloprid by using *Azospirillium* biofertilizer and *Rhizobium* biofertilizer was investigated at different conditions using batch experimentation. Optimization of parameters, such as dosage, time, temperature, pH, and agitation speed, was carried out. Equilibrium adsorption was illustrated by Langmuir and Freundlich isotherms. The kinetic data was best described by intraparticle diffusion and pseudo-second-order model. Reusability study showed good removal efficiency of imidacloprid after fourth use also. The investigations show that these materials have potential to be an excellent alternative for removal of pesticides while supporting plant growth.

Keywords: Imidacloprid, Adsorption, Removal Efficiency, Biofertilizer

INTRODUCTION

Pesticides are widely used in the majority of agricultural production sectors to increase crop production. Most of the active components have long balance and as a result can easily enter water sources such as streams and shallow groundwater. Another common way of polluting the water assets is through the pesticide manufacturing industries. Toxicity of pesticides released in the environment damages the ecological balance [1]. Pesticides cause serious concern to the farmers and workers who get direct exposure and the general population who indirectly get exposed through food and water [2-6]. Because of non-biodegradability and toxicity, control of pesticides is essential to avoid contamination of food, water sources and damage to the environment [7,8]. It is most essential to have alternative technologies for the treatment of pesticides. Use of pesticides is directly done on soil or on the flora so that their action can be received easily into the environment. Harmful effect of pesticides has been observed on the natural habitat as well as community health. Ecosystem, health of human beings and fauna is mostly affected by dangerous pesticides. Adverse effect of these pesticides was seen after penetration to the applied field [9].

Several methods are employed for the treatment of pesticides, such as advanced oxidation processes [10,11], ozonation [12], photolysis [13], electrocatalytic oxidation [14], photo Fenton [15], biodegradation [16,17] photocatalytic degradation [18,19], nano filtration [20], hydrodynamic cavitation [21] and adsorption [22-26]. Due to high operational cost, less efficiency and hazardous waste generation make these methods unsuitable for the treatment of pesticides [27,28]; consequently, it is required to explore new methods which are effective, safe to environment and effective [29]. Among these methods, adsorption is supposed to be an alternative for the removal of pesticides and other pollutants because of being ecofriendly, simple, and low-cost technology [30]. Biosorption technology is a substitute for the removal of pesticides [31]. Biosorption is a fast process in which interaction between cell surface and adsorbate and live, alive, or immobile biomass. When live biomass is used, the removal mechanism may involve biodegradation along with sorption phenomena [32]. Various natural materials have been utilized for the removal of pollutants, such as agricultural residue, raw plants, animal material, and microalgae sludge [33-36]. Plant based materials have been widely used for the wastewater treatment, like peanut shell, phytolacca Americana biomass, Marula seed husk, cedar leaf, olive tree pruning, cork waste, maize stover [37-43].

Imidacloprid is a pesticide normally used for seed therapy to control sucking and biting insects. Also, it flows rapidly all through plant tissue, and provides protection to crops from insects [44,45]. Imidacloprid is extremely toxic, and globally its surface water concentration is in the range between 0.001 to 320 μg/L [46,47]. Imidacloprid (IMD) is commonly detected in surface waters and floor waters due to its excessive persistence, bioaccumulation and low biodegradability, which poses an extremely top threat to various ecological surroundings and human health [48-50]. Imidacloprid

---

[†] To whom correspondence should be addressed.
E-mail: kavitashreya@gmail.com, kskulkarni@bvucoep.edu.in

is an insecticide that comes under the group of neonicotinoids. Imidacloprid is applied to kill the insects on the crops by attacking the central nervous system of the insects [51]. Removal of imidacloprid has been tried by various methods. Activated carbon was utilized for the removal of imidacloprid by performing static experiments. From green tea infusion, removal of imidacloprid and acetamiprid was attempted. Rate of removal was reduced with initial concentration and also with tea concentration. For imidacloprid the removal was 85% and for acetamiprid, 87.5%. Pseudo-second-order model was appropriate for the adsorption process [52]. For the treatment of effective activator, water treatment remains were utilized as precursor. Hydrothermal treatment was used for the treatment of imidacloprid. The optimized parameters gave 97.64% removal of imidacloprid [53]. Comparison of regular rice straw biochar and rice straw treated with phosphoric acid was employed as adsorbent for the removal of imidacloprid and atrazine. From the optimized parameters the removal efficiency was 95% for imidacloprid and atrazine. Modelling of the data was done for three stage adsorber process. Reduction in quantity of adsorbent was observed for two stage model [54]. The main purpose of this study is to check the feasibility of two biofertilizers as an adsorbent for the removal of imidacloprid.

MATERIALS AND METHODS

In the present study, all chemicals were of analytical grade. All chemicals were procured from Merck. Imidacloprid (insecticide) was purchased from Dhanuka Agritech Ltd, Chiplun. Chemical composition is as shown in Table 1.

Imidacloprid maximum wavelength was 269 nm, which was used for evaluation of adsorbed pesticide quantity. Beer - Lambert law was applied to the calibration curve for further diluting various concentrations. Precise amount of imidacloprid was taken for the preparation of stock solution. Chemicals used to adjust the pH were NaOH and HCL. Azospirillium biofertilizer (AZB) and Rhizobium biofertilizer (RZB) was procured from Agriculture College, M.P.K.V. Rahuri, Pune. AZB is mixture of lignite and *Azospirillum* bacteria to get the cell number of 10^8 and RZB is the blend of lignite and Rhizobium bacteria which will meet 10^8 cell counts. To perform batch experiments, stock solution was diluted for various concentrations.

1. Characterization

Surface morphology of the adsorbents was studied by scanning electron microscopy (COMP.JEOL, model). Fourier-transform infrared spectroscopy (FTIR) was used to identify the unknown components.

Table 1. Chemical composition of Imidacloprid

Compound	% W/W
Imidacloprid A.I.	17.800
Nonionic emulsifier (Ethoxylated alkyl aryl phenol derivative)	2.500
Polyvinyl pyrrolidone copolymer	1.00
Dimethyl sulfoxide	38.400
N methyl pyrrolidone	Q.S.

EXPERIMENTAL

Adsorption experiments were carried out in batch mode. A horizontal shaker (Uni -Tech) was used to carry out all the experiments by using AZB and RZB as adsorbent for the removal of imidacloprid. For batch adsorption experiments, 100 ml imidacloprid solution of varied concentration from 50 ppm to 150 ppm was used. Stock solution of 1,000 ppm was prepared and appropriate dilution was used for batch experiments. Systematic study of optimization of parameters was carried out. Detail information for parameters optimized is given below

1. Adsorbent dosage: For AZB and RZB (0.5 g-3 g)
2. pH: (2-10)
3. RPM: (100-260)
4. Temperature: (30 °C-60 °C)
5. Contact time: (20 min-140 min)
6. Initial Concentration: (50 ppm-150 ppm)

All experiments were performed in triplicate for accuracy. The residual concentration was filtered with nylon syringe filter and analyzed using UV spectrophotometer. Reproducibility of batch experimentation results was analyzed.

At defined intervals and at equilibrium, adsorption capacity was calculated by the use of Eqs. (1) and (2):

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where C_0 is initial concentration; C_e and C_t are concentration at equilibrium and concentration at regular interval in mg/l respectively. Adsorptive uptake is represented by q_t and q_e at regular intervals and at equilibrium, respectively. V is volume of solution in ml and m is mass of adsorbent in g.

RESULTS AND DISCUSSION

1. Adsorbent Characterization

1-1. Scanning Electron Microscopy

Morphology of AZB and RZB: Scanning electron microscopy of AZB and RZB was analyzed. Spongy material with many stackings was seen in the micrograph for RZB, as seen in Fig. 1. Irregular particle size with porous structure was observed.

For AZB, combined particles of uneven form with springy arrangement were observed as seen in Fig. 2.

1-2. Fourier-transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) is a method used to get an infrared spectrum for identification unknown sample. From the FTIR spectroscopy studies, the given two adsorbents Azospirillium and Rhizobium biofertilizer have the same functional groups like hydroxyl, carbon oxygen (C=O) bonding, double bonded carbon atoms (C=C), carbon single oxygen bonding (C-O) atoms, aromatic rings, aliphatic and also the bonding formed between carbon, oxygen and hydrogen (C-OH) atoms. Along with these groups,

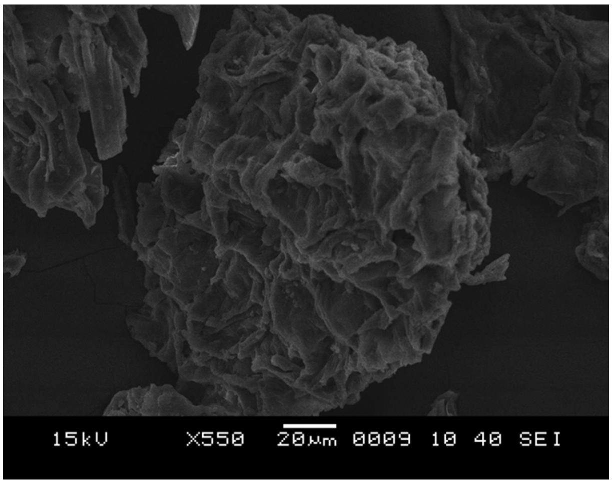


Fig. 1. Scanning electron microscopy of *Rhizobium* biofertilizer.

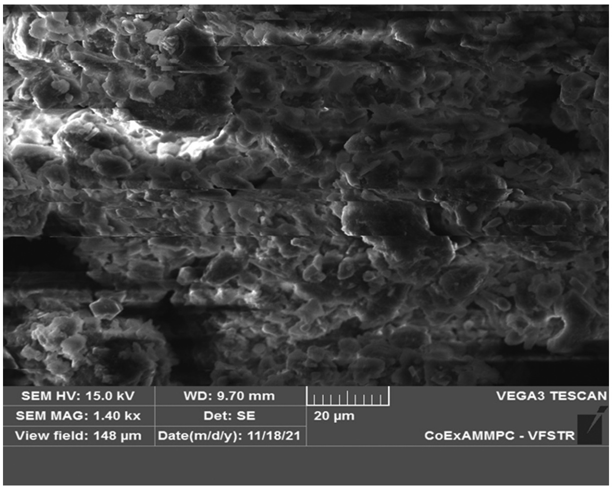


Fig. 2. Scanning electron microscopy of *Azospirillium* biofertilizer.

ethers, alcohols, and esters are also present. Due to loading with lignite, the aromatic rings played a major role in all aspects. From Fig. 3, there is a reduction of aliphatic carbon bonding from 3,700-3,550/cm, and there is some enhancement from 1,640-1,540/cm, which explains that there is some presence of aromatic structures and which was more at 510/cm. In Fig. 4, there is less symmetrical stretching of carbon hydrogen atoms bonding and the maximum presence of aromatic groups at 510/cm like Rhizobium adsorbent. Out of two adsorbents, the stretching is more in Rhizobium biofertilizer.

2. Parameters Optimization

2-1. Adsorbent Dose Optimization

For AZB and RZB dose optimization was checked, as adsorbent dose plays a significant role in removal of any pollutant by adsorption [55]. Fig. 5(a) and 5(b) depict the adsorbent dosage and removal efficiency.

As adsorbent dose was increased, removal efficiency was observed in increasing trend but in small variation. Variation of AZB and RZB dose was done from 0.5 g to 3 g. Optimized dose of AZB and RZB was 1.5 g and 2 g, respectively. Maybe at higher adsorbent dose, the saturation of active sites was the reason for decreased in removal efficiency [56].

2-2. Optimization of Contact Time

Time is a significant parameter which predicts adsorption process kinetics. It is very important to study time dependency, as contact time between adsorbate and adsorbent gives the adsorption

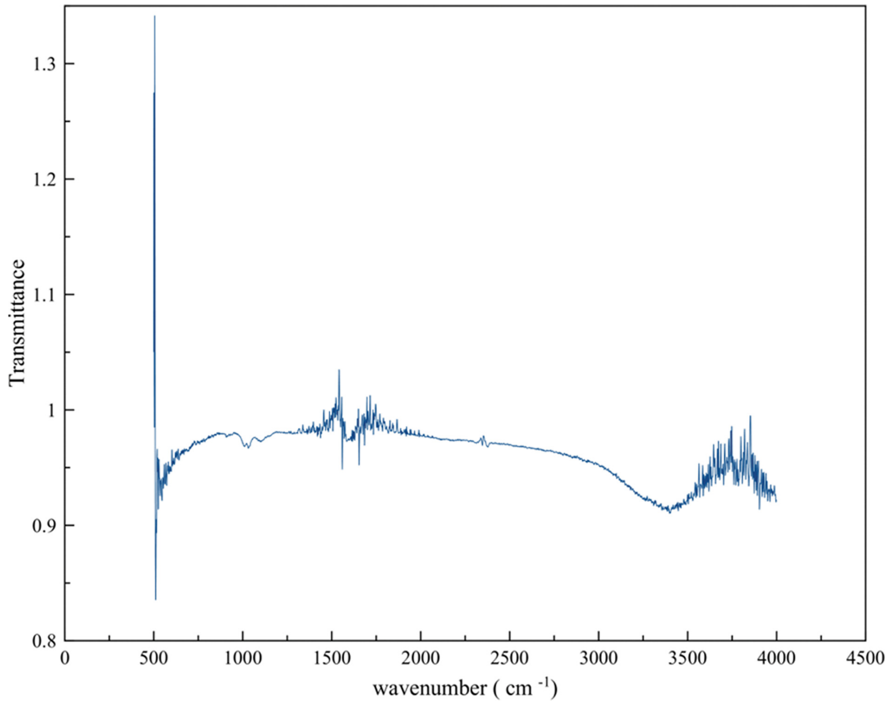


Fig. 3. FTIR of *Rhizobium* biofertilizer.

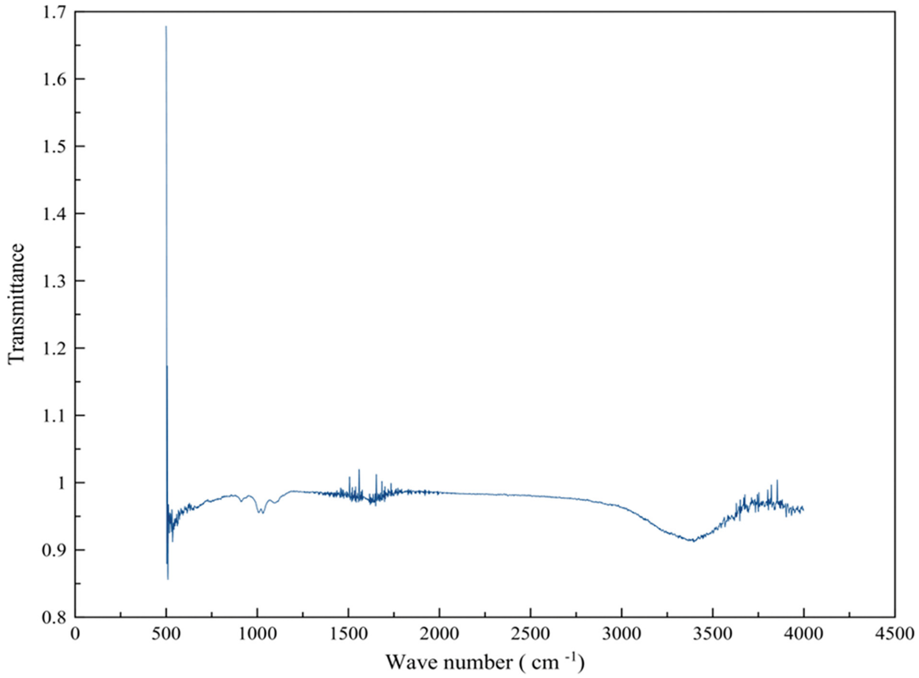


Fig. 4. FTIR of *Azospirillium* biofertilizer.

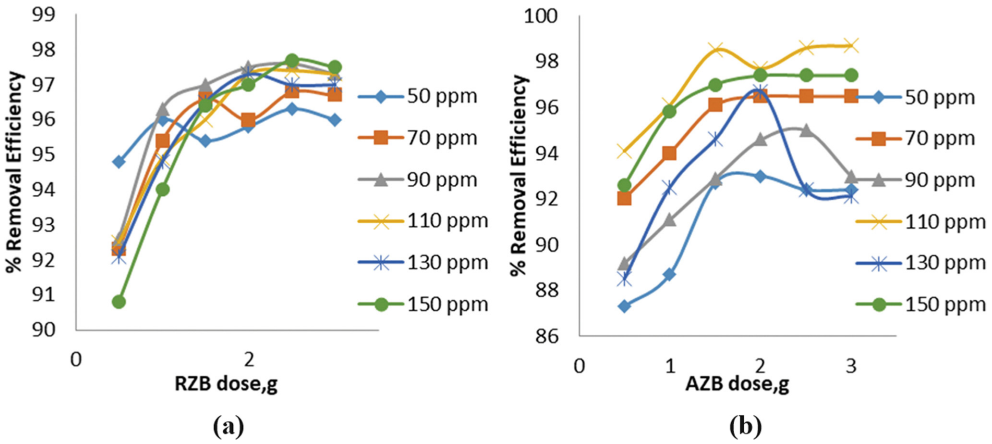


Fig. 5. Effect of dosage by (a) RZB (b) AZB on removal of Imidacloprid.

ability of the adsorbent. Fig. 6(a) and 6(b) show the effect of time on removal efficiency of imidacloprid.

The initial concentration was varied from 50 ppm to 150 ppm, and contact time for adsorption process was studied from 20 minutes to 140 minutes. For RZB, for 50 ppm concentration there was sharp increasing trend in removal efficiency for imidacloprid, but as the initial concentration was increased, the removal efficiency was greater but somewhat stable and not increased for RZB. For AZB, the removal efficiency trend was fairly the same for all initial concentrations. Optimized time for RZB and AZB was 20 minutes.

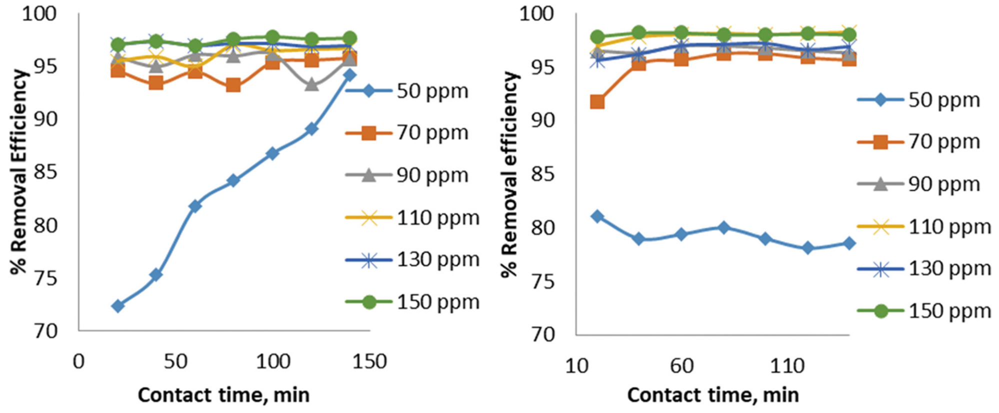
2-3. Temperature Effect

Temperature is one of the important factors that controls the adsorption capacity in the process of adsorption [57]. Fig. 7(a) and 7(b) depict the effect of temperature by RZB and AZB, respectively.

For RZB, decreasing trend of adsorption with temperature indicated the exothermicity of the adsorption process. Weakening of adsorptive bonds between RZB surface and imidacloprid may be the reason for reduced removal efficiency. Similar results were observed for different adsorption systems [58]. Temperature effect showed heterogeneity of the RZB surface [59]. For AZB, the removal efficiency was seen as increasing tendency with very small difference at 30 °C and 50 °C, but at 40 °C and 50 °C the removal efficiency was decreased with very little variation. The optimum temperature for the process was 50 °C, at which removal efficiency was higher.

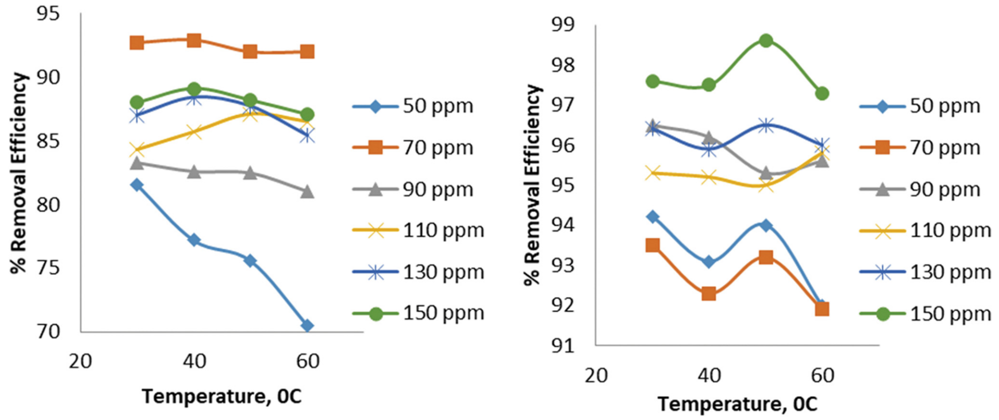
2-4. Effect of pH

Solution pH plays a very important role in the adsorption process. Adsorption experiments were carried out at various pH values (2-10). Fig. 8(a) and 8(b) represent the effect of pH on removal of imidacloprid for RZB and AZB, respectively. For RZB, there



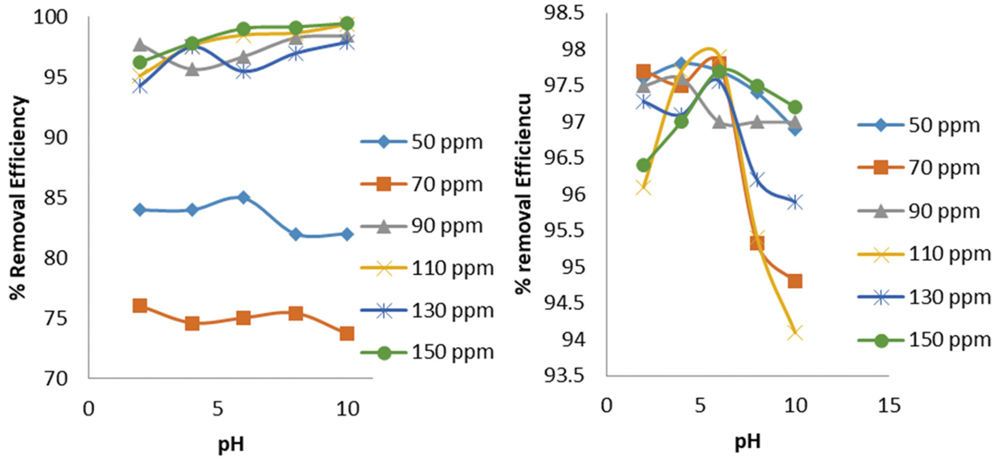
(a) (b)

Fig. 6. Effect of contact time for (a) RZB (b) AZB on removal of Imidacloprid.



(a) (b)

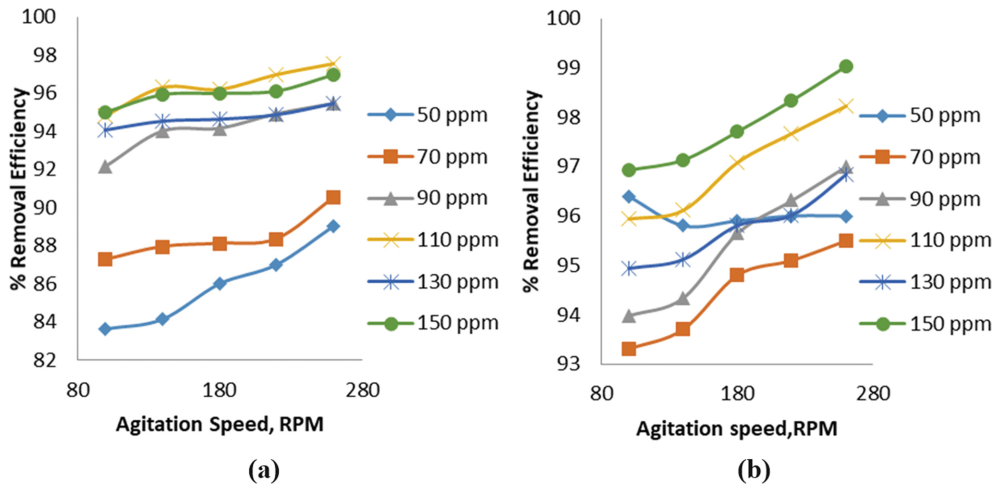
Fig. 7. Effect of temperature for (a) RZB (b) AZB on removal of Imidacloprid.



(a) (b)

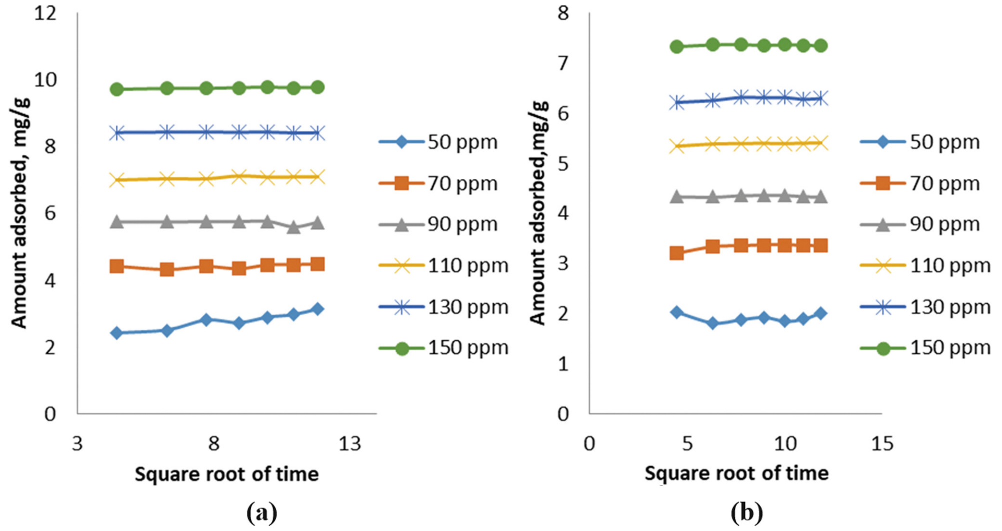
Fig. 8. Effect of pH for (a) RZB (b) AZB on removal of Imidacloprid.

was no sharp decrease in removal efficiency. A small difference in removal efficiency was observed as pH was increased. Higher removal efficiency was observed between 6 to 7 pH. Similar result was observed for adsorption of imidacloprid [60]. For AZB, as pH was increased the removal efficiency was increased, but after 7 pH the removal efficiency decreased. With pH variation there is change



(a) (b)

Fig. 9. Effect of agitation speed for (a) RZB (b) AZB on removal of Imidacloprid.



(a) (b)

Fig. 10. Intra particle diffusion model for (a) RZB (b) AZB for removal of Imidacloprid.

in surface charge with H^+ and OH^-. Maybe the change in H^+ ions in acidic medium and change in OH^- ions in basic medium competed with imidacloprid for adsorption and contributed to effect of pH [61].

2-5. Influence of Agitation Speed

In solid liquid transport, agitation has important role. Agitation reduces the boundary layer and increases contact time between adsorbent and adsorbate [62]. At five different agitation speeds (100, 140, 180, 220, 260) adsorption experiments were conducted. From Fig. 9(a) and 9(b), it was observed that adsorption rate was increased with increase in agitation speed for RZB and AZB. Maximum removal efficiency was 97% for AZB and RZB at 260 rpm.

ADSORPTION KINETICS

1. Study of Adsorption at Equilibrium

For large scale applicability, a kinetic study is necessary. For the adsorption of imidacloprid, the data from batch experiments were checked for two kinetic models, like intraparticle diffusion model [63] and pseudo-second-order model [64].

1-1. Intraparticle Diffusion Model

Intraparticle diffusion model was proposed by Weber and Morris [65]. According to the intraparticle model, the existence of a boundary layer as well as intraparticle diffusion was assumed. Eq. (3) represents the linear form of intra particle diffusion.

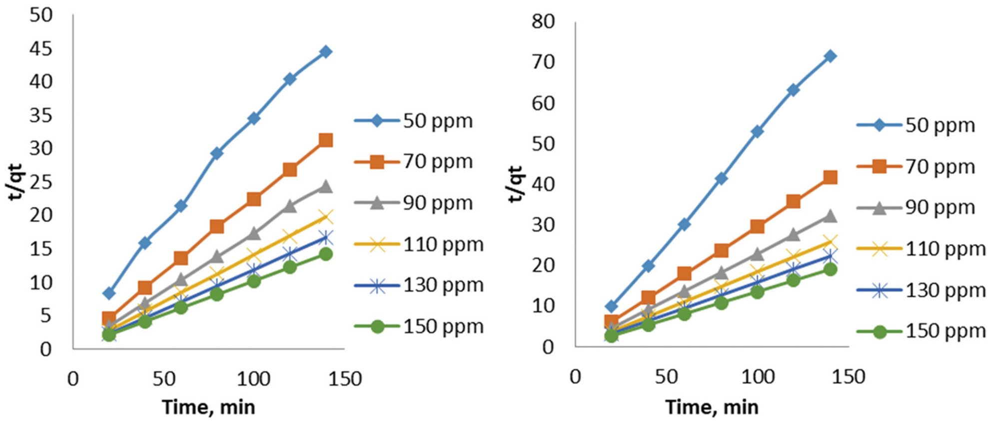
$$q_t = k_p t^{0.5} + C \tag{3}$$

where

k_p=Rate constant for Intra particle diffusion, (mg/g $min^{-0.5}$)
q_t=Fraction of metal adsorbed, mg/g
t=Contact time, min
C=Thickness of boundary layer, Constant

Boundary layer effect will be increased with higher value of C.

A straight line plot between qt and square root of time indicates intraparticle diffusion rate as controlling. Graphical representation



(a) (b)

Fig. 11. Pseudo-second-order model for (a) RZB (b) AZB for removal of Imidacloprid.

Table 2. Rate constant and correlation coefficient for intra particle diffusion model and for pseudo-second-order model

Pseudo-second-order model (RZB)		
Initial concentration, mg/L	Rate constant g/mg min^{-1}	R^2
50	0.305	0.99
70	0.222	0.99
90	0.18	0.99
110	0.14	1
130	0.12	1
150	0.10	1
Pseudo-second-order model (AZB)		
Initial concentration, mg/L	Rate constant g/mg min^{-1}	R^2
50	0.53	0.99
70	0.3	0.99
90	0.23	1
110	0.18	1
130	0.16	1
150	0.14	1

of intraparticle diffusion model is shown in Fig. 10(a) and 10(b) for RZB and AZB.

From the linearity of the graph, it can be predicted that for all initial concentrations, intraparticle diffusion was rate controlling. For low concentration, 50 ppm minor change was observed in linearity of plot.

1-2. Pseudo-second-order Model

In the pseudo-second-order model two assumptions are considered, as the rate limiting step is chemisorption and rate of adsorption does not depend on adsorbate concentration [66,67]. The arithmetical form for the pseudo-second-order model is represented by Eq. (4).

$$\frac{t}{q_t}=\frac{1}{k_2q_e^2}+\frac{1}{q_e}t \qquad (4)$$

q_e=amount adsorbed at equilibrium, mg/g

t=time, min and k_2 is pseudo-second-order rate constant, (g/mg·min)

A graph was plotted between t/qt and time as shown in Fig. 11(a) and 11(b) for RZB and AZB, respectively.

The correlation coefficients for the pseudo-second-order model are presented in Table 2. From all the values for all concentrations, it can be concluded that, the pseudo-second-order model was perfectly fit to the adsorption of imidacloprid by RZB and AZB.

2. Adsorption Kinetics

2-1. Langmuir Isotherm

For assessment of adsorption capacity, and to check the adsorption mechanism, the isotherm is considered a vital tool. The Langmuir adsorption assumptions include complete monolayer adsorption and no interaction with other molecules [68]. The mathematical form of the Langmuir equation is presented by Eq. (5):

$$\frac{C_e}{Q_e}=\frac{1}{k_aQ_m}+\frac{C_e}{Q_m} \qquad (5)$$

where

C_e=Concentration of imidacloprid at equilibrium, mg/l

Q_m=Amount adsorbed at constant interval of time, mg/g

Q_e=Amount adsorbed at equilibrium, mg/g

k_a=Langmuir constant, 1/mg

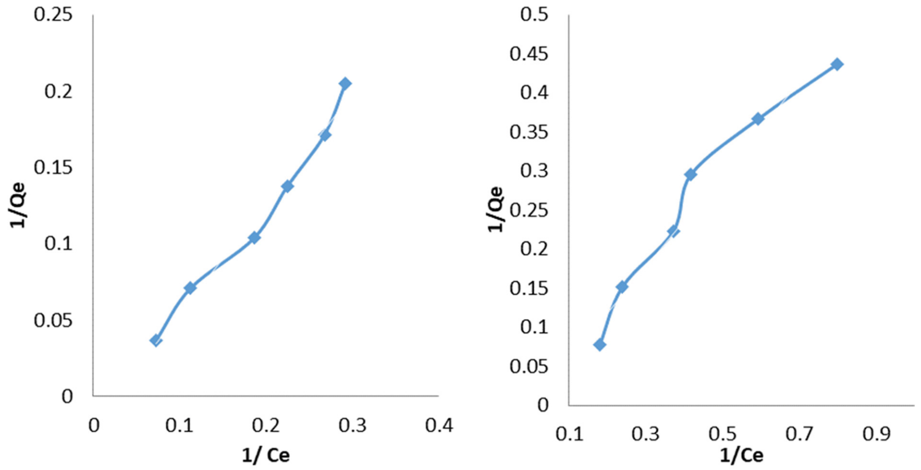
Fig. 12(a) and 12(b) represent Langmuir isotherm plot of $1/Q_e$ and $1/C_e$ for RZB and AZB.

For both adsorbents, the Langmuir isotherm was best fitted with correlation coefficient of 0.98 and 0.95. The Langmuir adsorption capacity for RZB and for AZB was 58.8 mg/g and 83.3 mg/g. The constant values are presented in Table 3.

Langmuir isotherm feasibility is checked by separation factor defined by Eq. (6).

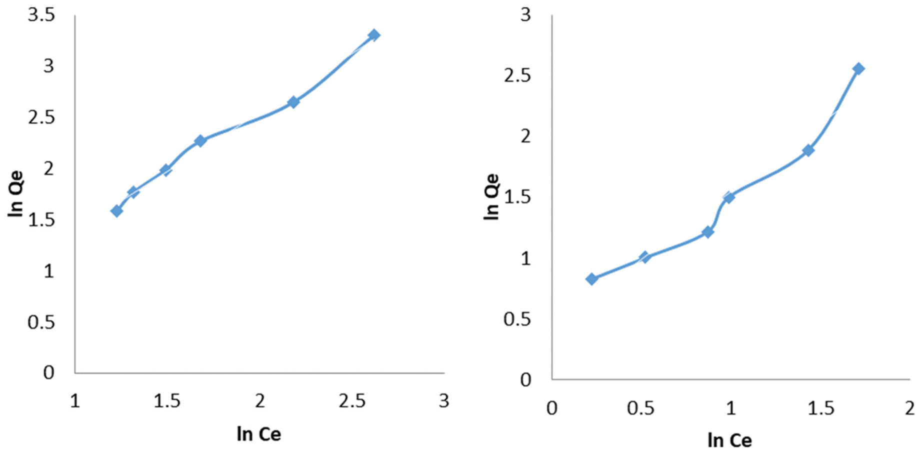
$$R_L=\frac{1}{1+k_aC_0} \qquad (6)$$

where R_L represents separation factor and C_0 corresponds to initial concentration.



(a) (b)

Fig. 12. Langmuir isotherm for (a) RZB (b) AZB for removal of Imidacloprid.



(a) (b)

Fig. 13. Freundlich isotherm for (a) RZB (b) AZB for removal of Imidacloprid.

Adsorption process favorability is shown by R_L. For the linear process, R_L value is 1 and non-favorability is observed above 1 ($R_L>1$). Favorability is observed between $0<R_L<1$, and for reversible process R_L tends to zero. For the adsorption of imidacloprid process by RZB and AZB, R_L values are found as 0.224 and 0.404 for RZB and AZB, respectively. For both the adsorbents the adsorption of imidacloprid was favorable.

2-2. Freundlich Isotherm

Analysis of adsorption data was also done by Freundlich model. Usually, the Freundlich isotherm is analyzed for a heterogeneous system [69]. The logarithmic equation for Freundlich isotherm is given by Eq. (7).

$$\log Q_e = \log K_f + \frac{1}{n} C_e \tag{7}$$

where

C_e=Equilibrium concentration, mg/l
Q_e=Amount adsorbed, mg/g
K_f=Freundlich Constant
n represents adsorption intensity

Fig. 13(a) and 13(b) depict the Freundlich isotherm suggesting applicability to the adsorption process. The correlation coefficients are shown in Table 3. For RZB the correlation coefficient was 0.99 and, for AZB 0.94 showed good fit to Freundlich isotherm; values for 1/n less than one suggest multilayer adsorption may be involved in the process.

2-3. Temkin Isotherm

Linear decrease in adsorption energy with increased surface coverage was assumed in the Temkin isotherm [70]. Linear form of the Temkin equation is presented by Eq. (8), where

$$q_e = B_1 \ln A + B_1 \ln C_e \tag{8}$$

A=Temkin constant, l/mg
B=Constant for heat of adsorption

Fig. 14(a) and 14(b) depict the Temkin isotherm for adsorption of imidacloprid by RZB and AZB, respectively. The correlation coefficient for RZB and AZB was 0.93 and 0.79. In Table 3 all con-

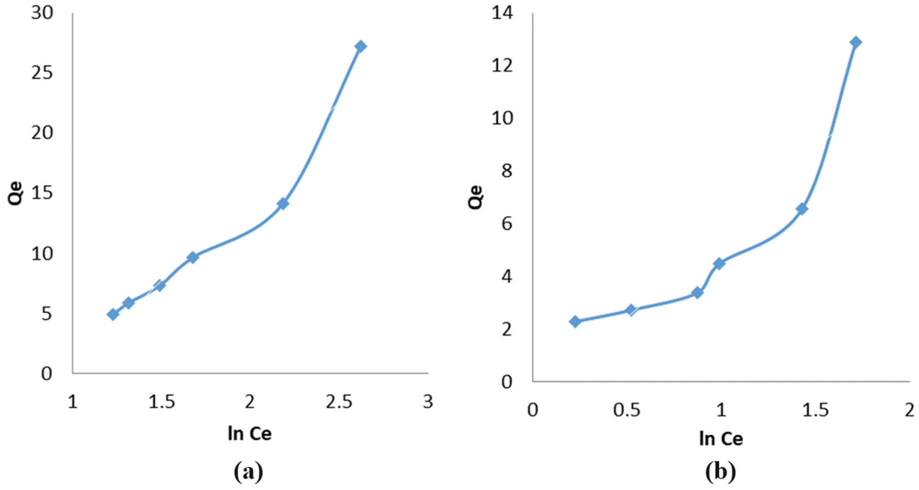


Fig. 14. Temkin isotherm for (a) RZB (b) AZB for removal of Imidacloprid.

Table 3. Isotherm parameter values and correlation coefficient for adsorption of Imidacloprid by RZB and AZB

Isotherm	Parameters	Values	Correlation coefficient
RZB			
Langmuir	Q_m (mg/g) Ka (l/mg)	58.8 0.023	0.98
Freundlich	n (g/L) K_F (L/mg)	0.8635 1.2535	0.99
Temkin	A (L/mg) B	0.3751 14.85	0.93
AZB			
Langmuir	Q_m (mg/g) Ka (l/mg)	83.3 0.021	0.95
Freundlich	n (g/L) K_F (L/mg)	1.529 0.8944	0.94
Temkin	A (L/m g) B	0.8882 6.407	0.79

stant values are presented for the Temkin isotherm. For RZB, the Temkin isotherm was suitable as compared to AZB.

From the data of the adsorption of imidacloprid by RZB and AZB, both Langmuir and Freundlich isotherm were suitable for the process and Temkin isotherm was suitable for RZB only.

Mechanism

Pesticide residue present in the water in the agricultural field may affect the soil and water body in the environment [71]. For the removal of pesticides, various mechanisms are reported, such as biodegradation, bioadsorption and bioaccumulation. Mishaqa reported that, 87-96% removal of pesticides by microorganisms was seen by bioadsorption [72]. In the bioadsorption process various mechanisms are also involved like electrostatic interaction [73,74] ion exchange, precipitation and adsorption [75], and surface complexation [76]. Active groups on the surface and characteristics of the microorganisms are the important parameters which decide the adsorption efficiency of pesticide [77]. Polysaccharides, carbohydrate intercellular spaces and fibril matrix are the components of cell wall of microorganisms, which could help in adsorption of organic pollutant from water [78]. In the microbial removal of pesticides, biodegradation is important, in which organic matter is converted into minute molecules. These small molecules are utilized as nutrient source by microorganisms [79,80]. Gokhan Onder Erguven reported bioremediation of imidacloprid by use of *Ochrobactrum thiophenivorans* and *Sphingomonas melonis*. The two types of bacteria showed high removal efficiency for imidacloprid [81]. Imidacloprid degradation was highest by using *Pseudomonas bacteria* [82]. Wastewater having *Rhodopseudomonas capsulate* could effectively remove imidacloprid [83]. *Pseudomonas* sp. 1G converted imidacloprid in urea metabolites with denitrification process [84]. Hydrolysis of imidacloprid to dechlorinated 6-chloronicotinic acid was observed by Bradyrhizobiaceae strain SG-6C. In the process, nicotinic acid metabolism path was seen, and as carbon source 6-CNA was utilized by microbial community [85]. Three important biodegradation pathways have been reported for the imidacloprid removal in which imidacloprid hydroxylation, nitro group reduction and nitro group loss were observed [86,87]. Microorganisms can react physically as well as chemically to the substance, resulting in change in structure or complete degradation of the substance was observed [88]. In the process of bioremediation of imidacloprid by use of RZB and AZB, investigation of adsorbent RZB and AZB for the content of imidacloprid after the reuse was carried out. Presence of imidacloprid was not observed on the adsorbent. Maybe due to bioadsorption, the removal of imidacloprid was seen. RZB and AZB is a combination of lignite and *Rhizobium* bacteria and *Azospirillium* bacteria, large fraction of imidacloprid may be consumed as food by bacteria [56]. Both adsorbents showed same type of mechanism for adsorption of imidacloprid.

REUSABILITY STUDY

Performance of the adsorbent was analyzed up to fourth cycle for RZB and AZB for adsorption of imidacloprid. Fig. 15 depicts the reusability study for both adsorbents. Both adsorbents show good

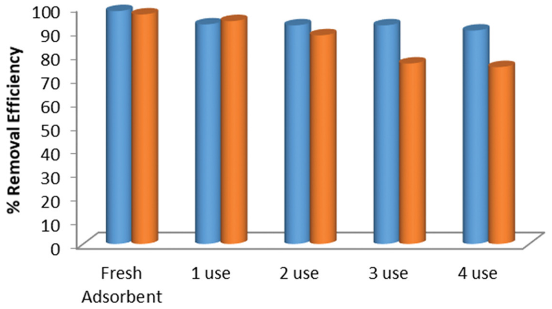


Fig. 15. Reusability of the RZB and AZB for removal of Imidacloprid.

removal efficiency at fourth cycle also.

CONCLUSIONS

Azospirillium biofertilizer and *Rhizobium* biofertilizer were utilized for the adsorption of imidacloprid. Batch experimentation was conducted using RZB and AZB. Time for maximum removal was 20 minutes for both adsorbents. The optimized pH value for AZB and RZB was 7. Removal efficiency was higher at the optimized value of 50 °C. Optimized dose for AZB, 1.5 g and for RZB 2 g was observed. Optimized agitation speed was 260 rpm. For the adsorption process, Langmuir and Freundlich isotherms were suitable. Langmuir adsorption capacity for AZB was 83.3 mg/g and for RZB 58.8 mg/g. Pseudo-second-order model was best fitted to the experimental data for both adsorbents. These biofertilizers were used to increase crop production. From experimental data, it can be concluded that, AZB and RZB can be used for removal of excess of imidacloprid from water. This study will be beneficial for the removal of excess insecticide quantity.

REFERENCES

1. T. D. Wilde, P. Spanoghe, J. Mertens, K. Sniegowksi, J. Ryckeboer, P. Jaeken and D. Springael, *Environ. Pollut.*, **157**, 1373 (2009).
2. C. A. Damalas, *Sci. Res. Essays.*, **4**, 945 (2009).
3. H. M. G. van der Werf, *Agr. Ecosyst. Environ.*, **60**, 81 (1996).
4. C. Wilson and C. Tisdell, *Ecol. Econ.*, **39**, 449 (2001).
5. D. Pimentel, *Environ. Dev. Sustain.*, **7**, 229 (2005).
6. M. Maroni, A. Fanetti and F. Metruccio, *Med. Lav.*, **97**, 430 (2006).
7. P. Alvarez-Zaldivar, S. Payraudeau, F. Meite, J. Masbou and G. Imfeld, *Water. Res.*, **139**, 198 (2018).
8. J. M. C. Diaz, L. Delgado-Moreno, R. Nunez, R. Nogales and E. Romero, *Bioresour. Technol.*, **214**, 234 (2016).
9. G. O. Erguven and N. Yildirim, *Curr. Microbiol.*, **76**, 1461 (2019).
10. I. Carra, J. A. Sanchez Perez, S. Malato, O. Autin, B. Jefferson and P. Jarvis, *J. Chem.Technol. Biotechnol.*, **91**, 72 (2016).
11. O. Iglesias, J. Gomez, M. Pazos and M. A. Sanroman, *Appl. Catal. B.*, **144**, 416 (2014).
12. S. Swami, R. Muzzammil, S. Saha, A. Shabeer, D. Oulkar, K. Banerjee and S. B. Singh, *Environ. Monit. Assess.*, **188**, 301 (2016).
13. P. N. Moza, K. Husteri, E. Feicht and A. Kettrup, *Chemosphere*, **36**, 497 (1998).
14. O. Iglesias, J. Gomez, M. Pazos and M. A. Sanroman, *Appl. Catal. B.*, **144**, 416 (2014).
15. C. Segura, C. Zaror, H. D. Mansilla and M. A. Mondoca, *J. Hazard. Mater.*, **150**, 679 (2018).
16. M. S. Fuentes, C. S. Benimeli, S. A. Cuozzo and M. J. Amoroso, *Int. Biodeterior. Biodegradation.*, **64**, 434 (2010).
17. A. T. Shawaqfeh, *Chin. J. Chem. Eng.*, **18**, 672 (2010).
18. H. Ikeura, F. Kobayashi and M. Tamaki, *J. Food Eng.*, **103**, 345 (2011).
19. A. T. Shawaqfeh and F. A. Al Momani, *Sol. Energy*, **84**, 1157 (2010).
20. K. V. Plakas, A. J. Karabelas, T. Wintgens and T. Melin, *J. Membr. Sci.*, **284**, 291 (2006).
21. P. Thanekar, M. Panda and P. R. Gogate, *Ultrason. Sonochem.*, **40**, 567 (2018).
22. L. U. Jianmei, Z. Zhuo, L. Xiaorong, C. Zhongzheng, L. Bin and Z. Yuanyuan, *Food Control*, **131**, 108 (2022).
23. Y. Yong, M. A. Xinxin, Y. Chunhong, W. Yanru, C. Jingli, Z. Jinhao, D. Xiaowa and Z. Qingming, *Chem. Eng. J.*, **430**, 132 (2022).
24. F. Ishtiaq, H. Nawaz Bhatti, A. Khan, I. Munawar and K. Abida, *Int. J. Biol. Macromol.*, **147**, 217 (2020).
25. K. Wang, J. Shu, V. K. Sharma, L. Cong, X. Xiping, N. Nasri and W. Hongyu, *Sci. Total Environ.*, **805**, 150 (2022).
26. S. Singh, S. Kaushal, J. Kaur, G. Kaur, S. K. Mittal and P. P. Singh, *Chemosphere*, **272**, 132707 (2021).
27. M. E. A. Abigail, M. S. Samuel and R. Chidambaram, *J. Taiwan Inst. Chem. Eng.*, **63**, 318 (2016).
28. M. S. Samuel, *Afr. J. Microbiol. Res.*, **7**, 3101 (2013).
29. A. Thevannan, R. Mungroo and C. H. Niu, *Bioresour. Technol.*, **101**, 1776 (2010).
30. P. Venkateswarlu, M. Venkata Ratnam, D. Rao and M. Rao, *Int. J. Phys. Sci.*, **2**, 188 (2007).
31. X. Chen, Q. Zhou, F. Liu, Q. Peng and P. Teng, *Chemosphere*, **233**, 49 (2019).
32. M. S. Samuel, *J. Photochem. Photobiol. B Biol.*, **204**, 111 (2020).
33. K. Vijayaraghavan and R. Balasubramanian, *J. Environ. Manag.*, **160**, 283 (2015).
34. M. Fomina and G. M. Gadd, *Bioresour. Technol.*, **160**, 3 (2014).
35. R. M. Hlihor, *New Biotechnol.*, **32**, 358 (2015).
36. K. Zhou, Z. Yang, Y. Liu and X. Kong, *J. Environ. Chem. Eng.*, **3**, 2219 (2015).
37. S. Tasar, F. Kaya and A. Ozer, *J. Environ. Chem. Eng.*, **2**, 1018 (2014).
38. G. Wang, *Arab. J. Chem.*, **11**, 99 (2018).
39. M. Moyo, U. Guyo, G. Mawenyiyo, N. P. Zinyama and B. C. Nyamunda, *J. Ind. Eng. Chem.*, **27**, 126 (2015).
40. L. D. Hafshejani, *J. Mol. Liq.*, **211**, 448 (2015).
41. A. Ronda, M. Calero, G. Blazquez, A. Perez and M. A. Martin-Lara, *J. Taiwan Inst. Chem. Eng.*, **51**, 109 (2015).
42. M. Lopez-Mesas, E. R. Navarrete, F. Carrillo and C. Palet, *Chem. Eng. J.*, **174**, 9 (2011).
43. U. Guyo, J. Mhonyera and M. Moyo, *Process Saf. Environ. Prot.*, **93**, 192 (2015).
44. T. Blacqui, G. Smagghe, C. A. M. Van Gestel and V. Mommaerts, *Ecotoxicology*, **21**, 973 (2012).
45. R. Sur and A. Stork, *Bull. Insectol.*, **56**, 35 (2003).
46. A. C. Morrissey, P. Mineau, H. J. Devries, F. Sanchez-Bayo, M. Liess, C. C. Michael and K. Liber, *Environ. Int.*, **74**, 291 (2015).
47. A. I. J. M. Dijk, H. E. Beck, R. S. Crosbie, R. A. M. De Jeu, Y. Y. Liu, G. M. Podger, B. Timbal and N. R. Viney, *Water Resour. Res.*, **49**,

1040 (2013).

48. K. Starner and K. S. Goh, *Bull. Environ. Contam. Toxicol.*, **88**, 316 (2012).
49. C. A. Morrissey, P. Mineau, J. H. Devries, F. Sanchez-Bayo, M. Liess, M. C. Cavallaro and K. Liber, *Environ. Int. Jan.*, **74**, 291 (2015).
50. C. M. Batikian, A. Lu, K. Watanabe, J. Pitt and R. M. Gersberg, *Chemosphere*, **223**, 83 (2019).
51. F. Martelli, Z. Zhongyuan, J. Wang, C. Wong, E. K. Nicholas, U. Roessner, T. Rupasinghe, K. Venkatachalam, T. Perry, H. J. Bellen and P. Batterham, *Acad. Sci.*, **117**, 25840 (2020).
52. J. Lu, Z. Zhang, X. Lin, Z. Chen, B. Li and Y. Zhang, *Food Control*, **131**, 108 (2022).
53. X. Cui, X. Liu, C. Liu, M. He and W. Ouyang, *Chemosphere*, **254**, 126 (2020).
54. A. Mandal and N. Singh, *Int. J. Hyg. Environ. Health*, **220**, 637 (2017).
55. A. Aamir, *Sep. Purif. Technol.*, **157**, 141 (2016).
56. K. Parashar, N. Ballay, S. Debnath, K. Pillay and A. Maity, *J. Colloid Interface Sci.*, **476**, 103 (2016).
57. G. Z. Menon, M. I. Bhanger, M. Akhtar, F. N. Talpur and J. R. Memom, *Chem. Eng. J.*, **138**, 616 (2008).
58. K. Kulkarni, G. Bhogale and R. Nalawade, *Korean J. Chem. Eng.*, **35**, 153 (2018).
59. D. P. Das, J. Das and K. Parida, *J. Colloid Interface Sci.*, **261**, 213 (2003).
60. N. Daneshwar, S. Aber and A. Khani, *J. Hazard. Mater.*, **144**, 47 (2007).
61. K. Azza, E. N. Ahmed, E. S. Amany and O. Abdelwahab, *Desalination*, **238**, 210 (2009).
62. W. T. Tsai, H. C. Hsu, T. Y. Su, T. Y. Lin, K. Y. Lin, C. M. Lin and T. H. Dai, *J. Hazard. Mater.*, **147**, 1056 (2007).
63. J. Walter, J. Weber and J. C. Morris, *J. Sanitary Eng.*, **89**, 31 (1963).
64. S. Lagergren, *Handlingar*, **24**, 1 (1898).
65. J. Weber, J. Walter and J. Carrell Morris, *J. Sanit. Eng. Div.*, **90**, 79 (1964).
66. Y. S. Ho and G. McKay, *Process Biochem.*, **34**, 451 (1999).
67. Y. S. Ho and G. McKay, *Process Saf. Environ. Protect.*, **76**, 183 (1998).
68. I. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
69. H. Z. Freundlich, *Phys. Chem.*, **57**, 384 (1906).
70. L. Tang, J. Yu, Y. Pang, G. Zeng, Y. Deng, J. Wang, X. Ren, S. Ye, B. Peng and H. Feng, *Chem. Eng. J.*, **336**, 160 (2018).
71. G. O. Erguven and U. Demirci, *J. Environ. Health Sci.*, **18**, 395 (2020).
72. E. S. I. Mishaqa, *J. Fertil. Pestic.*, **8**, 5 (2017).
73. E. Ardal, Slu Department of Biosystems & Technology (2014).
74. M. Bilal, T. Rasheed, J. E. Sosahernández, A. Raza, F. Nabeel and H. M. N. Iqbal, *Mar. Drugs*, **16**, 65 (2018).
75. S. S. G. Ungureanu, R. Boaventura and C. Botelho, *Environ. Eng. Manag. J.*, **14**, 455 (2015).
76. M. Fomina and G. M. Gadd, *Bioresour. Technol.*, **160**, 3 (2014).
77. A. Ata, O. O. Nalcaci and B. Ovez, *Algal Res.*, **1**, 194 (2012).
78. A. M. Hammed, S. K. Prajapati, S. Simsek and H. Simsek, *Algae*, **31**, 189 (2016).
79. V. Matamoros and Y. RodraGuez, *J. Hazard. Mater.*, **309**, 126 (2016).
80. I. A. Perez-Legaspi, L. A. Ortega-Clemente, J. D. Moha-Leon, E. Ríos-Leal, S. C. Gutierrez and I. Rubio-Franchini, *J. Environ. Sci. Health B*, **51**, 103 (2016).
81. G. O. Erguven and U. Demirci, *Environ. Technol. Innov.*, **21**, 101236 (2021).
82. M. Gupta, S. Mathur, T. K. Sharma, M. Rana, A. Gairola, N. K. Navani and R. A. Pathania, *J. Hazard. Mater.*, **301**, 250 (2016).
83. P. Wu, X. Zhang, T. Niu, Y. Wang, R. Liu and Y. Zhang, *Environ. Pollut.*, **257**, 114254 (2020).
84. G. Pandey, S. J. Dorrian, R. J. Russell and J. G. Oakeshott, *Biochem. Biophys. Res. Commun.*, **380**, 710 (2009).
85. M. Shettigar, S. Pearce, R. Pandey, F. Khan, S. J. Dorrian, S. Balotra, R. J. Russell, J. G. Oakeshot and G. Pandey, *PLoS One*, **7**, e51162 (2012).
86. D. A. Schulz-Jander and J. E. Casida, *Toxicol. Lett.*, **132**, 65 (2002).
87. J. E. Casida, *J. Agric. Food Chem.*, **59**, 2923 (2011).
88. G. Briceno, G. Palma and N. Duran, *Crit. Rev. Environ. Sci. Technol.*, **37**, 233 (2007).