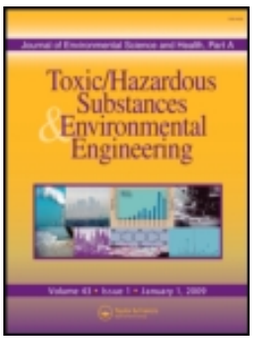

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Removal of BPA model compounds and related substances by means of column chromatography using Octolig®

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Octolig®, a polyethylenediimine ligand covalently attached to high-surface area silica gel, was used to study the removal of phenolic compounds from aqueous samples by column chromatography. Model phenolic compounds of Bisphenol A (BPA), 4-isopropylphenol and 4-(*t*-butyl) phenol, were selected for this study due to their similarities in pKa and log P values. The percent removal of these compounds by Octolig® was 26 ± 2 and 22 ± 2, respectively. Furthermore, the three isomers of nitrophenol were investigated as well as additional phenolic compounds, such as amoxicillin and five phenolic dyes. These compounds have a pKa range of 2–10.2. The compounds that have pKa values less than 8.3 were able to be completely removed by Octolig®, yet compounds with pKa values of 8.3 and higher resulted in approximately 20–26% removal.

Keywords: BPA, polycarbonates, Octolig®, chromatography, phenols.

Introduction

Bisphenol A (BPA) shown in (Eq. 1) is a component in the synthesis of polycarbonate plastics and epoxy resins[1–5] shown in (Eqs. 2, 3) that have a variety of significant uses.[6]

$$2C_6H_5OH + (CH_3)_2C{=}O \rightarrow HOC_6H_4C(CH_3)_2C_6H_4OH + H_2O \quad (1)$$

phenol acetone BPA

$$BPA + Cl_2C{=}O \rightarrow -[O{-}C_6H_4C(CH_3)_2C_6H_4O(C{=}O){-}]_n \quad (2)$$

phosgene polycarbonate

$$BPA + CH_2CHOCH_2Cl \rightarrow -[O{-}C_6H_4C(CH_3)_2C_6H_4O{-}CH_2C(OH)CH_2{-}]_n \quad (3)$$

epichlorohydrin epoxy resin

Unfortunately, these plastics can degrade with age, and BPA or other substances possessing estrogenic activity (EA) can be released.[1–4] BPA is also present in human bodies in detectable amounts in the human blood stream. Despite its low solubility in water it is present in the rivers and estuaries in detectable amounts. Although BPA may have a short half-life in soil,[7,8] the ubiquity of the substance provides a continuous supply in the environment.[1–4,9] BPA in the environment raises concern due to the toxicity of the material, which has become a matter of significant debate, which seemingly leads to three choices: ban, restrict, ignore.[5] To minimize the possible adverse health effects due to BPA it has been suggested to either avoid exposure to EA-containing polycarbonates[9] or treatment of EA-containing polycarbonates.[10]

The potential control of EA materials in plastics needs to be considered because the volume of plastics used annually means that there will be no sudden cessation of use. Based on results of a survey of 455 commercially available plastic products for release of EA materials researchers discovered that EA materials could be removed by extraction with two solvents, e.g., ethanol and saline.[10] The potential for control of EA materials in plastics may be considered. These findings raise a question of how the EA materials in the two solvents could be safely disposed.

One possibility is the use of column chromatography using commercially available Octolig®, a polyethylenediimine ligand covalently attached to a high surface area silica gel. The proposed structure of the Octolig® ligand is indicated in Figure 1, where A^- is considered to be an anion either simple (phosphate, sulfate, nitrate, nitrate), or more complex. This material was designed to remove transition metal ions, and it does so effectively.[11] We, however, have studied Octolig® for the ability to remove anions[12–14] and its potential commercial applications.[15]

Previously we have demonstrated that phenolic compounds with low pKa values, such as xanthylbenzenes

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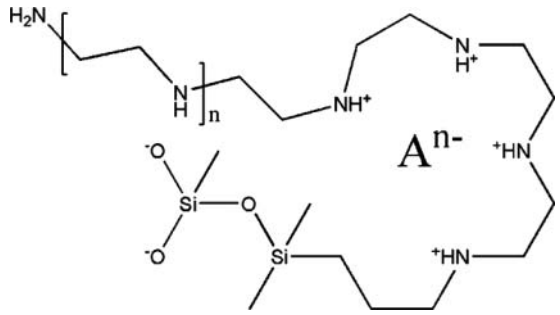


Fig. 1. Proposed structure of Octolig®-anion interaction (redrawn from Stull and Martin[12]).

(Rose Bengal, eosin Y, and erythrosine), could be quantitatively removed.[16] Moreover, Lissamine Green B, as well as amoxicillin, a phenolic dye and a phenolic antibiotic can be removed in similar quantities.[17]

In this work we have studied the removal of phenolic compounds with higher pKa values, such as 4-isopropylphenol, 4-(*t*-butyl) phenol, and nitrophenols. The results obtained from the current study as well as previous studies of the removal of phenolic compounds by Octolig® may provide a predictive guide for the removal of similar compounds. Specifically, 4-isopropylphenol and 4-(*t*-butyl) phenol may serve as model compounds of BPA suggesting the removal rates of BPA from aqueous samples using Octolig®.

Materials and methods

Source of reagents and materials

Octolig® (CAS registry number 404899–06-5) was a gift from Metre-General, Inc (Frederick, CO). The 4-(*t*-butyl) phenol and 4-isopropylphenol were selected as model compounds of BPA.[18] Both 4-(*t*-butyl) phenol and 4-isopropylphenol were obtained from Sigma-Aldrich.

Samples of 4-nitrophenol, 3-nitrophenol and 2- nitrophenol, used to test electronic effects were obtained from Acros Organic or Aldrich Chemical Company. For pH adjustments aqueous sodium hydroxide, dilute phosphoric acid or a sodium phosphate buffer was used. Solid NaOH pellets and phosphoric acid were obtained from Fisher Scientific. For the buffer, sodium phosphate monobasic mono hydrate $NaH_2PO_4 \cdot H_2O$, and sodium phosphate dibasic Na_2HPO_4, were obtained from Mallinckrodt Chemical Works, and Matheson Coleman & Bell, respectively.

Sample preparation

Stock solutions of the compounds of 500 ppm were made with DI water as the matrix. The solubility of 4-(*t*-butyl) phenol and 4-isopropylphenol in water is negligible as noted visually and from various MSDSs. In order to dissolve the compounds in water, aqueous NaOH (5 *M*) was added drop- wise to a suspension of the solid in DI water until the solid particles appeared to be dissolved. The solutions were checked for a Tyndall effect, which was absent. The stock solutions were diluted with the matrix of interest prior to being passed through the chromatographic column. The pH of the diluted solutions was adjusted using aqueous 0.1 M or 0.2 M NaOH if necessary.

Column chromatography

Octolig®, as received, was washed with DI water several times to remove fines until the water rinsed clear before further use for chromatographic analysis. The Octolig® was then used to pack a Chemglass 2.0 cm (i.d.) chromatographic column fitted with a glass frit to an approximate height of 23–24 cm (72.3 – 75.4 cm^3). The prepared column was then washed with DI water or the desired matrix. Aqueous samples at desired pH values of BPA model compounds were passed through the column at a flow rate of 10 mL/min using a Masterflex® L/S™ or a Spectra/Chrom ™ Macroflow peristaltic pump. A series of 50-mL fractions of eluent were collected and pH and UV-Vis analysis measurements were made.

Batch method of separation

A sample of Octolig ® (5 g as received) was washed with DI water until the water rinsed clear and placed in a 250-mL Erlenmeyer flask. Then, 100 mL of 10 ppm aqueous solution of the desired compound at a known pH was added. The samples were placed in a New Brunswick gyrotatory water bath (Model G76) and subjected to shaking at a rate of 240 rpm. At various intervals of shaking time, 10- mL aliquots were removed for analysis; results were plotted as percent removed as a function of time. The results indicated that the maximum removal had occurred by 5 min and remained unchanged thereafter. For subsequent batch methods, aliquots were taken from the sample after 5 minutes of shaking.

Analyses

All pH measurements were made using an Orion pH meter model 420A with an Orion pH electrode model 9107BN. The pH of the aqueous samples of model compounds was measured prior to chromatographic analysis. If necessary, the pH was adjusted with aqueous NaOH. The pH of the 50-mL fractions was measured.

Ultraviolet-visible light (UV-Vis) measurements were obtained using a Perkin Elmer Lambda 950 UV-Vis spectrophotometer or a Shimadzu UV-2401 PC UV-Vis spectrophotometer. For UV-Vis analysis, aliquots of the fractions were diluted 1:1 with the sodium phosphate buffer to maintain a desired wavelength of maximum absorption.

The determined ppm of the fractions (typically fraction 4–10) was compared to the concentration of the solution that was introduced to the column, and the percent removal was calculated and recorded.

Statistical analysis

To determine if the different matrices had an effect on the removal of the compounds by Octolig®. Student's *t*-tests were performed with confidence interval of 95%. A Student's *t*-test was performed to determine at each pH studied if there was a significant difference in the removal of 4-isopropylphenol between DI water and well water as the matrix. In order to compare the percent removal between all three different matrices at the studied pH, a one-way Analysis Of Variance (ANOVA) test was performed. A Student's *t*-test was also used to determine if the maximum percent removal of 3-nitrophenol differed significantly from the maximum percent removal of the BPA model compounds 4-isopropylphenol and 4-(*t*-butyl) phenol.

Molar extinction coefficient measurements

Dilutions from the 500 ppm solution were made for each model compound to generate a calibration curve. The absorbance values at the determined wavelength of maximum absorption, λ_{max}, for each dilution were recorded. Using the Beer-Lambert law the molar extinction coefficient was determined in which the slope of absorbance versus concentration gives the extinction coefficient times the path length. The molar extinction coefficient value for each model compound is shown in Table 1.

Results and discussion

Selection of model compounds

There are two important criteria for the selection of model compounds, one being the acidity of BPA as reflected in the pKa, and the second the lipophilicity as reflected in the value of the octanol/water partition coefficient, P. The pKa value of the compound is important for the formation of anions; a higher pKa value requires a higher solution pH for anion formation. The log P value, a measure of lipophilicity, was chosen as an important criterion because it may aid in the migration of the compound from the aqueous phase to being associated with Octolig®.

BPA has pKa values of 9.59 and 11.3, and a log P value of 3.32. The pKa and log P values of 4-(*t*-butyl) phenol are 10.16 and 3.31, respectively. Therefore, the compound serves as a good model compound of BPA based on the criteria. Similarly, 4-isopropylphenol is relatively similar to BPA and was also selected as a model compound.[19–21]

Additionally, 4-nitrophenol and 2-nitrophenol that have lower pKa values, summarized in Table 2, were studied to test the effect of acidity. Both of these compounds are stronger acids, as well as being less lipophilic. The 3-Nitrophenol has a pKa value and log P value that is between that of the BPA model compounds and the other nitrophenol isomers. Although these compounds do not directly resemble BPA they could be useful model compounds if a process for BPA removal involved formation of a nitro derivative.

Table 1. Molar extinction coefficient values of BPA model compounds.

Model compound	λ_{max} *(nm)*	*Extinction coefficent* (M^{-1})
4-tert-butylphenol	274	1586.5
4-isopropylphenol	275	1651.2
2-nitrophenol	278	6353.9
3-nitrophenol	273	5988.4
4-nitrophenol	317	9734.1

Matrix effects

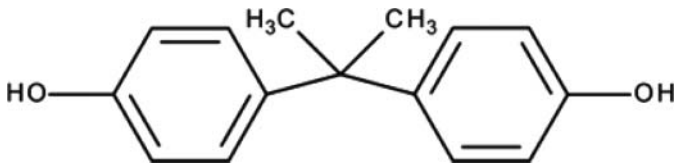
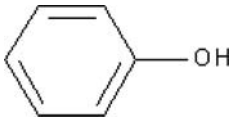
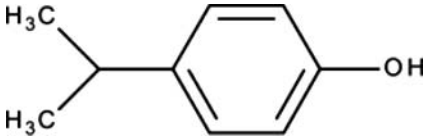
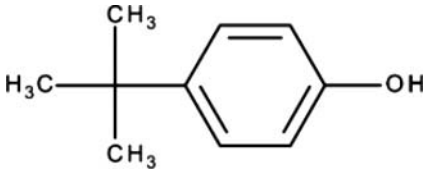
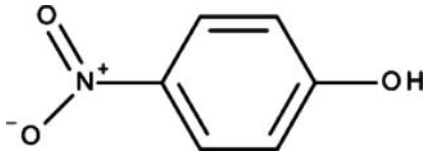
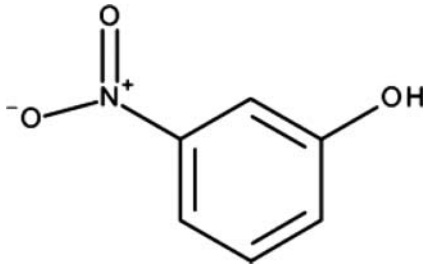
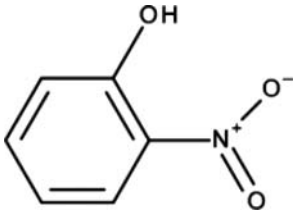
The removal of 4-isopropylphenol was tested using three solutions: deionized (DI) water, well water, and a 0.9% (w/v) saline solution (Table 3). At a pH of approximately 7.0, the results of a Student's *t*-test revealed that the percent removal of 4-isopropylphenol from DI water or well water did not differ significantly. However, at pH approximately 9.0, the matrix (DI water or well water) does have an effect on the removal of 4-isopropylphenol. An ANOVA test indicated that the three matrices differed in the removal of 4-isopropylphenol. Further analysis, using a difference between a means *t*-test, revealed that the matrices DI water and well water do not differ significantly in removal tendency but the removal from 0.9% (w/v/) saline differs significantly. The results indicate the possible removal of BPA from an extraction solvent such as saline solution.

Percent removal and pH

The percent removal of 4-isopropylphenol as a function of pH is shown in Figure 2. According to the data in Figure 2 the percent removed increases in the pH range of 5.5–8, reaching a maximum percent removal, and then decreased linearly from pH 8–10. Further examination of Figure 1 and Figure 2 suggests two effects are involved in the removal process of the model compounds. One key process is the removal of protons from the compound to form anions that would be attracted to protonated nitrogens on Octolig®. A second key process is the presence of protonated nitrogens on Octolig®, which is reportedly stable over a wide range of pH values, specifically 0.5–10.5.[23]

The first process is increasingly likely with increasing pH as predicted from the Henderson-Hasselbalch equation. The second key process, the likelihood of the protonation of the amines, decreases with increasing pH. The pKa of the

Table 2. Comparison of BPA with selected model compound.[25–28]

Compound name	*Structure*	*pKa*	*Log P*
Bisphenol A		9.59, 11.3	3.32
Phenol		9.95	1.50
4-isopropylphenol		10.19	2.82
4-(*t*-butyl)phenol		10.16	3.31
4-nitrophenol (*p*-nitrophenol)		7.15	1.91
3-nitrophenol(*m*-nitriophenol)		8.36	2.00
2-nitrophenol (*o*-nitrophenol)		7.22	1.77

ethylenediimine ligand of Octolig® may be similar to that of aliphatic diamines reported by Bryantsev et al.[24] where the pKa value for aliphatic internal ethylenediamines was 9.9–10.3 in aqueous phase.[24] Therefore, an equation that is indicative of the second process may be derived from the Henderson-Hasselbalch equation:

$$\log[HL^+] - \log[L] = pK_{HL} - pH. \quad (4)$$

Log [L] may be regarded as 0 because the activity of the non-protonated species remains constant. Accordingly, Eq. (4) indicates that as the pH increases, the effective concentration of protonated species, as log [HL^+] is reduced, and an approximate value could be calculated assuming that pK_{HL} would equal approximately 10. This would quantitatively indicate the concentration of protonated species in Octolig®, which decreases with increasing pH, though not on a 1:1 basis.

pKa as a predictive guide

A plot of percent removal as a function of pKa shows a drop in removal at pKa values greater than 8 (Fig. 3). Lissamine Green has sulfonate groups that provide an ample concentration of anions.[17] Similarly, three

Table 3. Removal of 4-isopropylphenol and 4-(*t*-butyl) phenol in different matrices over a chromatographic column (2 cm × 30 cm) packed with ~70 mL of Octolig® at a flow rate of 10 mL per min.

Model compound	*pH_i of stock solution*	*n, No. of trials*	*Matrix*	*Fraction*	*ppm*	*% Removed*
4-isopropylphenol	7.01 ± 0.07	2	DI water	Stock	68 ± 2	ND
				6–10	55 ± 2	18 ± 2
	7.17 ± 0.04	2	Well water	Stock	38 ± 1	ND
				6–10	31 ± 1	18 ± 3
	8.11 ± 0.03	4	DI water	Stock	100 ± 5	ND
				6–10	79 ± 4	22 ± 2
	8.08 ± 0.00	2	Well water	Stock	98 ± 3	ND
				6–10	78 ± 1	20 ± 1
	8.13 ± 0.06	2	Saline	Stock	96 ± 2	ND
				6–10	78 ± 1	19 ± 1
	9.02 ± 0.04	4	DI water	Stock	98 ± 1	ND
				6–10	84 ± 1	14 ± 2
	9.02 ± 0.07	2	Well water	Stock	101 ± 2	ND
				6–10	82 ± 1	19 ± 1
4-(*t*-butyl) phenol	8.70 ± 0.00	5[a]	DI water	Stock	8.4 ± 0.0	ND
				Aliquot	6.2 ± 0.2	26 ± 2
	8.99 ± 0.00	5^0	DI water	Stock	23.5 ± 0.0	ND
				Aliquot	17.6 ± 0.3	25 ± 1
	9.70 ± 0.00	4[a]	DI water	Stock	92.6 ± 0.0	ND
				Aliquot	79 ± 3	15 ± 2
	9.84 ± 0.07	4	DI water	Stock	93 ± 1	ND
				6–10	78 ± 2	16 ± 2

Here, 50-mL aliquots were collected.

xanthenylbenzenes (Rose Bengal, erythrosine, and eosin) may be phenols, but they also have carboxylate groups present that probably assist in the quantitative removal of these compounds.[16] A final example, amoxicillin, a popular antibiotic, is a phenol which has a carboxylic group that assist in the quantitative removal of the compound. [17]

At higher pKa values of the model compounds, higher pH values of the solutions are required to achieve the anionic form of the compound. As the pH of the solution increases the likelihood that Octolig® becomes deprotonated as well increases, resulting in a decrease in ability to remove the anionic compound.

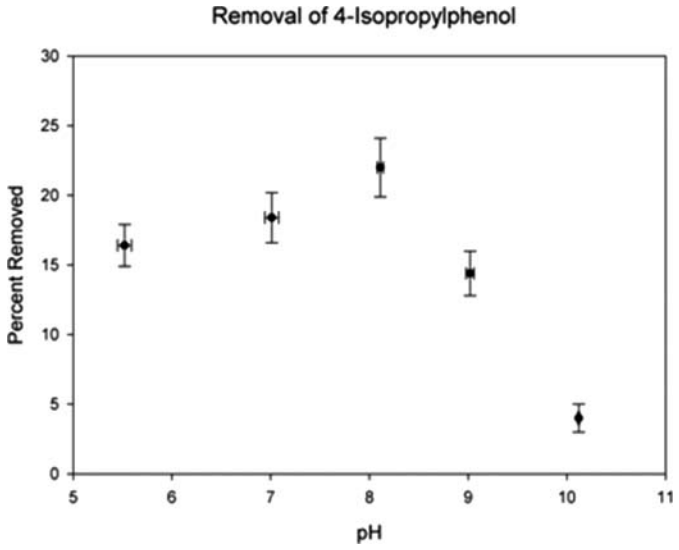


Fig. 2. Percent 4-isopropyl phenol removed as a function of initial pH. Average percent removed was determined from fractions 6–10 from all trials, that is $n = 4$.

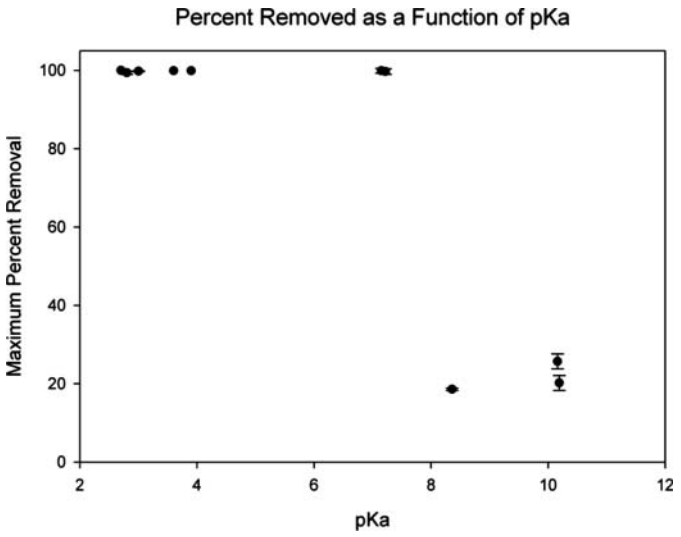


Fig. 3. Percent removal of selected compounds (Table 5) as a function of the pKa.

Table 4. Passage of aqueous nitrophenol solutions over a chromatographic column (2 cm × 30 cm) packed with ~70 mL of Octlig® at a flow rate of 10 mL/min.

Compound (matrix)	*n, No. of trials*	*pH_i of stock solution*	*Fraction*	*ppm*	*% Removed*
2-nitrophenol (DI water)	2	4.83 ± 0.02	Stock	9.2 ± 0.1	ND
			4–10	0.06 ± 0.02	99.3 ± 0.4
	2	6.04 ± 0.05	Stock	9.30 ± 0.04	ND
			4–10	0.01 ± 0.03	99.9 ± 0.2
	4	7.65 ± 0.06	Stock	9.31 ± 0.03	ND
			4–10	0.04 ± 0.05	99.5 ± 0.5
3-nitrophenol (DI water)	3[a]	5.13 ± 0.00	Stock	9.7 ± 0.0	ND
			Aliquot	7.9 ± 0.1	18.5 ± 0.6
	3[a]	7.10 ±0.08	Stock	9.7 ± 0.0	ND
			Aliquot	7.7 ± 0.1	19.3 ± 0.1
	3[a]	8.35 ± 0.00	Stock	9.6 ± 0.0	ND
			Aliquot	7.8 ± 0.0	18.4 ± 0.4
	3[a]	9.40 ± 0.00	Stock	9.5 ± 0.0	ND
			Aliquot	7.8 ± 0.0	18.0 ± 0.3
4-nitrophenol (DI water)	2	4.62 ± 0.02	Stock	9.8 ± 0.1	ND
			4–10	0.2 ± 0.1	98.1 ± 0.7
	3	6.02 ± 0.04	Stock	99.9 (trial 1)	ND
				9.6 ± 0.1 (trial 2 & 3)	ND
			4–10	0.1 ± 0.1	99.4 ± 0.9
	2	7.58 ± 0.01	Stock	9.9 ± 0.4	ND
			4–10	0.01 ± 0.02	99.9 ± 0.2
(Well water)	2	7.58 ± 0.01	Stock	11.0 ± 0.4	ND
			4–10	0.01 ± 0.02	99.9 ± 0.1

[a]Indicates batch method, as described previously, was used to study removal. ND (not determined). Fractions of 50 mL were collected.

A Student's *t*-test showed that the maximum removal of 3-nitrophenol was significantly less than 4-(*t*-butyl) phenol but did not differ significantly from the percent removal for 4-isopropylphenol. The pKa of 3-nitrophenol is lower than that of either 4-isopropylphenol or 4-(*t*-butyl) phenol, which would suggest the percent removal may be higher. However, the log P of 3-nitrophenol is lower than the two model compounds, which may reduce its partitioning to the Octolig® stationary phase. On the other hand, 4-nitrophenol and 2-nitrophenol were almost completely removed by Octolig® (Tables 4 and 5).

Table 5. Maximum percent removal achieved with corresponding pH by column chromatography using Octolig® as a function of pKa.

Compound	*pKa*	*pH*	*% Removal*
Rose Bengal[16]	3.9	6.6	99.2 ± 0.7
Erythrosine[16]	3.6	8.7	99.9 ± 0.0
Eosin Y[16]	2.7	6.7–6.8	100.0 ± 0.1
Lissamine Green B[17]	~3	6.3–8	99.9 ± 0.1
Amoxicillin[17]	9.48	6.2–7.1	99.0 ± 0.7
4-isopropyl phenol	10.19	7–8	20 ± 2
4- t-Butyl phenol	10.16	8.7–9	26 ± 2
4-Nitrophenol	7.15	6–7.6	99.9 ± 0.6
3-Nitrophenol	8.36	7–9.4	18.6 ± 0.3
2-Nitrophenol	7.22	6–7.6	99.7 ± 0.7

A possible explanation is that the isomers 4-nitrophenol and 2-nitrophenol provide more resonance stabilization than 3-nitrophenol. The stability of the phenolate anion of the two isomers compared to 3-nitrophenol may contribute to the high removal observed. In addition to the phenolate anion the nitrophenols contain the nitro group which provides another source of anion formation. The complete removal of 4-nitrophenol and 2-nitrophenol at pH values less than that of the pKa values (pKa values are that of the phenol group) can be attributed to the nitro group anion.

To further examine the effect of pKa on removal, three xanthenylbenzenes (Rose Bengal, erythrosine, and eosin Y) were previously investigated for the removal by Octolig®.[16] The xanthenylbenzenes contain a phenolic group as well as a carboxylic acid group. These three dyes are more acidic than the chosen BPA model compounds and thus have lower pKa values. All three were removed by Octolig® effectively. Additionally, Lissamine Green B and the pharmaceutical amoxicillin both have amine and phenolic groups and were also removed effectively by Octolig®.[16,17] All the examples cited for their successful removal had pKa values of less than 7.2.

In contrast, for a pKa value between 7.2–8.3, there is a value at which the pH required to deprotonate the compounds to yield the anionic form simultaneously results in the deprotonation of Octolig® to a significant amount, and the compounds cannot be effectively removed. In fact,

removal of approximately 25% was observed for those compounds with pKa values greater than 8.3. Given that BPA has pKa values of 9.6 and 11.3 indicates an approximate removal of 25% based on experimental results.

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