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Peach resin coated silica particles for Imidacloprid removal as a greener approach to water remediation

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ABSTRACT

Pesticides are one of the major toxic pollutants that can be lethal even at trace levels. They generally enter into the water reservoirs through agricultural run-off and hence pose serious threat to flora and fauna of aquatic system. Development of green techniques for pesticide removal is of high importance due to the environmental advantages they offer. In the present work, a green adsorbent was developed for the removal of Imidacloprid from water samples collected from industrial waste. The adsorbent was synthesized by coating peach gum resin on silica particles and was found to effectively remove Imidacloprid from water. Fourier-transform infrared spectra confirmed the desired coating of the resin by indicating the presence of characteristic functional. The adsorption studies showed that the pesticide could be efficiently removed from water with a percentage recovery of about 65% at pH 8. These coated particles are eco-friendly, cost effective as well as facile to prepare through simple ultrasonication method.

Keywords: Peach gum coated silica; Pesticide removal; Adsorption; Green technique

1. Introduction

Excessive application of pesticides has recently become a trend among the farmers throughout the world in order to protect the plants from pests including insects, weeds, rodents and fungus. The pesticides are bioaccumulative in nature and hence possess long lasting toxic effects [1–3]. As they are extensively used for the treatment of crops, therefore, surface water pollution is caused by water run-off, and return flow from irrigated fields. The flowing water carries pesticides with it and ultimately mixes up with surface water, that is, ponds, lakes, river and also groundwater. Pesticides concentration in agricultural and industrial areas generally occurs up to the level of 290 μg/L [4,5]. This can lead to adverse environmental issues, decrease of biodiversity and command on organic resources, ecological imbalance and water contamination [6]. Even lower concentration levels of pesticides can change organoleptic properties of water. Pesticides in water produce smell of earth, onion, mould and chlorine. Some pesticides are cause of foaming, turbidity and change of water colour. They can produce carcinogenic materials by reacting with oxidants, thus making water unfit for drinking [7]. European Union directive has tightened the standard of drinkable water and hence for a single type of pesticide, the concentration should never exceed 0.1 μg/L and for collective pesticides, it should not be more than 0.5 μg/L [4].

Imidacloprid is one of the most extensively used pesticides because of high insecticidal efficiency [8]. It is an

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insecticide with wide range of effectiveness and possesses systematic properties. Imidacloprid is absorbed easily from soil by plants and is translocated to stem and other aerial parts [9]. Hence, Imidacloprid is considered very effective for the pests which affect plants by sucking and penetrating, for example, leafhoppers, aphids, flees, trips, household insects, etc. [7–14]. Polluting environmental water with Imidacloprid is a matter of imperative concern and when used in field, it may accumulate in water and soil, reaching human and other organisms and affecting the nervous system [15]. The literature describes the presence of Imidacloprid in water [16–18]. Imidacloprid and its degraded species also enter into water stream by decomposition of parts of plants over which pesticide has been applied, therefore, the use of Imidacloprid for crops may affect the quality of freshwater [18,19]. Hence, a special consideration needs to be paid to the treatment of affected water through greener methods. Commonly used techniques to purify water from microorganism, dust particle and organic pollutants include filtration, ozonization, flocculation, chlorination and coagulation [20]. Coagulation and flocculation processes are used for the removal of microorganisms, sand particles, dust and other organic matter [21]. But at the same time, these processes remove useful entities by damaging the quality water. In chlorination and ozonation, the oxidizing agents are used for oxidation of organic matter and produce by-products which are reported carcinogenic [22]. So, it is necessary to propose a more appropriate procedure of water purification, which can overcome foresaid drawbacks.

Adsorption is a better replaceable technique for conventional purification method of removing pollutants from water. This technique is portable, low cost and is without adverse effects that may pollute water further. Variety of adsorption techniques have been used for removal of pollutants. Nowadays, adsorption material such as carbon (activated), agricultural waste and biopolymers are being used [23–25]. Presently, biopolymer-based composites are handy and considered efficient for removing pollutants from water.

In past, many biopolymers have been used for removal of dyes and other pollutants from water [26–28]. Nowadays, a keen interest is being taken for the synthesis of low cost and high adsorption capacity materials. Some adsorbents such as peanut shell, castor seed shell and wheat shell have been used for the removal of dyes from water. These low cost adsorbents presented high percentage removal, for example, peanut shell has been applied for the adsorption of cationic dyes with a removal efficiency of 90%–96% [29]. Similarly, castor and wheat shells were found efficient to adsorb basic dyes presenting a percentage removal of 91%–97% [30,31]. Agrowastes such as Eucalyptus bark, etc. have been found to adsorb pesticides such as Imidacloprid in the range of 70%–75% [32]. Peach gum is a substance that is extracted from plant stems (peach tree). It belongs to the family Rosacea and has scientific name *Prunus persica* [33]. Peach gum, a widely spread material as plant tree is present throughout the world. It is commonly found all over the world as the second fruit producing tree after apple. Chemically, peach gum possesses polysaccharides with high molecular mass and has branched structure. Peach gum has large number of –COOH groups, so can be used as an efficient adsorbent material for pollutants such as dyes.

In this work, we prepared an adsorbent using peach gum (*P. persica*) resin with silica particles. Silica possesses silanol groups which facilitate the coating of resin on their surface. Moreover, they provide a higher surface area, which is easily available, cost effective, eco-friendly and non-toxic in nature.

2. Materials and methods

2.1. Chemicals

Imidacloprid standard with 99% purity was purchased from Sigma-Aldrich, Germany. Silica particles, acetonitrile, methanol, sodium hydroxide and hydrochloric acid were purchased from Merck, Germany. Potassium bromide and acetone were also bought from Merck. Crude peach gum was collected personally from peach tree of local garden. It was dried in air and was grounded into fine powder before using for coating. All the experiments were carried out in double deionized water (Milli-Q).

2.2. Preparation of peach gum on silica particles

100 mL solution of peach gum (20 mg/mL) was prepared in deionized water. This solution was stirred for 24 h at 40°C. Peach gum was left to swell in water, meshed by using blender and then filtered with nylon cloth. For coating silica particles, 10 mL of peach gum solution was added separately to 10 test tubes. After washing five times with water, 20 mg of silica particles were added to each test tube. This mixture was sonicated for 30 min; particles were filtered, washed 5–6 times with deionized water and dried in air.

2.3. Characterization of adsorbent

The coated particles were characterized using FTIR spectroscopy and scanning electron microscopy (SEM). Spectra of pure silica particles and coated silica particles were taken using spectrophotometer, Shimadzu model 1800S between 500 and 4,000 cm^{-1}.

2.4. Adsorption studies of Imidacloprid

The parameters such as pH and time were optimized before determining maximum adsorption capacity of the adsorbent. During optimization, 0.2 g of adsorbent was added in each flask having 5 mL of 0.2 mmol/L Imidacloprid solution. The samples from the flasks were withdrawn one after the other at the interval of 60 min between each sample.

Similarly, in order to study the effect of pH variation on adsorption of Imidacloprid on coated particles, pH range 4–12 was maintained by using 0.1 M solution of NaOH or HCl as desired. The abovementioned process was performed using 0.2 g of coated particles in 5 mL solution of 0.2 mmol/L Imidacloprid. The optimized conditions were then used for further studies and the effect of concentration was determined by using concentrations of Imidacloprid from 0.23 to 0.04 mmol/L. 5 mL of each concentration of Imidacloprid solution was then taken and 0.2 g of the adsorbent was added to each flask. All the solutions were separated from coated silica particles after predetermined time using centrifugation process at 5,000 rpm for 10 min. Supernatant was filtered using micronylon filter to ensure that filtrate is free from coated particles. All these experiments were performed in triplicate. Concentration of Imidacloprid was measured using UV/Visible spectrophotometer. Wavelength of the detector was adjusted at 245 nm.

3. Results and discussion

3.1. Characterization of peach gum coated silica particles

3.1.1. FTIR spectroscopy

Spectra of peach gum coated silica particles and pure silica particles are shown in Figs. 1(A) and (B), respectively. Some new absorption bands appeared in the spectrum of coated particles which were absent in case of pure silica particles. The common bands to both spectra were at 3,417.10 cm^{-1} due to stretching vibration of O–H group and broad prominent band at 1,111 cm^{-1} can be due to Si–O–Si asymmetric stretching vibration while 800 cm^{-1} is assigned to Si–O–Si symmetric stretching vibrations.

Band at 2,920.27 cm^{-1} was observed in the spectrum of coated particles only and can be assigned to stretching vibration of C–H. A CH_2 bending can also be predicted in the spectrum A at 1,450 cm^{-1}.

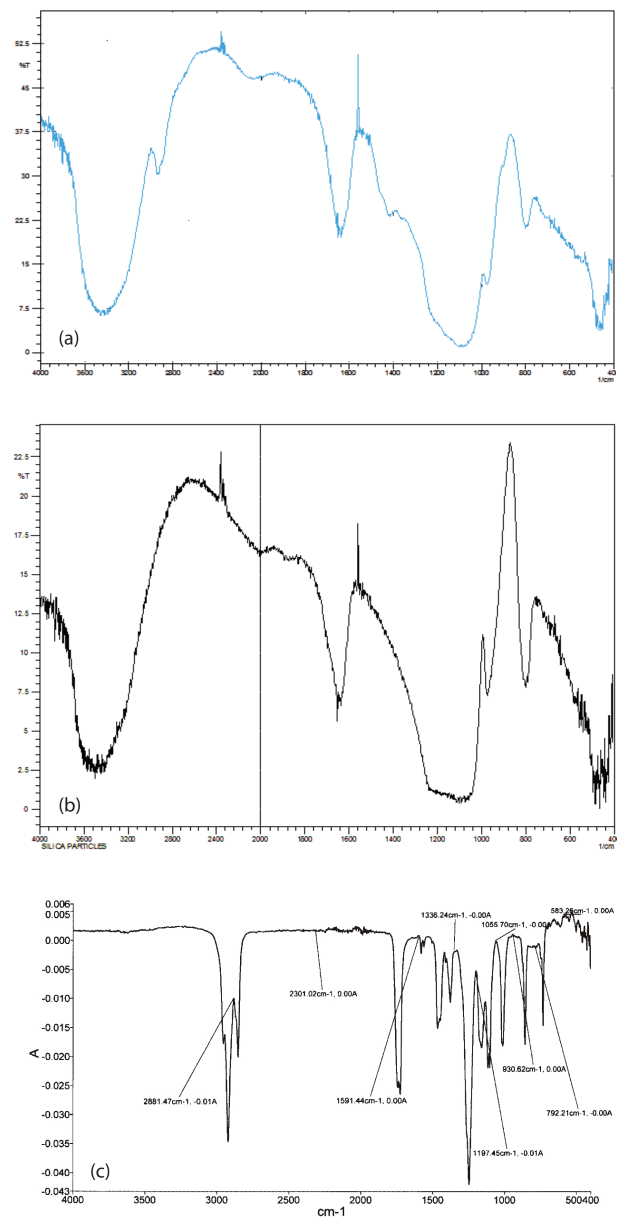

Fig. 1. (A) Spectra of peach coated silica particles, (B) spectra of silica particles and (C) spectra of peach gum.

3.1.2. Scanning electron microscopy

SEM micrograph for silica particles after coating with peach gum was scanned at 200 and 500 magnification as shown in Figs. 2(A) and (B). Surface of silica particles is irregularly enveloped by unequal biomass of peach gum polysaccharide. Morphology of adsorbent appears rough and the presence of oddly located abrasions makes it suitable for adsorption.

3.1.3. Thermogravimetry

Thermogravimetric analysis was performed to determine the stability of the coated particles. Thermogram shows first

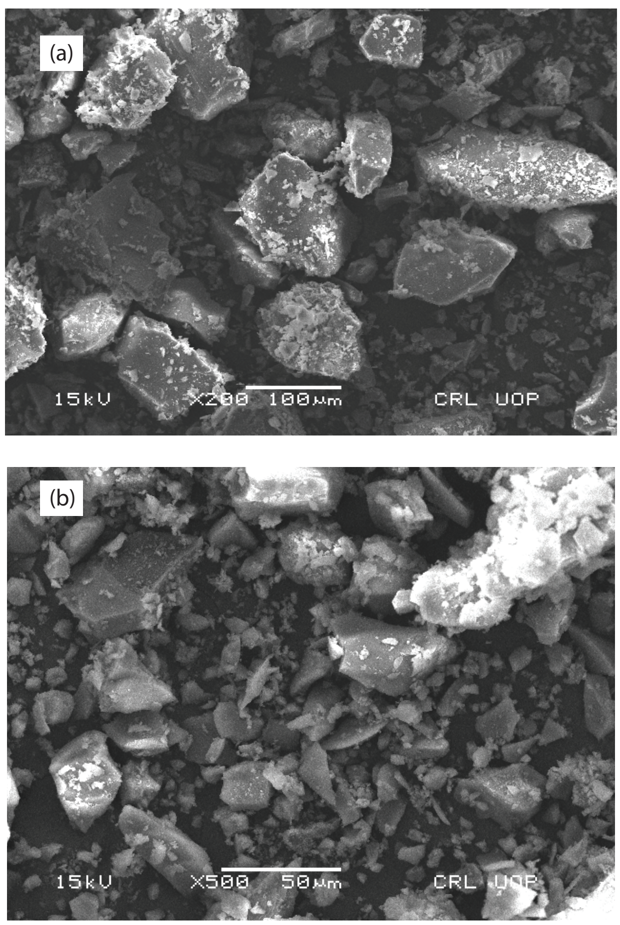

Fig. 2. SEM images of the surface of peach gum coated silica particles at different magnifications (a and b).

mass drop due to water loss at 100°C. Later, two main events occur during decomposition in the range of 220°C–350°C and 400°C–550°C (Fig. 3) so it is preferable to use the adsorbent below 220°C for adsorption process.

3.2. Adsorption

The amount of Imidacloprid adsorbed on to the adsorbent during various experiments was calculated by using the following formula:

$$q_e = \left(\frac{C_i - C_e}{M}\right)V \tag{1}$$

where q_e is the amount of Imidacloprid adsorbed in mg/g, C_i and C_e are initial and final concentrations in mg/L, M is the amount of adsorbent in g and V is the volume of solution in L.

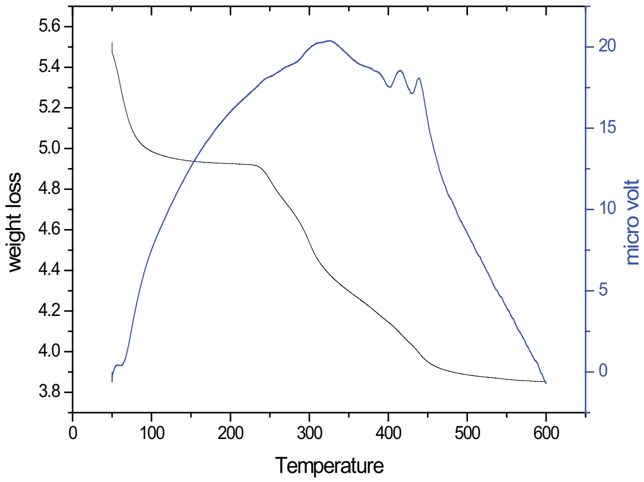

Fig. 3. Thermogravimetric analysis of peach gum coated silica particles.

3.2.1. Effect of contact time

Effect of contact time on adsorption of insecticide is shown in Fig. 4. During the studied time interval, the adsorption of insecticide was found to increase till it became almost constant at 4 h. Hence, the time required for the insecticide to reach equilibrium was 4 h and this time interval was selected for further studies.

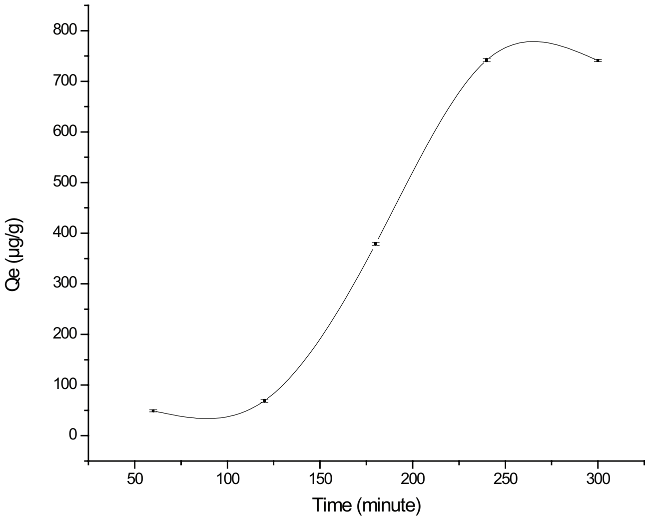

Fig. 4. Effect of contact time on the adsorption of Imidacloprid.

3.2.2. Effect of pH

pH plays a major role in adsorption process by affecting the surface charges of active sites of adsorbent. We studied pH effect for adsorption of Imidacloprid on peach gum coated silica particles in the range of 6–11 (Fig. 5), because Imidacloprid is most stable with in this pH range. The pH studies showed that the adsorption process gradually increased with an increase in pH and maximum adsorption occurred at pH 8. Further increase in pH led to a decrease in adsorption of Imidacloprid which probably is due to the reason that the insecticide is less stable at higher pH. Adsorption of insecticide can be affected as pH change affects the active sites of adsorbent material. All this can be explained from chemistry of peach gum as carbohydrates, hydroxyl, carbonyl and amine groups are present in peach gum whose charges are affected with an increase in pH of the solution [34,35].

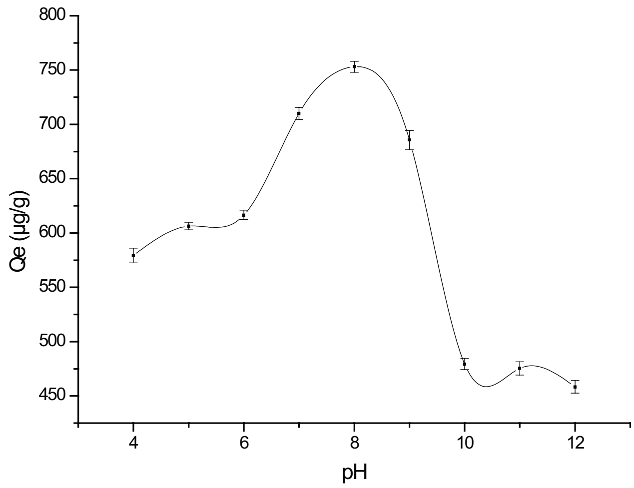

Fig. 5. Effect of pH on the adsorption of Imidacloprid.

3.2.3. Effect of concentration

Insecticide solutions of various concentrations from 10 to 60 µg/mL were prepared (Fig. 6). pH 9 was adjusted by adding 0.1 M NaOH solution drop wise. Time for adsorption was adjusted to 4 h. Adsorption increased with the increase in concentration of Imidacloprid till equilibrium was attained.

3.3. Adsorption isotherms

3.3.1. Langmuir adsorption isotherm

Adsorption data were analyzed by Langmuir and Freundlich isotherms. To apply isotherms, we need relation between C_e/q_e and C_e at equilibrium as initial concentration of adsorbate is increased. To get equilibrium data, concentration of pesticide was varied and the amount of adsorbent was kept constant at 9 pH for 4 h of contact time in static condition. Table 1 depicts the values of different factors. The fitting of Langmuir for adsorption of Imidacloprid on peach gum coated silica particles is presented in Fig. 7.

3.3.2. Freundlich adsorption isotherm

The adsorption isotherms of Imidacloprid on peach gum coated silica particles are shown in Fig. 8, suggesting a high affinity of Imidacloprid on peach gum coated silica particles for this herbicide leading to a progressive saturation of the surface. Freundlich adsorption isotherm model accounts for heterogeneous surfaces. Linear form of equation is given (Eq. (2)). Graph is plotted between $\log C_e$ vs. q_e. Data for Imidacloprid adsorption on peach gum coated silica particles were applied on non-linear isotherm. Freundlich adsorption isotherm presented high values of "R^2" suggesting that the adsorption process fits this isotherm.

$$\log q_e = \log K_F + 1/n \log C_e \tag{2}$$

Values are given in Table 2.

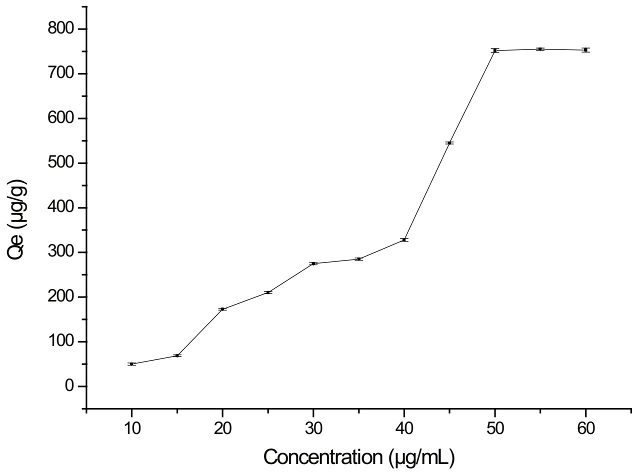

Fig. 6. Effect of increase in concentration of Imidacloprid on adsorption.

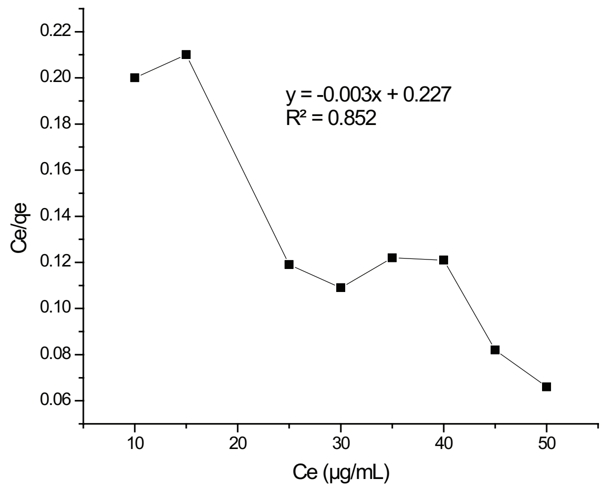

Fig. 7. Langmuir isotherm.

Table 1
Parameters of Langmuir adsorption isotherm

K_L (dm^3/g)	X_m (mg/g)	R^2
73.26	333	0.852

Note: K_L is the maximum binding per L and X_m is the maximum monolayer binding capacity.

4. Regeneration of material

A good adsorbent should have property of regenerability; a loaded adsorbent can be regenerated for further removal of pollutants. This makes material economical for industrial uses. Coated silica particles were collected by technique of centrifugation. Separated particles were washed with methanol and water. Reusability result of peach gum coated silica particles is almost the same as used in first cycle and shown in Fig. 9. Regenerated peach gum coated silica particles presented almost similar adsorption characteristics.

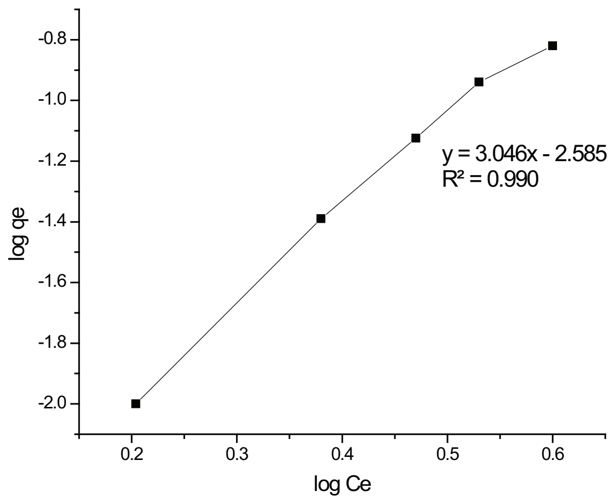

Fig. 8. Freundlich adsorption isotherm.

Table 2
Parameters of Freundlich adsorption isotherm

K_F	0.57
$1/n$	3.04
n	0.32
R^2	0.99

Note: K_F is the Freundlich isotherm constant adsorption capacity (mg/g); $1/n$ is the isotherm sorption intensity; and n is the linearity from deviation.

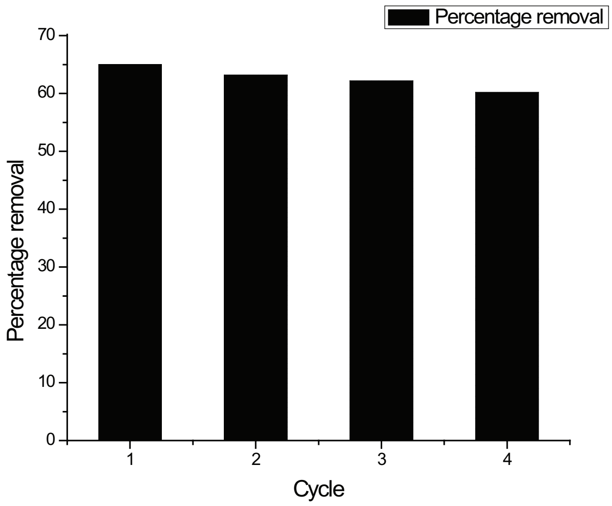

Fig. 9. Percentage removal in different cycles.

5. Conclusion

Peach gum coated silica particles successfully adsorbed Imidacloprid from aqueous solutions. The functional groups such as carbonyl, hydroxyl and carboxyl present on the surface of adsorbent have a prime role in adsorption. Adsorption is affected by parameters including time of contact between coated particles and Imidacloprid solution, pH, concentration of the Imidacloprid. Maximum adsorption of Imidacloprid on coated particles was at 240 min of contact time. A q_e of 725 µg/g was achieved with a percentage removal of 65%. The system followed Freundlich isotherm model.

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