Removal of bisphenol A from aqueous solutions using magnetic nanoparticles: Investigation of adsorption isotherms

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Aims: The purpose of this study was to investigate adsorption isotherms of removing bisphenol A (BPA) from aqueous solutions using magnetic nanoparticles Fe3O4 and SiO2. BPA is an endocrine disrupting chemical that has caused great concern because of its potential risk to human health.

Materials and Methods: The combined of magnetic nanoparticles Fe3O4 and SiO2 were applied to remove BPA from aqueous solution at a dose of 2 g/L. Isotherm Fitting Tool software was used for isotherm study in contact time 20 min, the initial concentration of BPA 0–10 (interval 1 mg/L), and pH 5.

Results: The maximum adsorption efficiency was found to be 55%. The results of our experiments showed that maximum adsorption efficiency was achieved at t = 20 min and pH 5.

Conclusion: The isotherm study showed that Langmuir isotherm described the equilibrium adsorption data better than other isotherms alternative.

Key words: Adsorption, aqueous solution, bisphenol A, magnetic nanoparticles, silica nanoparticles

INTRODUCTION

In the recent years, advances in environmental chemistry have increased focus on the presence of anthropogenic substances in the environment. These compounds have adverse effects on human health in low concentration.1 Many of the thousands of anthropogenic substances currently released into the environment are classified as “endocrine-disrupting chemicals.” These are defined as exogenous chemicals or chemical mixtures that impact endocrine system structure or function and cause adverse effects.2 Bisphenol A (BPA) is a highest volume production chemical primarily used as an intermediate and monomer in the production of epoxy resins and polycarbonates which are additives to a number of consumer products.3 BPA is widely used industrially in some dental materials, dental sealants, lining of food, and beverage containers as well as numerous other products. Additional uses for BPA include items that we come in contact with daily at home and in the workplace including the coating of CDs, DVDs, electrical and electronic equipment, automobiles, sports safety equipment, recycled paper, and carbonless paper often used in register receipts.4

The significance problem of BPA in the environment is intensified by physicochemical properties of this compound.
such as low solubility and high hydrophobicity characteristics. These properties suggest that BPA has low biodegradability and accumulates in living organism.\cite{1} The solubility of BPA in water ranges from 120 to 300 \(\mu\text{g/mL}\).\cite{6} A number of methodologies based on physical and chemical treatment processes are currently continued to apply the removal of BPA.\cite{7} Among these methods, adsorption is a superior and promising method for removing low-concentration contaminants from water systems in terms of cost, ease of operation, and lack of harmful secondary products.\cite{8} Dehghan et al. demonstrated that the maximum adsorption capacity of BPA by single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) was 71 and 111 mg/g, respectively. It can be concluded that the MWCNTs were more efficient for the absorbance of BPA than the SWCNTs.\cite{9} Amin et al. used magnetic nanoparticles for removal of benzene and showed that the Brunauer–Emmett–Teller (BET) model fit more closely and produced an isotherm constant (b) < 1, indicating favorable adsorption.\cite{10} Zhou et al. demonstrated the sorption behavior of BPA from aqueous solutions onto biosorbent peat. The sorption capacity notably increased to a level higher than that of activated carbon after modification with a quaternary ammonium surfactant.\cite{11} Lin et al. applied a combined molecularly-imprinted polymer with a superparamagnetic core-shell nanoparticle for extraction of BPA from aqueous solution. The novel nanoparticles showed excellent magnetic properties and high selectivity for the target BPA molecule.\cite{12}

In this study, the isotherm behavior of BPA adsorption onto composite Fe\(_2\)O\(_3\)/SiO\(_2\) nanoparticles from aqueous solution was investigated. The novel isotherm idea of the study was to use combined Fe\(_2\)O\(_3\)/SiO\(_2\) for BPA removal which allows easy separation of the polluted absorbent from the solution to control its release into the environment after use.

**MATERIALS AND METHODS**

**Materials**

BPA (2, 2-[4, 4-dihydroxydiphenyl]) propane with 99% purity was obtained from Sigma-Aldrich (USA). Methanol (high purity for gas chromatography [GC] analysis), NaOH (99% purity; Mallinckrodt Chemical; USA), and HCl 37% (wt) were obtained from Merck (Germany). Solid-phase extraction (SPE) cartridges (3 ml/500 mg) were purchased from Macherey-Nagel (Germany).

**Experimental procedure**

The stock solution of BPA was prepared by dissolving 100 mg of BPA in deionized water, after which it was stored in a refrigerator before use. The other diluted solutions were resulted from this stock solution. Before each experiment, the pH of the aqueous solution was adjusted use 0.1 M HCl or 0.1 M NaOH.

Solutions including 0–10 mg/L (concentration intervals 1 mg/L) BPA concentrations were prepared in vitro. In the first phase, with BPA concentration and absorbent dose being constant, optimum pH was determined from a range of predefined pH (3–11). The initial concentration of BPA was adjusted at 10 mg/L in all samples. BPA samples were analyzed at each phase to determine the optimal value of effective parameters including pH, contact times, and initial concentrations. A shaker apparatus in 300 rpm was used for solution mixing. The absorbent was extracted from the studied solutions by separation with a magnetic field and then by centrifuge at 10,000 rpm for 20 min. Finally, the resulted solutions were analyzed.

Absorbent dose was selected by determining the optimum absorbent dose for Fe\(_2\)O\(_3\) and SiO\(_2\) separately. Finally, the ratio of 500–1500 or (1:3) was determined for Fe\(_2\)O\(_3\)/SiO\(_2\), respectively. The level of BPA in the aqueous solution was determined using standard curves (\(R^2 = 0.99\)) by injecting known amounts of standard solution (10, 4, 1, and 0.1 mg/L) and measuring the areas under the peaks.

The amount of BPA adsorbed \(q_\text{e} \text{mg/g}\) and percentage of removal \(R\) were calculated as follows:

\[
R = \frac{C_0 - C_\text{e}}{C_0} \times 100
\]

\[
q_\text{e} = \frac{C_0 - C_\text{e}}{m} \times V
\]

Where, \(C_0\) and \(C_\text{e}\) (mg/L) are the BPA concentrations at the start and end of each run, respectively, \(V\) (l) is the initial solution volume, and \(m\) (g) is the adsorbent weight.

Isotherm study was evaluated for BPA adsorption by Fe\(_2\)O\(_3\)/SiO\(_2\) in optimum condition with initial concentration of 0–10 mg/L (interval 1 mg/L), Fe\(_2\)O\(_3\)/SiO\(_2\) dose 1 g/L, contact time 20 min, and pH 5. Water solubility \(S_\text{w}\) of BPA was estimated 210 mg/L at pH 5. Isotherm Fitting Tool (ISOFIT) software (State University of New York at Buffalo Department of Civil) was used to fit isotherm parameters to experimental data. ISOFIT is a software program that fits isotherm parameters to experimental data via the minimization of a weighted sum of squared error (WSSE) objective function.

ISOFIT supports a number of isotherms including (1) BET, (2) Freundlich, (3) Langmuir, and (4) linear.

**Extraction and analysis**

Samples were extracted using SPE C\(_18\) cartridges. The SPE cartridges were initially conditioned with 5 ml methanol and 10 ml milli-Q water. Then, samples were passed through the wet cartridges at a flow rate of 20 ml/min. First, 2 ml of methanol was passed through the cartridge. Next, the sample was evaporated to dryness under gentle nitrogen gas, 100 \(\mu\text{l}\) of methyl tert-butyl ether was added to tube, and 5 \(\mu\text{l}\) was
injected into the GC system (GC/flame ionization detector 5975B; Agilent Technologies; USA). An HP-5 ms fused silica column (30 m × 0.25 mm ID, 0.25 μm) was employed with helium (99.995% purity) as the carrier gas at a flow rate of 1 ml/min. The injector temperature was set at 250°C, and the sample was injected in splitless mode. The column temperature was set at 100°C for 2 min, heated to 230°C at a rate of 10°C/min and then to 280°C at 5°C/min for a total run time of 25 min.

RESULTS

Effect of pH on removal of bisphenol A
The results of changes in pH to remove the BPA from aqueous solution under constant conditions are shown in Figure 1. As it can be seen, with increasing pH from 3 to 5, the removal efficiency rate was increased. In pH 11, it was reduced to 38.9%, and in pH 7, the minimum rate of 29% was achieved. Which in pH 5, elimination rate was more effective. According to the results, pH 5 was selected as the optimum pH. Table 1 depicts the results obtained at various initial pH.

Effect of contact time on removal of bisphenol A
The contact time was examined as another factor influencing absorption. The range of contact time was selected as 5–30 min. By increasing contact time from 5 to 20 min, the efficacy of removal was increased from 32% to 55%. However, in 30 min, the removal efficiency of BPA was reduced to 42%.

Figure 2 shows the effect of contact time on elimination efficiency. The results of BPA removal by Fe₃O₄-SiO₂ nanoparticles at various contact times are shown in Table 2.

Effect of initial concentration on bisphenol A sorption
Figure 3 shows the effect of initial concentration on removal efficiency rate. As it can be seen, under determined conditions, by increasing the initial concentration of BPA from 0.1 to 10 mg/L, elimination rate showed an increasing trend, which is suggestive of increased efficacy in higher concentrations. The experimental results using Fe₃O₄/SiO₂ nanoparticles at various initial concentrations are shown in Table 3.

Table 1: Bisphenol a removal by combined of Fe₃O₄/SiO₂ nanoparticles at various initial pH

| Run | BPA concentration (mg/L) | Adsorbent dose (ratio of Fe₃O₄ to SiO₂) (mg/L) | Time (min) | pH  | Cₑ (mg/L) | R % | SD | qₑ (mg/g) |
|-----|--------------------------|---------------------------------------------|------------|-----|------------|-----|-----|-----------|
| 1   | 10                       | 500/1500                                    | 20         | 3   | 6.5        | 35  | ±0.37| 1.75      |
| 2   | 10                       | 500/1500                                    | 20         | 5   | 4.5        | 55  | ±4.16| 2.75      |
| 3   | 10                       | 500/1500                                    | 20         | 7   | 7.1        | 29  | ±0.52| 1.45      |
| 4   | 10                       | 500/1500                                    | 20         | 11  | 6.1        | 38.9| ±0.57| 1.94      |

BPA: Bisphenol A, SD: Standard deviation

In this study, ISOFIT was applied to involving the adsorption of BPA by Fe₃O₄-SiO₂ in batch condition. Water solubility (Sₑ) of BPA was estimated 210 mg/L at pH 5.

Table 4 summarizes some of the diagnostic statistics computed by ISOFIT and reported in the output file.

In Table 5, the Linssen measure indicates significant WSSE nonlinearity near the optimal parameter values. The statistical measures such as and Durbin–Watson test (D) imply normally distributed weighted residuals with no serial autocorrelation.

Figures 4-7 contain plots of the fitted isotherms, organized into visually indistinguishable groups, along with the observed data points.
DISCUSSION

The effect of pH in this study showed that elimination in pH 5 occurred with 55% efficiency which is higher than elimination efficiency in normal pH [Figure 1]. Brugnera et al. showed that the highest rate of absorption using TiO$_2$ nanotubes was at pH 6.\cite{14} Furthermore, Fan et al. demonstrated similar results and selected pH 6 as the optimum pH for bisphenol elimination. They suggested that high pH is not suitable for bisphenol absorption.\cite{15}

Contact time is an important parameter in the absorption process. The maximum contact time for bisphenol absorption is at 20 min [Figure 2]. With increase in contact time, the absorption rate is higher which reaches to the maximum level at 20 min and afterward, at 30 min, slowly declines. Because absorbent surface sites are occupied with the absorbing material and are not accessible anymore.\cite{15} Wirasnita et al. used activated carbon for removal of BPA and showed that the maximum absorption rate
occurred at the first 18 h due to the availability of absorption sites but between 18 and 48 h, this trend was declined.\(^\text{[16]}\) Ghosh \emph{et al.} observed that adsorption increased instantly in the initial stage from rapid attachment of adsorbate to the surface of the adsorbent. For BPA, >95% of equilibrium adsorption occurred in the first 40 min.\(^\text{[17]}\)

The initial concentration of the contaminant is an important parameter to overcome mass transfer deterrent force between liquid and solid phases.\(^\text{[15]}\) By increasing the initial concentration, the removal efficiency is increased. The elimination efficacy increases from 40% at 0.1 mg/L to 55% at 10 mg/L [Figure 3]. In the study of Dehghani \emph{et al.}, similar results were obtained using single wall nanotubes to eliminate bisphenol.\(^\text{[18]}\)

In this study, the \(q_e\) of \(\text{Fe}_3\text{O}_4/\text{SiO}_2\) was compared with that of adsorbents such as granular activated carbon (GAC) and modified peat. The sorption studies were performed at 25°C and pH 7.0 using an initial BPA concentration of 2 mg/L, a sorbent dosage of 0.05 g, and an agitation rate of 200 rpm at a sorption time of 4 h. The BPA removal capacities of the GAC and modified peat were significantly lower at 1.67 and 1.71, respectively.\(^\text{[11]}\) This study indicated that the performance of BPA adsorption by \(\text{Fe}_3\text{O}_4/\text{SiO}_2\) was better than the other adsorbents.

Table 4 shows that the corrected Akaike information criterion values indicate that the Langmuir isotherm expression provides the best fit of the sorption data based on its relatively lowest value of multimodel ranking. The Langmuir constant \(b\) was calculated to be less than unity for the majority of the adsorbate and adsorbent combinations, indicating that the adsorption of the selected contaminants onto the \(\text{Fe}_3\text{O}_4/\text{SiO}_2\) samples is favorable. Linear regression techniques overcome many of the deficiencies associated with trial-and-error and linearization approaches to isotherm fitting. However, the performance of linear regression techniques can be impeded by the presence of local minima or excessive parameter correlation.

Table 5 contains selected ISOFIT output for the Langmuir isotherm. ISOFIT provides two “standard” measures for evaluating isotherm goodness of fit, namely the root mean squared error (RMSE, Equation 4) and the correlation between measured and fitted observations (\(R_\text{y}\) Equation 5).
RMSE = \sqrt{\frac{\text{WSSE}}{m-p}} \tag{4}

R_y = \frac{\sum_{i=1}^{m} (w_i S_{\text{obs}} - S_{\text{avg}}) (w_i S_i - S^{\text{avg}})}{\sum_{i=1}^{m} (w_i S_{\text{obs}} - S_{\text{avg}})^2 \sum_{i=1}^{m} (w_i S_i - S^{\text{avg}})^2} \tag{5}

Where, WSSE is weighted sum of squared error, \( m \) is the total number of isotherm parameters, \( p \) is the weight given to observation \( i \), \( S_{\text{obs}} \) is the \( i \)-th experimentally measured sorbed concentration, \( S_i \) is the \( i \)-th simulated sorbed concentration computed via an isotherm expression, \( S_{\text{avg}} \) and \( S^{\text{avg}} \) are the averages of the weighted measured and weighted isotherm simulated adsorbed concentrations, respectively.

**CONCLUSION**

The aim of this study was to examine the efficiency of BPA elimination from primary solutions by means of a combination of magnetic \( \text{Fe}_3\text{O}_4 \) nanoparticles and \( \text{SiO}_2 \) nanoparticles. Furthermore, absorptive capacity was studied. The results showed that BPA elimination was more effective under optimum conditions in pH 5, with the initial concentration of 10 and the contact time of 20 min, and under this condition, a BPA removal efficiency of 55% can be achieved. The maximum adsorption capacity was found to be 2.75 mg/g.

The Langmuir isotherm described the equilibrium adsorption data better than other isotherms alternative.

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**Conflicts of interest**

There are no conflicts of interest.

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