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Amberlite Resin Functionalized with Phosphorous Based Solvent for the Separation of Bisphenol-A: Batch Studies

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Exposure of endocrine disrupting chemicals into the environment is harmful for the human as well as wildlife. Bisphenol-A (BPA) is mainly used as a monomer for the manufacture of epoxy resins, polysulfone, polycarbonate, etc. Separation of pollutants using solvent impregnated resins becomes an attractive alternative as it combines adsorption, ion exchange and solvent extraction. In this study, removal of BPA was done using tri-n-butyl phosphate, an organophosphorous compound, impregnated Amberlite XAD-7HP resin (PX7). Effect of contact time, adsorbent dosage, initial concentration of BPA, and temperature were investigated on the separation efficiency of the resin. Experiments were performed in batch mode.

Keywords: Amberlite XAD-7HP, batch, bisphenol-A, tri-butyl phosphate, solvent impregnated resin

Introduction

Water is essential for all living beings. In 21st century, plastic waste in aquatic bodies has become a known fact which has serious health effects to the humans and aquatic life. Moreover, no technology is available for the complete eradication of these plastics, hence their persistency and durability has led to the accumulation of these materials into the aquatic environment[1]. These materials when degraded releases several smaller chemical compounds that include endocrine disrupting chemicals (EDCs).

EDCs are substances present in the environment either naturally or anthropogenically. These substances have potential to disrupt the endocrine system in many ways like under or over production of hormones, mimicking or repressing a natural hormone[2]. BPA is one of the EDCs mainly used industrially for the production of flame retardants, polycarbonates, epoxy resins, and unsaturated-polyester styrene resins. Thus, BPA causes severe harm. Therefore, an effective technology for the removal of BPA is the need of the hour. Solvent impregnated resin technique was used in this study to remove BPA. In this technique a solvent is physically adhered to the surface of a solid support. The advantages include specificity, high efficiency, no loss of solvent and good regenerability[3].

Experimental

Material and method

Amberlite resin manufactured name XAD-7HP, Bisphenol-A salt of purity greater than 99 wt % and Tri butyl phosphate of purity > 97% procured from Sigma Aldrich company. Grade-1, 125 mm filter paper of Whatman purchased from GE healthcare UK, Ltd was

utilized for filtration purpose. For all experimental purpose Deionized water obtained from Millipore Milli-Q was used.

Adsorption experiments

Equilibrium and kinetic studies were performed to evaluate the potential of prepared SIR for BPA separation. In kinetic study, percentage removal was calculated with respect to time with 6 g/L resin dosage. 10 mg/L to 50 mg/L of BPA was taken to examine the adsorption equilibrium. To find out the temperature dependency on the separation behavior, experiments were performed by changing the temperature from 298 K to 323 K. Determination of concentration of BPA was done using UV-VIS Spectrophotometer at 276 nm. The percentage removal and adsorption capacity were calculated using following formulas.

$$\% R = \left(\frac{C_o - C_{\mathrm{e}}}{C_{\mathrm{o}}}\right) \times 100$$

$$q_{\mathrm{e}} \mathrm{or} q_{\mathrm{t}} = \left(\frac{C_{\mathrm{o}} - C_{\mathrm{e}}}{m}\right) V$$

Here, C_o, is initial and $C_e$is equilibrium concentration of BPA in mg/L. V(in L)is the volume of BPA aqueous solution and m(in g) is the mass of resin.

Results and discussion

Effect of contact time

To observe the effect of contact time on BPA separation, experiments were performed using PX7 and results are shown in Figure 1. It was seen from the figure that firstly, when time was less (5 min) separation of BPA was found to be less (41.09 %) due to less interaction between the PX7 and BPA. Later, when time increased from 5 to 60 min, BPA separation increased from 41.09 % to 89.14%. Further, after 60 min, separation was found to be constant (89.14 %). This increase in adsorption occurred because of the high multitude of active sites on the PX7 surface which leads to the increase in the removal of BPA after 60 min, all the adsorption sites present on the surface of PX7 interacted with BPA. Therefore, equilibrium time for further BPA adsorption was taken as 60 min. To determine the BPA adsorption different kinetic models were applied. The value of $R^2$was observed to 0.998 for pseudo-second order.

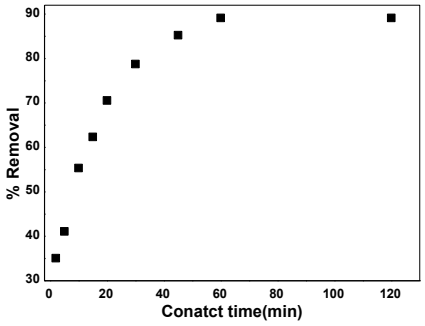

Fig. 1. Effect of contact time on adsorption of BPA using PX7 (m = 6g/L; C_o = 10 mg/L; T = 298 K; and speed of shaker = 100 rpm).

Effect of adsorbent dosage

To observe the effect of PX7 dosage on the BPA separation, studies were carried out at a BPA concentration of 10 mg/L for 60 min at 298 K and at 100 rpm. Dosage of PX7 was varied from 1 g/L to 8 g/L (Figure 2). It was concluded from the figure that the percentage removal of BPA increased from 55.81% to 81.39%. Further, increase in the dosage, there was a slight decrease in the percentage removal. Initially, when dosage of PX7 was less, due to presence of less adsorption sites the removal of BPA was observed to be less. But at higher dosage due to availability of more adsorption sites separation of BPA enhanced. Therefore, 6 g/L dosage of PX7 was taken to conduct further adsorption experiments.

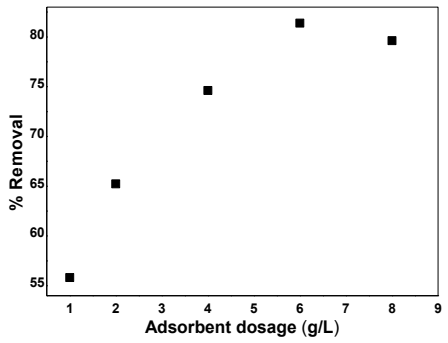

Fig. 2. Effect of mass of adsorbent on adsorption of BPA using PX7 (C_o = 10 mg/L; T = 298 K; and speed of shaker = 100 rpm)

Effect of initial BPA concentration

To find out the effect of concentration on BPA seperation, experiments were conducted with 6 g/L of PX7 dosage and by varying concentration of BPA from 10 to 50 mg/L for 60 min at 298 K and setting the speed of shaker at 100 rpm. (Figure 3). From the figure it can be seen that with an increase in the initial BPA concentration from 10 to 50 mg/L, the percentage removal of BPA decreased from 89.14% to 63.26%.This may be due to the abundance of BPA molecule with constant adsorbent dosage which leads to decrease in percentage removal. Four equilibrium isotherm models like Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) were used to fit the concentration experimental data. . Among these models the equilibrium data were matched with Freundlich model (R^2 = 0.994). This concluded that BPA separation follows multilayer adsorption on the surface of PX7 with heterogeneous surface. Energies of their active sites were distributed exponentially. Initially, molecules of BPA occupied the stronger sites of PX7 decreasing the adsorption energy exponentially while completion of the BPA adsorption process.

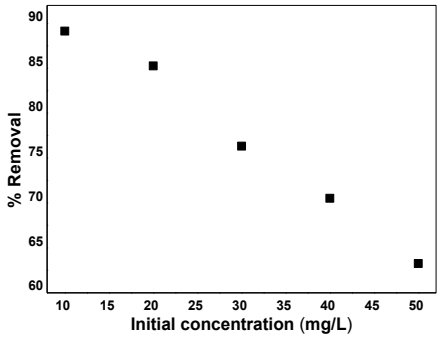

Fig. 3. Effect of concentration on BPA adsorption using PX7 (m = 6 g/L; T = 298 K; and speed of shaker = 100 rpm

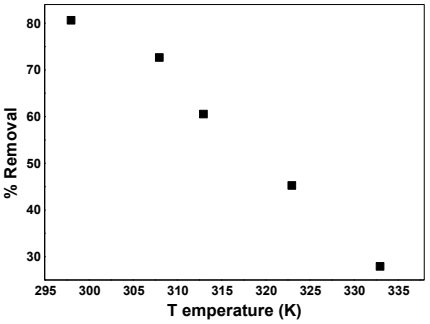

Fig. 4. Effect of temperature on BPA adsorption using PX7 (m = 6 g/L; t = 60 min; C_o = 10 mg/L; and speed of shaker = 100 rpm)

Effect of temperature

Effect of temperature study on the separation of BPA was performed by varying the temperature between 298 and 333 K (Figure 4). Experiments were performed using 6 g/L of PX7 dosage mixed with 10 mg/L of BPA and kept in water bath shaker at 100 rpm for 60 min. From figure 4, it was observed that there is an inverse trend between temperature and the percentage removal of BPA. At higher temperature due to higher kinetic energy very less interaction was observed between the

molecules of BPA and PX7. At 333 K, the percentage removal of BPA was less (27.90%) compared to the percentage removal at 298 K (80.62%).

Thermodynamics parameters like change in the standard Gibb's free energy (Δ*G*°), change in standard enthalpy (Δ*H*°), and change in standard entropy (Δ*S*°) was calculated at different experimental temperatures by using eqs.1 and 2. Values of Δ*H*° and Δ*S*° were calculated using eq. 2 by plotting a graph between Δ*G*° and *T* as per eq.1.

$$\Delta G^\circ = -RT\, ln\left(\frac{q_e}{C_e}\right) \quad (1)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (2)$$

where, *R* is the universal gas constant (8.314 J/mol·K), and *T* is the temperature in K. Value of Δ*H*° and Δ*S*° are found to be -54.89 kJ/mol and -128.35 J/mol·K respectively. Negative values of Δ*H*° and Δ*S*° shows that adsorption of BPA using PX7 is exothermic and spontaneous.

Conclusion

Separation of BPA was done using PX7. From the kinetic study it was observed that higher the contact time higher percentage removal obtained. Later, no change in the percentage removal was observed with increase in the contact time till 120 min. Pseudo-second-order gave the best fit with the experimental data points compared to pseudo-first-order and intra-particle diffusion model (R^2 = 0.998). Percentage removal of BPA was observed to be higher (89.14%) at lower concentration of BPA (10 mg/L). Freundlich isotherm gave best fit with the equilibrium data points. Dosage study revealed that at higher dosage percentage removal of BPA enhanced. Maximum percentage removal was obtained at 6 g/L which was considered for the further adsorption experiments. Negative effect on the percentage removal of BPA was observed at higher temperature. Adsorption of BPA was observed to be exothermic and spontaneous in nature.

Acknowledgement

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