

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

Tahereh Safabakhsh^{1,2}, Hamidreza Pourzamani^{1,3}

¹Department of Environmental Health Engineering, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran, ²Student Research Committee, Isfahan University of Medical Sciences, Isfahan, Iran, ³Environment Research Center, Research Institute for Primordial Prevention of Non-communicable Disease, Isfahan University of Medical Sciences, Isfahan, Iran

Address for correspondence:

Dr. Hamidreza Pourzamani,
Department of Environmental Health Engineering,
School of Health, Isfahan University of Medical
Sciences, Hezar Jerib Ave, Isfahan, Iran.
E-mail: pourzamani@hlth.mui.ac.ir

ABSTRACT

Aims: The purpose of this study was to investigate adsorption isotherms of removing bisphenol A (BPA) from aqueous solutions using magnetic nanoparticles Fe_3O_4 and SiO_2 . 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 Fe_3O_4 and SiO_2 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

This is an open access article distributed under the terms of the Creative Commons Attribution-NonCommercial-ShareAlike 3.0 License, which allows others to remix, tweak, and build upon the work non-commercially, as long as the author is credited and the new creations are licensed under the identical terms.

For reprints contact: reprints@medknow.com

This article may be cited as: Safabakhsh T, Pourzamani H. Removal of bisphenol A from aqueous solutions using magnetic nanoparticles: Investigation of adsorption isotherms. *Int J Env Health Eng* 2016;5:25.

Access this article online	
Quick Response Code: 	Website: www.ijehe.org
	DOI: 10.4103/2277-9183.196668

such as low solubility and high hydrophobicity characteristics. These properties suggest that BPA has low biodegradability and accumulates in living organism.^[5] The solubility of BPA in water ranges from 120 to 300 µg/ml.^[6] A number of methodologies based on physical and chemical treatment processes are currently continued to apply the removal of BPA.^[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.^[8] Dehghani *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.^[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.^[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,^[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.^[12]

In this study, the isotherm behavior of BPA adsorption onto composite Fe₃O₄/SiO₂ nanoparticles from aqueous solution was investigated. The novel idea of the study was to use combined Fe₃O₄/SiO₂ for BPA removal which allows easy separation of the polluted adsorbent 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 adsorbent 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 Fe₃O₄ and SiO₂, separately. Finally, the ratio of 500–1500 or (1:3) was determined for Fe₃O₄:SiO₂, 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_e ; mg/g) and percentage of removal (R) were calculated as follows:

$$R = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{C_o - C_t}{m} \times v \quad (2)$$

Where, C_o and C_t (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 Fe₃O₄-SiO₂ in optimum condition with initial concentration of 0–10 mg/L (interval 1 mg/L), Fe₃O₄-SiO₂ dose 1 g/L, contact time 20 min, and pH 5. Water solubility (S_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 C₁₈ 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 µl of methyl tert-butyl ether was added to tube, and 3 µl 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 adsorption. 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.

Bisphenol A isotherm-Fe₃O₄/SiO₂

In this study, ISOFIT was applied to involving the adsorption of BPA by Fe₃O₄-SiO₂ in batch condition. Water solubility (S_w) 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 Linszen 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.

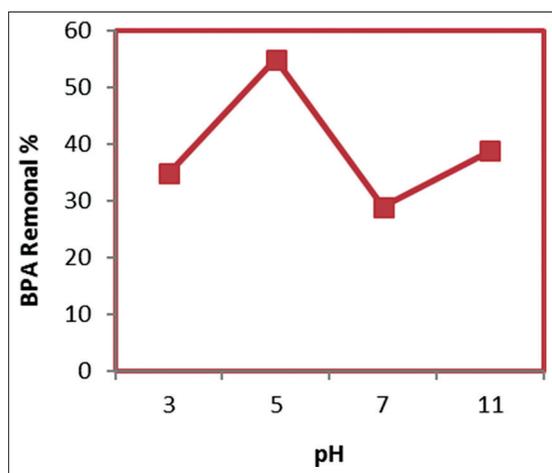


Figure 1: pH effect on bisphenol A removal

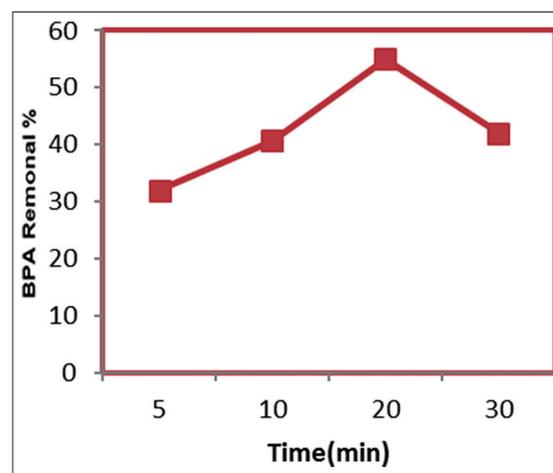


Figure 2: Effect of contact time on bisphenol A removal

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

Run	Factors				Response: BPA			
	BPA concentration (mg/L)	Adsorbent dose (ratio of Fe ₃ O ₄ to SiO ₂) (mg/L)	Time (min)	pH	C _t (mg/L)	R %	SD	q _e (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

Table 2: Bisphenol a removal by Fe₃O₄/SiO₂ nanoparticles at various contact times

Run	Factors				Response: BPA			
	BPA concentration (mg/L)	Adsorbent dose (ratio of Fe ₃ O ₄ to SiO ₂) (mg/L)	Time (min)	pH	C _t (mg/L)	R %	SD	q _e (mg/g)
1	10	500/1500	5	5	6.8	32	±0.55	1.6
2	10	500/1500	10	5	5.9	40.7	±0.47	2
3	10	500/1500	20	5	4.5	55	±4.16	2.75
4	10	500/1500	30	5	5.8	42	±0.32	2.1

BPA: Bisphenol A, SD: Standard deviation

Table 3: Bisphenol a removal by Fe₃O₄/SiO₂ nanoparticles at various initial concentrations

Run	Factors				Response: BPA			
	BPA concentration (mg/L)	Adsorbent dose (ratio of Fe ₃ O ₄ to SiO ₂) (mg/L)	Time (min)	pH	C _t (mg/L)	R %	SD	q _e (mg/g)
1	10	500/1500	20	5	4.5	55	±4.19	2.75
2	1	500/1500	20	5	0.51	49	±0.67	0.26
3	0.1	500/1500	20	5	0.06	40	0.54	0.02

BPA: Bisphenol A, SD: Standard deviation

Table 4: Summary of selected diagnostics for bisphenol A adsorbed by Fe₃O₄-SiO₂

Isotherms	AICc	R _y ²	R _N ²	M ²	Linearity assessment
Langmuir	6.2	0.986	0.850	4.5 × 10 ⁻⁹	Linear
BET	8.2	0.976	0.863	2.5 × 10 ¹	Nonlinear
Linear	8.2	0.975	0.890	9.04 × 10 ⁻⁹	Linear
Freundlich	9.4	0.875	0.890	3.57	Nonlinear

AICc: Multimodel ranking, R_y²: Correlation between measured and simulated observation, R_N²: Correlation between residual and normality, M²: Linssen measure of nonlinearity. BET: Brunauer–Emmett–Teller, AICc: Akaike information criterion

Table 5: Selected isotherm fitting tool postregression output (Langmuir isotherm)

Parameter or statistic	ISOFIT result
Overall quality of fit	
WSSE	2.6 × 10 ⁻¹
RMSE	0.057
R _y	0.988
Parameter statistics	
bQ ₀	2.8 × 10 ⁻¹
b	4.6 × 10 ⁻⁹
Parameter standard error	
bQ ₀	9.8 × 10 ⁻³
b	1.7 × 10 ⁻¹⁷
Test of assumptions Linssen (M ²)	
M ²	4.6 × 10 ⁻⁹
Threshold	0.02 × 10 ⁻⁹
Assessment	Linear
Normality (R _N ²)	
R _N ²	0.850
Critical value	0.71
Assessment	Normal residuals
Runs test	
Number of runs	3
P	0.955
Assessment	No correlation
Durbin–Watson test (D)	
D	0.98
P	0.017
Assessment	Correlation

WSSE: Weighted sum squared error, RMSE: Root mean squared error, ISOFIT: Isotherm Fitting Tool

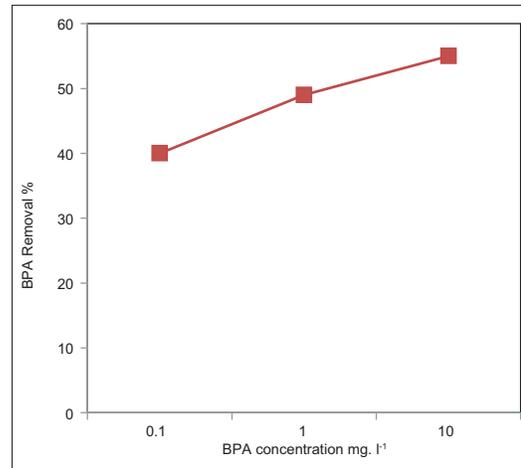


Figure 3: Bisphenol A concentration effect on bisphenol A removal

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 TiO₂ nanotubes was at pH 6.^[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.^[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 adsorbent surface sites are occupied with the absorbing material and are not accessible anymore.^[15] Wirasmita *et al.* used activated carbon for removal of BPA and showed that the maximum absorption rate

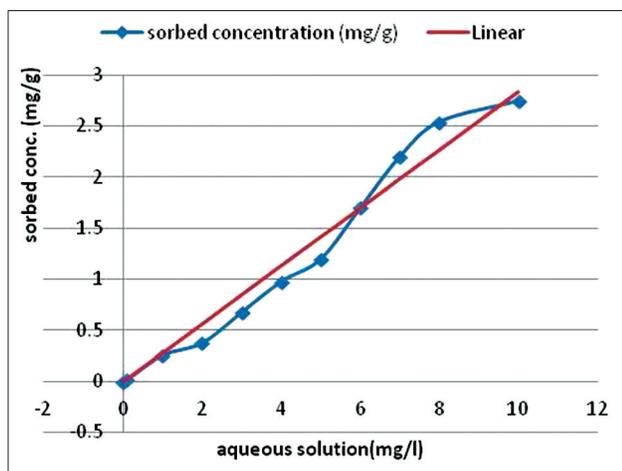


Figure 4: Plots of the linear isotherm

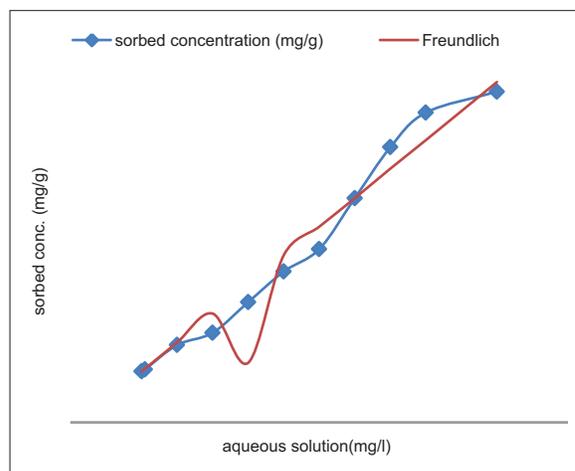


Figure 5: Plots of the Freundlich isotherm

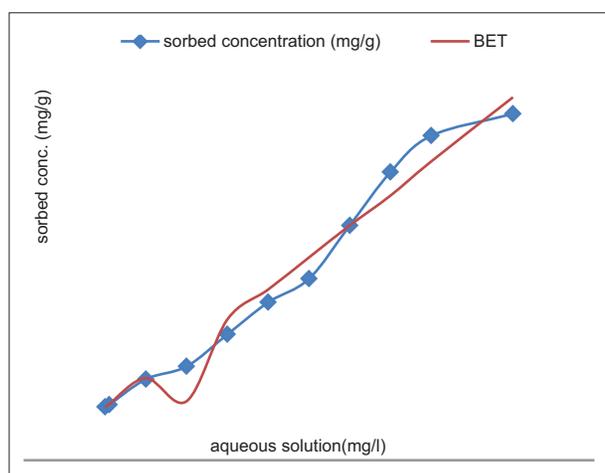


Figure 6: Plots of the Brunauer–Emmett–Teller isotherm

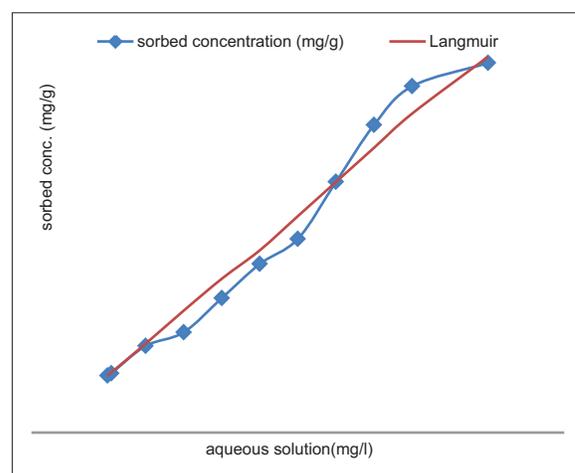


Figure 7: Plots of the Langmuir isotherm

occurred at the first 18 h due to the availability of absorption sites but between 18 and 48 h, this trend was declined.^[16] Ghosh *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.^[17]

The initial concentration of the contaminant is an important parameter to overcome mass transfer deterrent force between liquid and solid phases.^[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 *et al.*, similar results were obtained using single wall nanotubes to eliminate bisphenol.^[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.^[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_y , Equation 5).

$$RMSE = \sqrt{\frac{WSSE}{(m-p)}} \quad (4)$$

$$R_y = \frac{\sum_{i=1}^m (w_i S_{i,obs} - S_{obs}^{avg})(w_i S_i - S^{avg})}{\sqrt{\sum_{i=1}^m (w_i S_{i,obs} - S_{obs}^{avg})^2 \sum_{i=1}^m (w_i S_i - S^{avg})^2}} \quad (5)$$

Where, WSSE is weighted sum of squared error, m is the total number of experimental observations, p is the number of isotherm parameters, w_i is the weight given to observation i , $S_{i,obs}$ is the i -th experimentally measured sorbed concentration, S_i is the i -th simulated sorbed concentration computed via an isotherm expression, S_{obs}^{avg} and S^{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 Fe_3O_4 nanoparticles and SiO_2 nanoparticles. Furthermore, adsorptive 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.

Financial support and sponsorship

Isfahan University of Medical Sciences, Isfahan, Iran.

Conflicts of interest

There are no conflicts of interest.

REFERENCES

- Bertanza G, Papa M, Pedrazzani R, Repice C, Mazzoleni G, Steimberg N, *et al.* EDCs, estrogenicity and genotoxicity reduction in a mixed (domestic+textile) secondary effluent by means of ozonation: A full-scale experience. *Sci Total Environ* 2013;458-460:160-8.
- Flint S, Markle T, Thompson S, Wallace E. Bisphenol A exposure, effects, and policy: A wildlife perspective. *J Environ Manage* 2012;104:19-34.
- Olmez-Hanci T, Arslan-Alaton I, Genc B. Bisphenol A treatment by the hot persulfate process: Oxidation products and acute toxicity. *J Hazard Mater* 2013;263(Pt 2):283-90.
- Rubin BS. Bisphenol A: An endocrine disruptor with widespread exposure and multiple effects. *J Steroid Biochem Mol Biol* 2011;127:27-34.
- Bohdziewicz J, Liszczyk G. Evaluation of effectiveness of bisphenol a removal on domestic and foreign activated carbons. *Ecol Chem Eng S* 2013;20:371-9.
- Kang JH, Kondo F, Katayama Y. Human exposure to bisphenol A. *Toxicology* 2006;226:79-89.
- Kusvuran E, Yildirim D. Degradation of bisphenol A by ozonation and determination of degradation intermediates by gas chromatography – Mass spectrometry and liquid chromatography – Mass spectrometry. *Chem Eng J* 2013;220:6-14.
- Nguyen-Huy C, Kim N, Nguyen-Phan TD, Yoo IK, Shin EW. Adsorptive interaction of bisphenol A with mesoporous titanasilicate/reduced graphene oxide nanocomposite materials: FT-IR and Raman analyses. *Nanoscale Res Lett* 2014;9:462.
- Dehghani MH, Mahvi AH, Rastkari N, Saeedi R, Nazmara SH, Irvani E. Adsorption of bisphenol A (BPA) from aqueous solutions by carbon nanotubes: Kinetic and equilibrium studies. *Desalination Water Treat* 2015;54:84-92.
- Amin MM, Bina B, Samani Majd AM, Pourzamani H. Benzene removal by nano magnetic particles under continuous condition from aqueous solutions. *Front Environ Sci Eng* 2014;8:345-56.
- Zhou Y, Lu P, Lu J. Application of natural biosorbent and modified peat for bisphenol a removal from aqueous solutions. *Carbohydr Polym* 2012;88:502-8.
- Lin Z, Cheng W, Li Y, Liu Z, Chen X, Huang C. A novel superparamagnetic surface molecularly imprinted nanoparticle adopting dummy template: An efficient solid-phase extraction adsorbent for bisphenol A. *Anal Chim Acta* 2012;720:71-6.
- Malakootian M, Mahvi AH, Jafari Mansoorian H, Alizadeh M, Hosseini AR. Study of application of alumina-coated carbon nanotube for removal of hydroxy benzene from aqueous solutions: Adsorption and determination of equilibrium and kinetics parameters. *Iran J Health Environ* 2015;8:127-40.
- Brugnera MF, Rajeshwar K, Cardoso JC, Zanon MV. Bisphenol A removal from wastewater using self-organized TiO₂ nanotubular array electrodes. *Chemosphere* 2010;78:569-75.
- Fan X, Tu B, Ma H, Wang X. Adsorption behavior of environmental hormone bisphenol A onto mesoporous silicon dioxide. *Bull Korean Chem Soc* 2011;32:2560-4.
- Wirasmita R, Hadibarata T, Yusoff A, Rahim M, Yusop Z. Removal of bisphenol a from aqueous solution by activated carbon from oil palm empty fruit bunch. *Water Air Soil Pollut* 2014;225:1-12.
- Ghosh S, Abu Zayed B, Kus H, Shahab M. Adsorptive removal of emerging contaminants from water using superparamagnetic Fe₃O₄ nanoparticles bearing aminated β -cyclodextrin. *J Environ Chem Eng* 2013;1:122-30.
- Irvani E, Dehghani MH, Mahvi H, Rastkari N. Removal of bisphenol A from aqueous solutions using single walled carbon nanotubes: Investigation of adsorption isotherms. *Iran J Health Environ* 2013;6:257-64.