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Sorption of Paraquat and 2,4-D by an *Oscillatoria* Sp.-Dominated Cyanobacterial Mat

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Abstract The present study characterises sorption of two pesticides, namely, paraquat (PQ) and 2,4-dichlorophenoxyacetic acid (2,4-D) by an *Oscillatoria* sp.-dominated cyanobacterial mat. Sorption of PQ onto the test mat was not significantly affected by the pH of the solution within the pH range 2–7. However, 2,4-D sorption was strongly influenced by the solution pH and was maximum at pH2. Whereas PQ sorption increased with increase in temperature, 2,4-D sorption showed an opposite trend. The sorption of PQ and 2,4-D achieved equilibrium within 1 h of incubation, independent of concentration of pesticide and mat biomass in the solution. The pseudo-second-order kinetic model better defined PQ sorption than the pseudo-first-order model, whereas 2,4-D sorption was well defined by both the models. Sorption isotherms of both the pesticides showed L-type curve. Freundlich model more precisely defined PQ sorption than Langmuir model, thereby suggesting heterogeneous distribution of PQ binding sites onto the biomass surface. However, the Langmuir model more correctly defined 2,4-D sorption, thus, indicating homogeneous distribution of 2,4-D binding sites onto the biomass surface. The test biomass is a good sorbent for the removal of PQ because it could, independent of pH of the solution, sorb substantial amount of PQ ($q_{\max}$=0.13 mmol g^{-1}).

Keywords Sorption · Paraquat · 2,4-D · *Oscillatoria* · Cyanobacterial mat

Introduction

Pesticides are widely used for eradicating undesirable insects, plant pathogens, weeds, molluscs, birds, mammals, fish, nematodes, etc., that compete with humans for food, destroy property, spread uncontrollably, or are vectors of disease or cause annoyance [1]. However, contamination of natural waters by pesticides is a serious environmental problem nowadays due to their unapproved use, poor agricultural practices, illegal operations, accidental releases, surface runoff from agriculture land, and direct release of effluents from pesticides manufacturing industries [2–4]. Pesticides deleteriously affect aquatic biota and, thus, may seriously disturb structure and function of aquatic ecosystems [5, 6]. The bioaccumulation and subsequent

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biomagnification of pesticides in fishes and other organisms through food chains might cause serious health risks to human beings [7]. Direct drinking of pesticide-polluted water may cause various types of chronic diseases associated with kidney, eye, skin, immune systems, nervous system, endocrine system, etc. [8]. Thus, the protection and remediation of pesticide-contaminated water bodies seem a very important task.

The methods commonly used for the removal of pesticides from wastewaters comprise destructive oxidation and sorption onto various materials [9]. Destructive oxidation of pesticides often generates secondary pollutants (degradation products), which are as toxic as their mother compounds [10], and so this process is not environment-friendly. Conversely, sorption process does not produce any secondary pollutant and, thus, seems a safe and effective alternative for the removal of pesticides. In this context, nonbiological and biological sorbents are receiving a great deal of attention recently. Granular-activated carbon has been often tested for the sorptive removal of pesticides from aqueous solutions [10–12]. However, it is expensive and often loses its pesticide sorption ability during successive cycles of sorption and desorption. Among biological materials, polymerin [13], oilseed press-cake [14], modified rice husk [15], wood residue [16], rice husk [17], vegetable biomass [18], and bituminous shale [19] have shown promising capability for the sorptive removal of pesticides from aqueous solutions. Other biological materials, such as cyanobacteria, bacteria, unicellular green algae, filamentous green algae, seaweeds, fungi, etc., have also shown remarkable capability to sorb metal ions and dye pollutants [20, 21], and they seem to be good candidates for the removal of pesticides as well.

In the present study, we have studied the sorption of 2,4-D and paraquat (hereafter referred to as PQ) by the dried biomass of an *Oscillatoria* sp.-dominated cyanobacterial mat in relation to pH, time, biomass and pesticide concentration, and temperature. The *Oscillatoria* sp.-dominated cyanobacterial mat was selected for the study due to the following reasons: (1) the self-immobilized biomass of *Oscillatoria* sp. is very common in our locality, distributed worldwide, and can be easily harvested from nature and (2) the species of *Oscillatoria* are well known to secrete exopolysaccharide-rich matrix endowed with numerous sites for the sorption of ionic pollutants [22, 23]. The pesticides selected for the study, 2,4-D and paraquat, are frequently used in agriculture; however, both are extremely toxic to nontarget organisms including humans at a very low concentration [24, 25].

Materials and Methods

Biosorbent

A cyanobacterial mat dominated by *Oscillatoria* sp. was collected from a pond close to the campus of the Banaras Hindu University, Varanasi, India. *Oscillatoria* sp. is a filamentous, unbranched, and non-heterocystous cyanobacterium that can be easily identified by its oscillatory movement and typical apical cell. The mat biomass was firstly washed with tap water and thereafter with Milli-Q water so as to remove dust, soil, and other materials sticking to the biomass. Then, it was dried in a hot-air oven at 80°C until constant weight, powdered, and sieved to get particles of 0.1 to 0.2 mm size.

The Test Pesticides (PQ and 2,4-D)

PQ is the trade name of 1,1′-dimethyl-4,4′-bipyridinium dichloride, a quaternary ammonium herbicide which is also known as methyl viologen. The molecular formula and molecular weight of PQ is $CH_3(C_5H_4N)_2CH_3Cl_2$ and 257.16 $\mathrm{g\,mol^{-1}}$, respectively. At room temperature, it appears as a solid (density=1.25 $\mathrm{g\,cm^{-3}}$), odorless, off-white powder and has a very high solubility in water. It remains in cationic form in aqueous solution and gives absorption maximum in UV range at 257 nm [13]. It quickly generates superoxide species when it enters a cell and, thus, causes severe damage to cellular membranes by oxidizing unsaturated membrane lipids.

2,4-D (2,4-dichlorophenoxyacetic acid), a synthetic auxin (plant growth hormone) with molecular formula $C_8H_6Cl_2O_3$ and molecular weight 221.04 $\mathrm{g\,mol^{-1}}$ is a widely used herbicide of phenoxy family. It is readily available in market in various formulations under a wide variety of brand names, such as Weedtrine-II, Aqua-Kleen, Barrage, Plantgard, etc. At room temperature, it appears as white to yellow powder and is soluble in water (900 mg $\mathrm{l^{-1}}$). It remains in anionic form in aqueous solution; however, equilibrium of ionization between anionic and molecular form is affected by pH of the solution [13]. It gives absorption maximum in UV range at 282 nm. It causes excessive growth of leafy parts of plants, thus, inducing curling or withering of leaf and stem and ultimate death of the affected plant.

Preparation of Stock Solution

Stock solutions of pesticides were prepared in Milli-Q water with analytical grade salts of 2,4-D and PQ. The stock solution (4.0 mM) was diluted with Milli-Q water to prepare solutions of the desired concentrations.

Sorption Methodology and Analysis of Residual Pesticide Content in the Solution

As a general procedure, sorption of both the test pesticides (PQ and 2,4-D) was determined in batch setup considering three replicates. Pre-weighted dried biomass (10 mg) of the test mat was added to 100-ml Erlenmeyer flasks each containing 10 ml of pesticide solution of known concentration (0.0–2.0 mM) and agitated on a shaker at 80 rpm and 25±2°C until the equilibrium was reached. Subsequently, the biomass was separated by centrifugation at 5,000 rpm. The supernatant was taken into clean-dried test tubes for determining the residual pesticide concentration. For residual pesticide analysis, the absorbance was recorded at 257 [13] and 282 nm [19], respectively, for PQ and 2,4-D. The effects of pH on the sorption of PQ and 2,4-D were studied within the pH range 2–7, and the desired pH values were obtained using 0.1 N HCl/NaOH. Since pH4 and 2 were, respectively, found optimum for the sorption of 2,4-D and PQ, they were selected for all other experiments. Independent sets of experiments were conducted at three different initial concentrations of pesticides (i.e., 0.045, 0.226, and 0.453 mM for 2,4-D and 0.039, 0.195, and 0.389 mM of PQ) and mat biomass (i.e., 1, 2.0, and 4.0 $\mathrm{g\,l^{-1}}$) to find out the time required for the establishment of the sorption equilibrium and also to assess the kinetic behavior of pesticide sorption by the mat biomass. However, the effect of biomass concentration was examined taking its four different concentrations (i.e., 0.5, 1.0, 2.0, and 4 $\mathrm{g\,l^{-1}}$). Similarly, influence of temperature on sorption was studied within the temperature range 10–40°C. Arrhenius activation energy has been calculated following the equation given in Alam et al. [26].

Kinetic and Isotherm Modelling of Sorption Data

Freundlich and Langmuir empirical equations were used to model the sorption isotherm data of both the test pesticides because they showed L-type sorption curve [27]. However, time course sorption data were fitted to pseudo-first-order and pseudo-second-order equations to identify kinetic order of the pesticide sorption reaction. The nonlinear method was used for regression analysis.

Results and Discussion

Sorption of PQ and 2,4-D in Relation to Solution pH

Sorption of PQ and 2,4-D was investigated as a function of pH of the solution (Fig. 1). Sorption of PQ onto the mat biomass was not significantly affected by the solution pH within the range 2–7, when the PQ concentration in the solution was 0.039 mM. However, a slight increase, i.e., from 0.071 to 0.086 mmol g^{-1}, in PQ sorption was noticed with increase in pH from 2 to 3 at 0.389 mM concentration of PQ. This observation suggests that binding sites for sorbing ~0.071 mmol g^{-1} PQ onto mat biomass were available at all the tested pH, and a small number of additional binding sites for sorbing ~0.015 mmol g^{-1} PQ appeared consequent upon change in pH of the solution from 2 to 3. A good amount of PQ sorption at pH2 suggests that the test biomass has sufficient negative charge even at pH2 because ionic bonding involving columbic attraction between opposite charged species is usually responsible for PQ sorption by biological materials [13]. It deserves mention that PQ, being a quaternary ammonium compound, always shows a specific character of complete ionization in the form of permanently charged cationic species in the solution independent to pH of the solution [28]. This particular property makes the mat biomass better than other sorbents, such as polymerin, for sorbing cationic species from aqueous solution. Polymerin is the humic acid-like fraction of olive mill wastewater that showed optimum and negligible sorption of PQ, respectively, at pH5.7 and 3 [13]. Contrary to PQ, sorption of 2,4-D onto the biomass was considerably lower and strongly affected by the pH at its both tested concentrations. The sorption of 2,4-D was maximum at pH2, and it declined with further increase in pH. The sorption of 2,4-D was almost negligible at pH>4. Sannino et al. [13] noted a similar behaviour of 2,4-D sorption by polymerin. They suggested that the sorption of 2,4-D onto biological materials, by the help of hydrogen bonding, occurs when it exists in unionized (molecular) form. When pH of the solution increases, the ratio of molecular 2,4-D to its anionic form decreases and simultaneously, the biomass gains more negative charge. These changes together cause repulsion of 2,4-D from the biomass surface and ultimately result in decreased sorption of 2,4-D by the biomass.

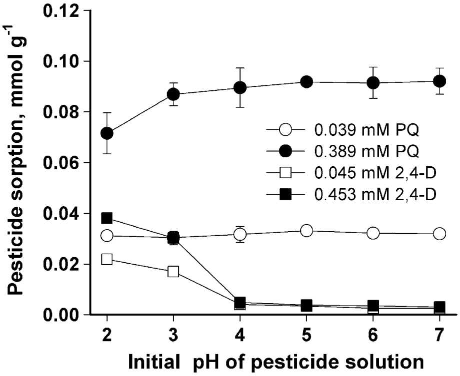


Fig. 1 Sorption of PQ and 2,4-D by *Oscillatoria* sp.-dominated cyanobacterial mat in relation to pH of the solution. The biomass concentration, contact time, and temperature were 1 gl^{-1}, 4 h, and 25±2°C, respectively. The *symbols* represent the means of three replicates, and *bars* represent the standard deviation, if larger than the dimensions of the symbols

Biomass Concentration-Dependent Sorption of PQ and 2,4-D from the Solution

The concentration of biomass greatly affected the sorption and removal of PQ and 2,4-D from the solution (Fig. 2). Per unit pesticide sorption (millimole pesticide sorbed per gram mat biomass) decreased at high concentration of biomass because of decreased availability of pesticide for per unit biomass (millimole pesticide available per gram of biomass). However, the removal of pesticide increased with increasing biomass concentration as it enhanced the availability of pesticide binding sites. PQ removal was 83.6–86.2% from the solution containing 0.039 mM PQ for the biomass concentration range 0.5–4 gl^{-1}. PQ removal by mat biomass occurred effectively at high PQ concentration also. At 4.0 gl^{-1} of mat biomass, 55% and 43% PQ removal, respectively, occurred at 0.195 and 0.389 mM of PQ. However, the mat biomass is not a good sorbent for the removal of 2,4-D as 4 gl^{-1} biomass could remove only 37% of 2,4-D from the solution containing 0.045 mM of 2,4-D.

Sorption of PQ and 2,4-D in Relation to Solution Temperature

The sorption of PQ increased with a rise in temperature from 10 to 40°C (Fig. 3). However, the sorption of 2,4-D followed a reverse trend as it declined with increase in temperature. A decrease in sorption of 2,4-D with increase in temperature is perhaps due to involvement of weak forces in the sorption process, like hydrogen bonding, which can easily break due to increase in the kinetic energy of the sorbate molecules with a rise in temperature. The activation energy (E_a) for the sorption of PQ and 2,4-D were calculated at the tested temperatures (see Table 1). The E_a denotes the minimum energy barrier that pesticides (PQ or 2,4-D) overcome for sorption on to the test mat biomass. The values of E_a are in the range of 3.66 to 3.72 kcal mol^{-1} for PQ and −1.45 to −1.35 kcal mol^{-1} for 2,4-D. Such

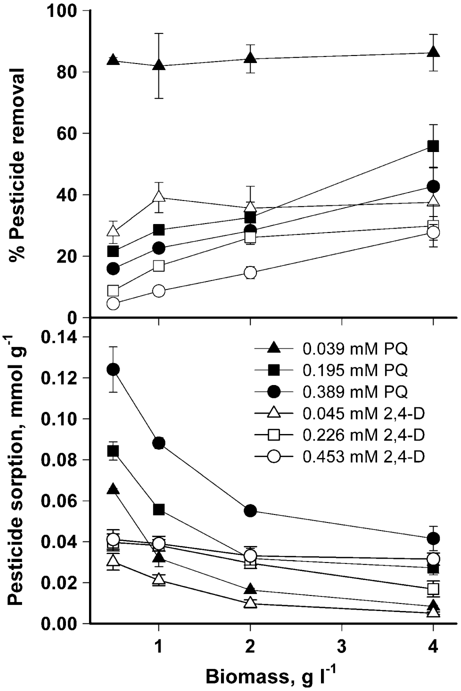
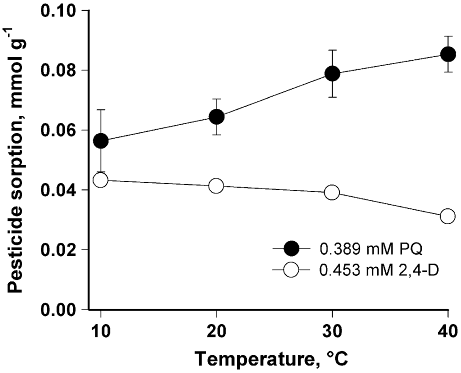


Fig. 2 Sorption and removal of PQ and 2,4-D as a function of biomass concentration of *Oscillatoria* sp.-dominated cyanobacterial mat. Experiments were conducted at 25±2°C for 4 h. The pH of pesticide solution was adjusted to 2 and 4, respectively, for 2,4-D and PQ because these were identified as the optimum pH for the two pesticides

Fig. 3 Temperature-dependent sorption of PQ and 2,4-D by *Oscillatoria* sp.-dominated cyanobacterial mat. All the experiments were conducted for 4 h taking biomass concentration 1 gl^{-1}. The concentration of PQ and 2,4-D were 0.389 and 0.453 mM, respectively. The pH of 2,4-D and PQ solution were adjusted to 2 and 4, respectively, for the reason given in Fig. 2



energy levels are equivalent to the bond energy of van der Waals forces and hydrogen bonding [26].

Time Required for the Establishment of Sorption Equilibrium of PQ and 2,4-D and Kinetic Modelling

Experiments were performed to find out the time required for the establishment of equilibrium of PQ and 2,4-D sorption by the mat biomass (Fig. 4). Sorption of PQ and 2,4-D achieved equilibrium within 1 h of incubation, regardless of the concentration of pesticide and mat biomass in the solution. In a similar way, establishment of equilibrium of Pb(II) sorption onto several plant materials was not significantly affected by the biomass and metal concentration [29]. A rapid attainment of sorption equilibrium is considered as a prerequisite of an ideal sorbent, and in this context, the test mat seems attractive because the time required for sorption of PQ and 2,4-D by mat biomass is lower than that of other reported sorbents. Polymerin required 4 and 24 h, respectively, for significantly sorbing PQ and 2,4-D. The mat biomass also has a considerably lower equilibrium time for 2,4-D sorption compared to other sorbents like bituminous shale (>2 h, [19]) and tire rubber granules (2 h, [26]).

The time course sorption data of PQ and 2,4-D were fitted to the pseudo-first-order and pseudo-second-order models. The pseudo-second-order model (see r^2 in Tables 2 and 3) better defined PQ sorption than the pseudo-first-order model. Thus, kinetic order of PQ sorption by mat biomass is 2. Several other workers have also noticed a greater suitability of the pseudo-second-order model in predicting sorption of various other pollutants, such as metal ions and

Table 1 Arrhenius activation energy (E_a) for the sorption of PQ and 2,4-D onto *Oscillatoria* sp.-dominated cyanobacterial mat.

Pesticide	Temp (°C)	E_a (Kcal mol^{-1})
PQ	10	+3.66
	20	+3.68
	30	+3.70
	40	+3.72
2,4-D	10	−1.44
	20	−1.42
	30	−1.38
	40	−1.35

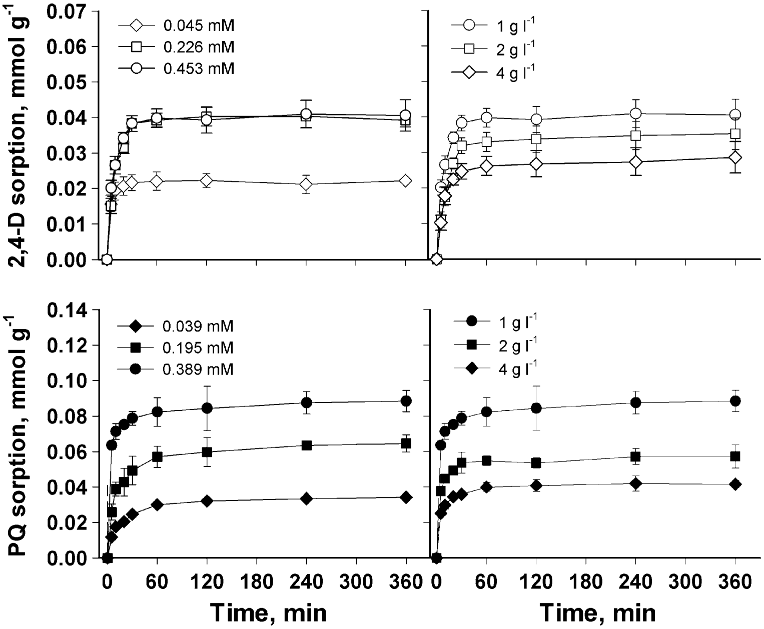


Fig. 4 Time course of PQ and 2,4-D sorption by *Oscillatoria* sp.-dominated cyanobacterial mat. The solution had 1 gl^{-1} biomass at three different concentrations of PQ and 2,4-D. However, concentrations of PQ and 2,4-D were 0.389 and 0.453 mM, respectively, when experiments were conducted at three different concentrations of the biomass. All other experimental conditions were as per Figs. 1 and 2

dyes. On the other hand, time course data of 2,4-D sorption were well defined by both the kinetic models; therefore, the order of sorption reaction is perhaps in a fraction that remains between 1 and 2. Vilar et al. [30] likewise noted a similar kinetic behavior of Cd(II) sorption by *Gelidium* biomass. Our unpublished data on the sorption of methylene blue, a cationic dye, by the same test mat biomass also showed similar sorption kinetics.

Both the kinetic models were used to determine the initial rates of PQ and 2,4-D sorption (Tables 2 and 3). However, the pseudo-second-order rate equation successfully predicted the kinetic behavior of sorption of both PQ and 2,4-D; thus, it could be considered as a more generalized model for kinetic modeling of time course sorption data of both the

Table 2 Parameters of the pseudo-first-order and the pseudo-second-order rate models for the sorption of PQ and 2,4-D onto *Oscillatoria sp.*-dominated cyanobacterial mat.

Pesticide	Conc. (mM)	Pseudo-first-order model				Pseudo-second-order model			
		q_E (mmol g^{-1})	k_{1S} (min^{-1})	Sorption rate (mmol g^{-1} min^{-1})	r^2	q_E (mmol g^{-1})	k_{2S} (min^{-1})	Sorption rate (mmol g^{-1} min^{-1})	r^2
PQ	0.04	0.032	0.061	0.002	0.965	0.035	2.56	0.003	0.994
	0.20	0.060	0.085	0.005	0.954	0.065	1.96	0.008	0.992
	0.40	0.082	0.262	0.025	0.973	0.086	5.74	0.043	0.995
2,4-D	0.04	0.022	0.244	0.005	0.995	0.022	2.33	0.001	0.995
	0.20	0.040	0.118	0.005	0.992	0.042	3.58	0.006	0.980
	0.40	0.040	0.098	0.004	0.993	0.042	4.57	0.008	0.993

Table 3 Parameters of the pseudo-first-order and the pseudo-second-order rate models for the sorption of PQ and 2,4-D onto *Oscillatoria sp.*-dominated cyanobacterial mat.

Pesticide	BC ($g\ l^{-1}$)	Pseudo-first-order model				Pseudo-second-order model			
		q_E ($mmol\ g^{-1}$)	k_{1S} (min^{-1})	Sorption rate ($mmol\ g^{-1}\ min^{-1}$)	r^2	q_E ($mmol\ g^{-1}$)	k_{1S} (min^{-1})	Sorption rate ($mmol\ g^{-1}\ min^{-1}$)	r^2
PQ	1	0.082	0.262	0.022	0.973	0.086	5.785	0.043	0.995
	2	0.054	0.206	0.011	0.982	0.060	6.678	0.024	0.997
	4	0.040	0.163	0.007	0.966	0.042	6.432	0.011	0.997
2,4-D	1	0.040	0.118	0.005	0.992	0.042	4.571	0.008	0.993
	2	0.035	0.076	0.003	0.997	0.037	2.927	0.004	0.980
	4	0.027	0.096	0.003	0.993	0.029	4.933	0.004	0.990

BC biomass concentration

pesticides. The pseudo-second-order rate equation suggests a rapid initial sorption of PQ and 2,4-D onto the biomass, and the initial sorption rates were higher at higher concentrations of pesticides in the solution. Increase in concentration of PQ or 2,4-D in the solution enhanced the chances of collision of these pesticides with binding sites, thus, resulting in their rapid sorption onto the biomass. However, the initial rates of PQ and 2,4-D sorption were lower at higher concentrations of the mat biomass in the solution. This apparently happened because the rate of pesticide sorption is expressed in terms of the amount of pesticide sorbed per unit weight of the biomass per unit time. At a particular external concentration of the pesticide, the availability of pesticide per unit biomass would decrease if there is an increase in biomass concentration. Hence, the rate of pesticide sorption (the amount of pesticide sorbed per unit weight of the biomass per unit time) will decrease with increase in biomass concentration.

Sorption of PQ and 2,4-D as a Function of Their Initial Concentration in the Solution and Isotherm Modeling

PQ and 2,4-D sorption were dependent on their initial concentration in the solution (Fig. 5). PQ sorption by the mat biomass increased rapidly with increasing concentration

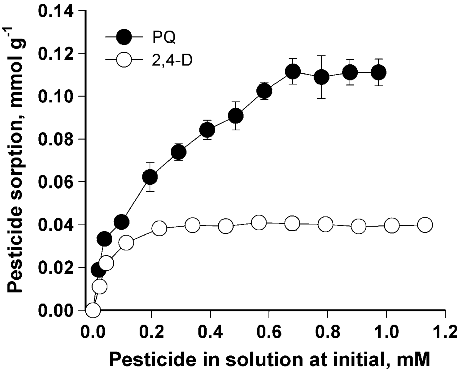


Fig. 5 Concentration-dependent sorption of PQ and 2,4-D by *Oscillatoria* sp.-dominated cyanobacterial mat. Experimental conditions were as in Figs. 1 and 2

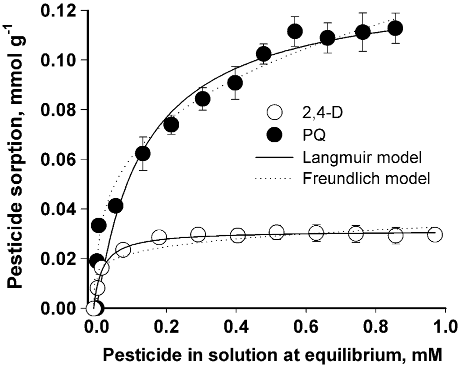


Fig. 6 Isotherm curves of PQ and 2,4-D sorption by *Oscillatoria* sp.-dominated cyanobacterial mat. Equilibrium sorption data were fitted to Freundlich and Langmuir empirical models using the non-linear regression method

of PQ in the solution up to 0.68 mM and thereafter changed little with further increase in its concentration. However, 2,4-D sorption by the mat biomass showed saturation at a very low concentration as no significant increase in sorption was noticed above 0.23 mM. Thus, the test mat biomass has a greater number of sites for the binding of PQ than for 2,4-D.

The sorption data of PQ and 2,4-D, as related to their concentration in the solution, have also been presented in the form of sorption isotherms, plotting sorption amount on Y-axis and the corresponding residual concentration of the test pesticides in the solution on X-axis (Fig. 6). The sorption isotherms of both the pesticides showed L-type curves; therefore, the mathematical modeling of these L-type curves was performed by two well-known empirical models, namely, Freundlich and Langmuir models [27]. The data of PQ and 2,4-D sorption could effectively fit both the models (Table 4). However, Freundlich model more accurately defined PQ sorption, thereby suggesting heterogeneous distribution of PQ binding sites onto the biomass surface [31]. Conversely, sorption isotherm data of 2,4-D more precisely fitted to the Langmuir model, thus, suggesting homogeneous distribution 2,4-D binding sites onto the biomass surface [31]. Langmuir sorption parameter $q_{\max}$ predicts the maximum monolayer sorption capacity [31] of the mat biomass for PQ and 2,4-D. The $q_{\max}$ for PQ is 0.13 mmol g^{-1}; however, it was only 0.04 mmol g^{-1} for 2,4-D sorption. Thus, the test mat biomass has threefold greater capacity to bind PQ from the solution in comparison to 2,4-D. The $q_{\max}$ of mat biomass for PQ compares favorably with the sorption capacity of the other sorbents, such as clays [32], activated bleaching earth [9], polymerin [13], acid-modified rice husk [15], etc. Similarly, $q_{\max}$ of the test mat biomass for 2,4-D also compares very well with sorption capacity of other sorbents like bituminous shale [19], polymerin [13], etc. Langmuir parameter b reveals the affinity of sorbent for the sorbate molecules [31]. The value of b for PQ and 2,4-D were 7.193 and 40.40, respectively. The Freundlich parameter K_f

Table 4 Freundlich and Langmuir parameters for the sorption of PQ and 2,4-D by *Oscillatoria sp.*-dominated cyanobacterial mat.

Pesticide	Freundlich isotherm			Langmuir isotherm		
	K_f (mmol^{1-n} g^{-1} l^n)	n	r^2	$q_{\max}$ (mmol g^{-1})	b (l mmol^{-1})	r^2
PQ	0.122	0.303	0.991	0.130	7.193	0.928
2,4-D	0.044	0.179	0.956	0.040	40.40	0.996

denotes the relative sorption capacity [29] of the mat biomass for PQ and 2,4-D. A higher value of K_f reflects ease in sorption of pesticides by the mat biomass. The present study showed that K_f is higher for PQ than for 2,4-D, thus, suggesting that PQ is more readily sorbed onto the mat biomass in comparison to 2,4-D. The parameter n of Freundlich isotherm is the measure of intensity of sorption, and its value between 0 and 1 is suggestive of the feasibility of the process [33]. In the present study, the value of n always remained <1 for the entire tested concentration range of PQ and 2,4-D.

Conclusions

A rapid attainment of sorption equilibrium is considered as a prerequisite of an ideal sorbent, and *Oscillatoria* sp.-dominated mat biomass successfully fulfils this requirement as sorption of PQ and 2,4-D reached equilibrium within 1 h. The mat biomass is an attractive sorbent for PQ due to the following features: (1) PQ sorption capacity ($q_{\max}$) of mat biomass is 0.13 mmol g^{-1}, which is three times higher than that of 2,4-D, (2) mat biomass is efficient in removing PQ from its low as well as high concentration in the solution, and (3) PQ sorption by mat biomass is independent of pH of the solution within the range 3–7. However, the biomass is not good for the sorption of 2,4-D from aqueous solution due to its low sorption capacity ($q_{\max}$=0.04 mmol g^{-1}), which significantly declined with a rise in temperature and pH.

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