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Phenol removal from aqueous solution by adsorption with resin technology

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ABSTRACT

Phenolic compounds are chemicals that appear quite frequently across a broad spectrum of industrial process streams and wastewaters such as those from the pharmaceutical, petrochemical and refineries, plastics, wood, paint, and paper industries. As phenol is both toxic and harmful to the environment, the discharge and disposal of wastewater containing phenol is strictly regulated across the world, leading to the universal need of treating phenolic wastewaters for their discharge and reuse. The aim of this paper was the study of phenol removal by adsorption with polymer resin DOWEX OPTIPORE™ L493 Adsorbent, focusing on the typical stumbling blocks of adsorption technologies: removal efficiency, adsorption capacity, and resin recovery. The potential of this resin for phenol removal was evaluated under different conditions at laboratory scale in packed-bed glass columns. Findings show that phenol removal was highly efficient, reaching values of 99.9% removal in single/solute studies and at least 95% in natural samples with high concentrations of additional total organic carbon. Equilibrium studies were carried out in order to build isotherm curves at 30°C and 60°C. The adsorption isotherm parameters were determined for various isotherm models through linear and nonlinear regression. Regeneration through temperature desorption has been tested on this resin, showing that quantitative desorption of phenol is possible at moderate temperature and pressure (100°C, 1 bar). In conclusion, the results have identified DOWEX OPTIPORE™ L493 as an appropriate adsorbent for phenol, which shows great potential as an alternative to less environmentally friendly materials.

Keywords: Phenol; Polymer resins; DOWEX OPTIPORE™ L493; Adsorption; Regeneration; Isotherm

1. Introduction

Phenol and phenolic derivatives are widespread in wastewaters from the chemical industry. As phenols and alkylphenols are a natural component of crude oil, they are ubiquitous in the wastewaters of the petrochemical and oil refining industries. The concentrations in which they are found can vary a lot depending on the type of operation, going from 6–500 mg/L (refineries), 28–3,900 mg/L (coking operations), 9–6,800 mg/L (coal processing), and to 2.8–1,220 mg/L (manufacture of petrochemicals). Additionally, phenols can be found in wastewater streams in concentrations of 0.1–1,600 mg/L in the pharmaceutical, plastics, wood products, paint, and pulp and paper industries [1]. The presence of phenol is so commonplace because it is the precursor of some very important dyes and polymers, including polyamides like nylon, polycarbonates, epoxy, and phenolic resins [2].

As the amounts of phenol in industrial wastewater usually exceed the acceptable levels for safe discharge or reuse, it becomes legally necessary for them to be treated. Phenolic compounds have been listed by the United States Environmental Protection Agency (USEPA) and the European Union (EU) as pollutants of priority concern due

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to their toxicity. The discharge of wastewaters into surface waters must not bring contaminant levels above acceptable environmental standards. In the case of the USEPA, the accepted environmental standard for phenol in surface waters is as low as 1 part per billion. The discharge and disposal of phenol is strictly regulated, by setting acceptable discharge limits, in most countries like China (0.2 mg/L), Brazil (0.5 mg/L), India (1 mg/L), Japan (5 mg/L), Mexico (0.3 mg/L), and EU countries such as France (0.3 mg/L) and Italy (1 mg/L) [3].

Conventional methods for phenol removal include steam distillation, solvent extraction, adsorption, chemical oxidation, wet air oxidation (WAO), and biodegradation, while more advanced technologies for removal of phenols include electrochemical oxidation, photooxidation, ozonation, the Fenton reaction, membrane processes, and enzymatic treatment [4]. The best technology to be applied strongly depends on each particular case, particularly on the concentration of phenol in the feed stream, the presence of other contaminants, and the nature of the plant where this problem is found. All existing technologies have some disadvantages that have to be considered in their implementation. Distillation at atmospheric pressures allows complete separation at the expense of a high energy consumption (temperatures between 98°C and 180°C) [5]. Therefore, distillation is used mainly for the purification of phenol but much more rarely when the aim is only to remove phenol from waste streams [6]. Liquid-liquid extraction is extensively used in phenol removal processes, but it introduces the use of extraneous solvents, which must also be treated and recovered. Furthermore, solvent extraction can also carry along other co-contaminants [7]. By changing the pH to achieve full dissociation of phenol in the feed solution, reverse osmosis membranes can be used to remove phenols from aqueous streams [8]. However, phenol, like most volatile organic compounds (VOCs), is a source of chronic organic fouling on reverse osmosis and nanofiltration membranes, which will cause system performance loss [9]. Oxidation with oxidants such as chlorine and chlorine dioxide or potassium permanganate is possible, but it is not an environmentally friendly method of phenol removal due to the formation of chlorinated organic compounds and the dispersion of Mn compounds. Moreover, it is also expensive due to the cost of the reagents, as well as the need for quite precise control of pH [10]. WAO is also used for the elimination of phenol and aromatic alcohols in water streams. The main drawback of this technology is the elevated pressures and temperatures required for significant removal rates: at 130°C and 5 bar total organic carbon (TOC) removal is ~5% after 2 h, whereas at 220°C and 30 bar removal is 88% [11]. A considerable amount of research has gone into catalysts that can overcome the costly, high-pressure, energy-intensive conditions required to achieve complete removal through WAO. A number of solid catalysts exist that have yielded good phenol removal rates, albeit at relatively milder conditions: 98% removal at ~150°C and ~10 bar. A relevant problem in heterogeneous catalytic WAO is that the associated leaching of the active metal species will further pollute the wastewater and result in the progressive loss of catalytic activity [12]. Compared with physicochemical treatments, biological abatement is environmentally friendly and energy saving. Most of the cultures tested for this purpose are capable of degrading phenol at low concentrations. However, phenol is toxic to most types of microorganisms, and at high concentration, it can be a growth inhibitory to those species that have the capacity to use it as a substrate. Therefore, to achieve good performances in biochemical treatments, it is necessary to keep phenol concentration below toxic limits, making it difficult to treat wastewaters with high or variable phenol contents [13]. Generally speaking, most of the more complex technologies – such as catalytic combustion, electrochemical oxidation, photooxidation, or Fenton's reaction – require advanced equipment. In such cases, the technical requirements for optimization and monitoring tend to be both complex and costly, hindering their large-scale implementation [1].

Adsorption onto solid media is one of the most common and long-standing methods for removal of phenol from water, in no small part because it is technologically quite simple to build and to operate. It has the advantage of having relatively low energy demands (20°C–50°C, ~1 atm) and the ability to treat feed streams with different concentrations: from very high to trace concentrations [1]. The main inconvenience in adsorption technologies is the regeneration of spent adsorbents, which may not be possible or even convenient, involving the use of additional chemicals. Commonly used media for phenol adsorption are activated carbon, zeolites, silica gel, activated alumina, organoclays, and polymer resins [14,15]. However, most adsorbent materials face the challenge of either poor regeneration capabilities or low adsorption capacities. Of these, activated carbon is by far the most widespread adsorbent material used for phenol removal. It is generally an inexpensive material, particularly some vegetable types, but its recovery is difficult and costly enough that it is often directly disposed of after a single use and as a consequence can be quite expensive and environmentally unfriendly [16]. Polymer resins are a classical alternative to activated carbon in adsorption processes. They can operate at conditions very similar to those of activated carbon (20°C–50°C, ~1 atm, neutral pH) and with the same type of fixed-bed column systems [1]. Typically, their overall adsorption capacities have been reported to be lower, but this is offset by much better avenues for in situ regeneration. Resins such as AMBERLITE™ XAD-2, AMBERLITE™ XAD-4, AMBERLITE™ XAD-7, and AMBERLITE™ XAD-16 have been shown to be capable of successfully removing phenol from water [16]. DOWEX OPTIPORE™ L493, a macroporous hyper-cross-linked polystyrene divinylbenzene resin, has more recently been proposed as a viable candidate for phenol removal applications. DOWEX OPTIPORE™ L493 has long been used for the removal of VOC in the gas phase and some types of organic compounds from water in some liquid applications, particularly aromatic compounds [17,18]. More recently, this resin has been identified as a good adsorbent for organics dissolved in wastewater originating from crude oil extraction [19,20]. As previously mentioned, phenolic compounds are naturally present in crude oil and much more soluble in water than other organic fractions and one of the main components of oil-contaminated wastewater [21]. In light of the existing literature, DOWEX OPTIPORE™ L493 shows high potential for phenol removal applications. The other reason DOWEX OPTIPORE™ L493 is attractive for this particular application is that desorption can easily be carried

out with steam, hot air, or ultrasound [22]. This compares favorably with most other adsorbents, where desorption and recovery can almost never be carried in situ. In the case of activated carbon, regeneration of spent adsorbent is almost always carried out off-site as it requires the use of large ovens in order to carry out the reactivation carbon particles at temperatures as high as 500°C–800°C [23]. In order to regenerate activated carbon in situ, it is necessary to either use organic solvents or meet very demanding conditions in order to implement thermal desorption in water (190°C and 25°bar) [24,25]. Most organoclays can be recovered through photochemical oxidation, but such a method would require an external setup; otherwise, the options are the use of organic solvents or thermal desorption in N_2 atmosphere [26].

2. Materials and methods

2.1. Materials

The adsorbent used in this study was the DOWEX OPTIPORE™ L493 Adsorbent, a highly cross-linked styrene-divinylbenzene copolymer with a high surface area (1,100 m^2/g) and porosity (1.16 cm^3/g), supplied by Dow (The Dow Chemical Company, USA). The resin was washed with ultrapure water prior to being used in the experiments. The study used synthesis-grade phenol (CAS 108-95-2, ≥99.9%) for preparation of synthetic samples and standards. The average properties of bulk DOWEX OPTIPORE™ L493 Adsorbent are provided in Table 1.

2.2. Screening tests

To test the resin for phenol removal, synthetic samples of known phenol concentration were eluted through a packed-bed glass column (5 cm diameter, 12 cm bed height) at different concentrations (10, 100, and 200 mg/L) and flow rates (15, 30, and 60 BV/h). The concentration of phenol in treated water was measured at the feed and effluent by taking aliquots and implementing standard phenol analysis method ISO 6439:1990 (Hach-Lange cuvettes LCK 346) and a UV-Vis Spectrometer (DR5000 Hach-Lange). The potential for phenol removal of the resin was also evaluated with real wastewater samples from the petrochemical industry of Tarragona (Spain) at 30 BV/h, containing variable amounts of BTEX (0–320 mg/L), phenol (90–120 mg/L), organic acids (20–250 mg/L), and generic TOC (230–670 mg/L). The removal efficiency was calculated as the ratio between the phenol removed between the inlet and the outlet and the concentration in the inlet.

$$E(\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (1)$$

Table 1
Typical properties of resin as specified by the supplier [27]

Matrix	Macroporous styrene polymer
Physical form	Orange to brown spheres
Particle size diameter	0.3–0.85 mm
BET surface area	1,100 m^2/g
Total porosity	1.16 cm^3/g
Average pore diameter	4.6 nm
Apparent density	0.33 g/cm^3
Moisture content	50%–65%

2.3. Adsorption equilibrium experiments

The method used for adsorption capacity determination was based on standard method by the American Society for Testing and Materials (ASTM) D3860-98 (2014). Adsorbents were ground to a fine particle size and dried at 105°C for 4 h. A stock solution of phenol of the desired concentration was prepared by mixing a known amount of pure crystalline phenol and diluting with ultrapure water. The batch mode experiments were conducted isothermally at 30°C and 60°C. Experiments were carried out by adding a known amount of adsorbent (M) to a series of sealed glass flasks, filled with 100 mL of the prepared solutions. The flasks were placed in a thermostatic shaker bath at 250 rpm to equilibrate. Four hours was considered sufficient time for proper equilibration after monitoring initial experiments for the duration. The initial (C_0) and equilibrium concentrations (C_e) of all liquid samples were analyzed (Standard Method ISO 6439:1990). The adsorption capacity (q_e) of the resin was calculated by normalizing the mass of phenol adsorbed onto the resin (m_e) by resin mass (M), as in the equation:

$$q_e = \frac{m_e}{M} = \frac{V(C_0 - C_e)}{M} \quad (2)$$

2.4. Desorption experiments

Desorption experiments were also conducted in batch mode, where spent adsorbent that had been saturated at an initial concentration of 500 mg/L and 30°C was submerged in a known volume of ultrapure water at high temperature (100°C). After 2 h, the concentration in the solution was measured. Afterward, the adsorption capacity of the regenerated resin was determined again at the same saturation conditions of 200 mg/L and 30°C. The recovery efficiency (R) of the resin was evaluated as the ratio between the difference in capacity between the fresh resin and that of the sample after recovery ($q_{e,0} - q_{e,r}$) and the capacity of fresh resin ($q_{e,0}$).

$$R(\%) = \frac{q_{e,0} - q_{e,r}}{q_{e,0}} \times 100 \quad (3)$$

3. Results

3.1. Screening

The screening tests with synthetic phenol solutions were carried out in conditions of increasing concentration (10, 100, and 200 mg/L) and flow rate (15, 30, and 60 BV/h). These experiments showed that the resin was capable of effectively removing phenol under increasingly harsh operating conditions. In all samples, concentrations registered

in the effluent were always below the limits of detection of the analytical method. This indicates a removal efficiency between, equal to, or above 99.5% and as high as 99.97% at high concentrations (Table 2).

The treatment of industrial wastewater samples with DOWEX OPTIPORE™ L493 Adsorbent also showed very low contents of phenol in the outlet. This indicates high selectivity toward phenol removal even in samples rich in organic content, where other molecules would also compete for adsorption in the active sites in the resin surface (Table 3). This is an indicator that the adsorbent shows high affinity for the adsorption of phenolic compounds. The removal efficiency with this type of samples was between 95.2% and 99.7%. Additionally, a high percentage of the TOC as measured through a TOC-L Shimadzu analyzer (Shimadzu Corporation, Japan), was also removed, although typically with a lower overall efficiency (62.2%–65.8%).

3.2. The effect of contact time and particle size

In order to establish the equilibrium time for phenol adsorption onto DOWEX OPTIPORE™ L493 Adsorbent, the influence of contact time over the process evolution was investigated in the first 24 h. Experiments were carried out in which the removal of phenol was plotted over the contact time. Typically, the amount of phenol adsorbed onto the resin increased rapidly in the first 1–2 h of the experiment. Afterward, it reached a plateau and further increased contact did not increase adsorption over time. A typical curve is shown in Fig. 1. In light of these results, the contact time was selected at 4 h.

Equilibrium experiments were carried out with ground resin (0.05 mm) as defined by method standards. This is typically done in order to minimize a bias introduced by the effect of internal mass transfer limitations as the existence of an inaccessible volume of resin inside the polymer beads would represent a capacity loss. However, later trials have shown that such mass transfer limitations are not significant when working with whole beads of DOWEX OPTIPORE™ L493 Adsorbent. Working with an initial concentration of 500 mg/L and 0.25 g of resin, the adsorption capacity obtained with ground resin was 106.8 ± 4.2 and 109.1 ± 3.1 mg/g when working with whole beads. This, along with the rapid equilibration time, indicates that the internal mass transfer in DOWEX OPTIPORE™ L493 Adsorbent is particularly favorable to phenol adsorption.

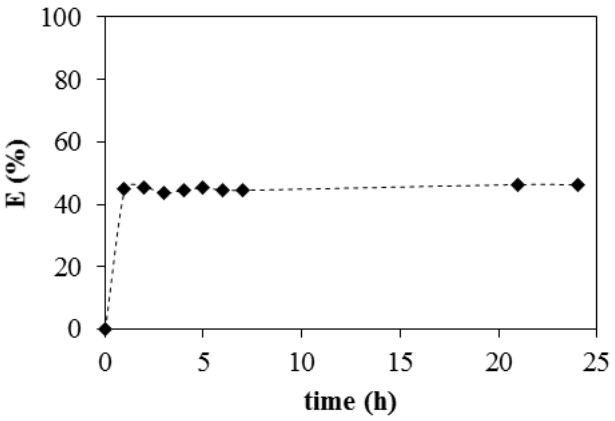

Fig. 1. Effect of contact time over removal efficiency at C_0 = 500 mg/L, 0.25 g resin, and 30°C.

3.3. The effect of temperature

The determination of resin adsorption capacity correlated to the corresponding equilibrium concentration – the adsorption isotherms – has been carried out at two different temperatures: at 30°C and 60°C. These temperature values were chosen because they are the extremes at which phenolic wastewater is most often found within the petrochemical industry. Fig. 2 shows the adsorption isotherms. The results obtained indicate a decrease in the adsorption capacity with increasing temperature. This suggests that at high temperatures, there is a displacement of the adsorption equilibrium which starts favoring desorption.

3.4. Adsorption isotherm models

There are a number of models that have been published to describe the experimental data of adsorption isotherms. Of all these models, the Langmuir and Freundlich isotherm

Table 2
Concentration of phenol in treated water (synthetic solutions)

Sample	Specific flow (BV/h)	C_{in} (mg/L)	C_{out} (mg/L)	E (%)
#1	15	10.0	<0.05	≥99.50
#2	15	89.5	<0.05	≥99.94
#3	15	199.5	<0.05	≥99.97
#4	30	191.5	<0.05	≥99.97
#5	60	195.0	<0.05	≥99.97

Table 3
Concentration of phenol in treated water (wastewater)

Sample point	Specific flow (BV/h)	Phenol			TOC		
		C_{in} (mg/L)	C_{out} (mg/L)	E (%)	C_{in} (mg/L)	C_{out} (mg/L)	E (%)
#1	30	75.0	3.6	95.2	209.1	73.6	64.80
#2	30	76.0	0.3	99.6	247.1	84.6	65.80
#3	30	83.0	0.2	99.7	226.9	78.1	65.60
#4	30	89.0	1.1	98.8	669.5	253.2	62.20

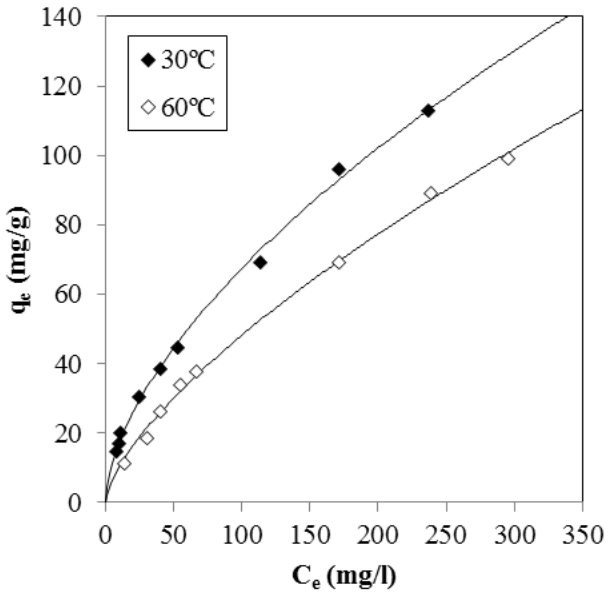

Fig. 2. Adsorption isotherms of phenol at 30°C and 60°C, fitted to a Freundlich isotherm.

models are the most frequently used for the adsorption of organic solutes. The Freundlich isotherm model is an empirical equation that best describes nonideal equilibrium adsorption on heterogeneous surfaces and has been used to model multilayer adsorption [28]. Langmuir isotherm model is based on the assumption that a monolayer of adsorbed solute is formed on the solid surface once adsorption takes place, with the active surface as a homogeneous ideal flat plane. This model assumes that all the adsorption sites have equal affinity for the solute; a site can hold at most one molecule of adsorbate, and adsorption at one site does not affect the adsorption at an adjacent site [29]. Thus, in the present study, both models have been used to describe the relationship between the amount of phenol adsorbed and the corresponding equilibrium concentration through linear regression analysis. The linear plots of the two isotherms considered are shown in Fig. 3.

The adsorption isotherm studies clearly indicate that experimental data show a good fit of the Freundlich model. The fit of the Langmuir model is far less adequate, as predicted values show a deviating trend from actual experimental data as shown in the plot of predicted vs. actual values in Fig. 4. The Freundlich and Langmuir coefficients calculated using linear regression have been given for 10–300 ppm, pH 7.8, 250 rpm, and 30°C–60°C and are given in Table 4.

The better fit of the Freundlich model indicates a nonideal reversible adsorption of the solute with a nonideal distribution or a heterogeneous surface of the adsorbent. This is in line with existing knowledge of typical polymer resin pore structures, which when compared with other adsorbent materials are highly heterogeneous. However, comparing only between two models for adsorption does not guarantee that one of them will indeed be the one that best describes adsorption in a given system. As most existing adsorption models cannot be properly linearized, it is necessary to use nonlinear regression in order to estimate model parameters. Several existing models have been analyzed for phenol adsorption with nonlinear regression through the least-squares method (Table 5).

Model parameters have been calculated for another 7 different models considered relevant for adsorption from the liquid phase (Table 6). The data have been presented alongside the calculated standard error of the regression (S_D) and the coefficient of determination (R^2), which have been used to compare regression analysis results. Fig. 5 shows the plot of predicted values in front of actual values for the different models considered.

The results indicate that the isotherm model equations with the worst fit are the Temkin and Dubinin–Radushkevich models. This was, in part, a predictable result as both isotherms are only truly suitable for an intermediate range of concentrations and do not predict well the behavior observed at low concentrations. They have both been typically used

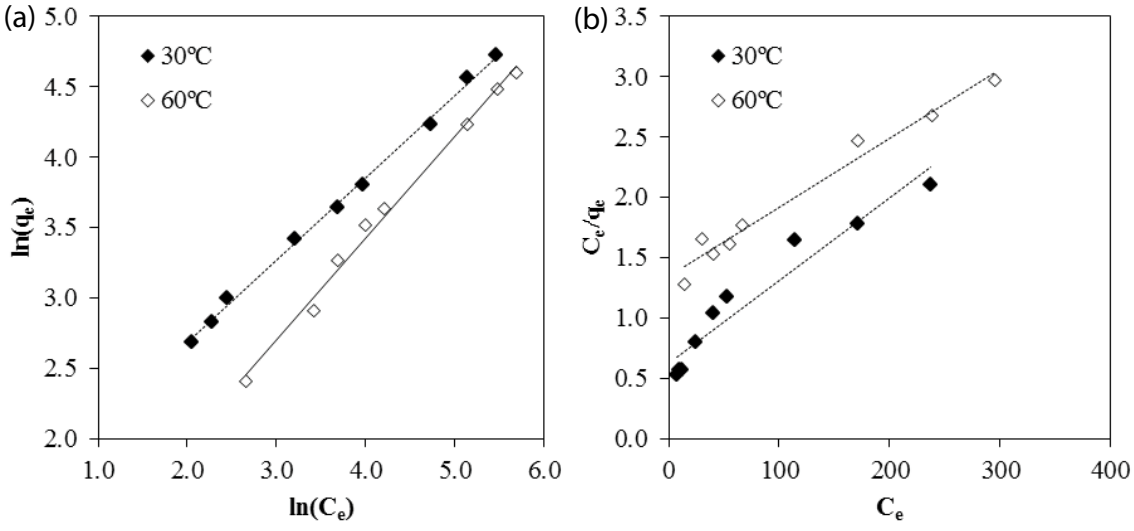

Fig. 3. Freundlich (a) and Langmuir (b) plots in the linear regression analysis for phenol adsorption at 30°C and 60°C.

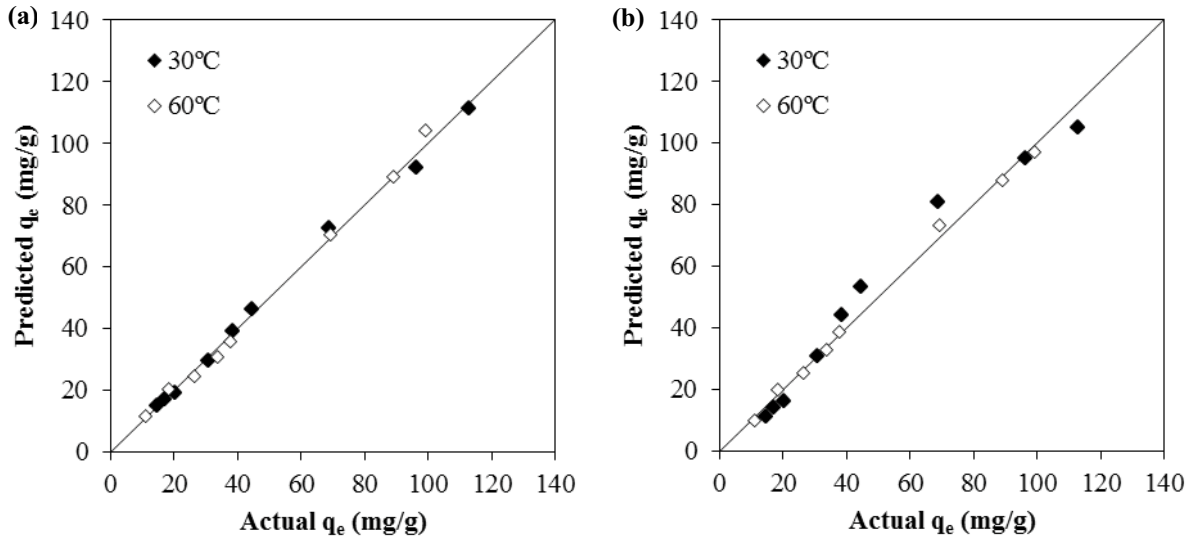

Fig. 4. Plot of predicted vs. actual values of adsorption capacity for the Freundlich (a) and Langmuir (b) isotherm models through linear regression.

Table 4
Freundlich and Langmuir's coefficients calculated using linear regression

Temperature (°C)	Freundlich			Langmuir		
	K_F[a]	n[b]	R^2	K_L[c]	q_0[d]	R^2
30	4.5 ± 0.3	1.71 ± 0.08	0.9968	0.011 ± 0.0030	146 ± 36	0.9188
60	1.7 ± 0.9	1.38 ± 0.12	0.9917	0.004 ± 0.0005	174 ± 29	0.9693

[a]Units of [(mg/g)/(mg/L)^n]; [b]Nondimensional; [c]Units of L/mg; [d]Units of mg/g.

to successfully model the adsorption of metal ions from the liquid phase, not organic molecules. Additionally, the Dubinin–Radushkevich isotherm is normally appropriate in the presence of microporous and mesoporous materials such as activated carbon. It is not strange then that it is inadequate to describe adsorption onto a hyper-cross-linked macroporous resin.

The rest of the models that have been used show a reasonably good fit for either one or both temperatures. However, a model that adequately describes one adsorption system should be able to fit the data at different temperatures. This requisite discards several of the analyzed models such as Langmuir, Brunauer–Emmett–Teller (BET), and Toth. This is because at 30°C, they all show a large deviation and a bias in the trend of actual vs. predicted value of capacity. The Langmuir model typically presents a plateau at high concentrations, which we do not see in the experimental data, at least at this range of concentrations. Therefore, the Langmuir model fit for the data is predictably poor. The BET equation model which describes multilayer adsorption on the assumption that the first layer is much more strongly adsorbed and subsequent layers all share the same energy of adsorption is shown to predict values within 0.002% of the predicted values for the Langmuir equation at both temperatures. As a result, the model presents a very similar bias and an equally poor fit.

At 30°C, we find that the best models available are the Freundlich and Sips models, going by the minimum value of standard deviation (S_D) and a maximum value of R^2. However, if we examine this result closely, we will find that with an a_S value of 0, the Sips model equation effectively collapses into the Freundlich model equation, with very similar parametric values. The Redlich-Peterson is also shown to adequately predict the behavior of phenol adsorption at 30°C. The values predicted by this model, however, are within 0.2% or less of the values predicted by the Freundlich model in the range of the experimental data (6.4–259 ppm), which cannot be considered a statistically significant difference.

At 60°C, we find that Freundlich and Redlich-Peterson still predict capacity values that are within 0.03% of each other. Of the three models (Freundlich, Sips, and Redlich-Peterson), a statistical analysis shows that Sips is the one that best fits the existing data. The Sips equation, which is also known as the Freundlich-Langmuir equation, is an empirical 3-parameter hybrid model of the 2-parameter models of Langmuir and Freundlich. At 60°C, it deviates from the Freundlich equation by gaining a constant in the denominator (a_S = 0.004), producing a model with a slightly flatter profile. As the emergence of an earlier plateau at lower concentrations with increasing temperature is a feature that would be expected of an adsorption system of this type, the Sips model can be considered a good fit. On the other hand,

Table 5
Linear and nonlinear isotherm model equations

Isotherm	Nonlinear equation	Linear equation	References
Freundlich	$q_e = K_F C_e^{1/n}$	$\ln(q_e) = \ln(K_F) + \frac{1}{n}\ln(C_e)$	[28]
Langmuir	$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_0 K_L} + \frac{C_e}{q_0}$	[29]
BET	$q_e = q_0 \frac{K_{BET,1} C_e}{(1 - K_{BET,2} C_e) + (1 - K_{BET,2} C_e + K_{BET,1} C_e)}$	–	[30]
Temkin	$q_e = a_{TE} \ln(K_{TE} C_e)$	$q_e = a_{TE} \ln(K_{TE}) + a_{TE} \ln(C_e)$	[31]
Sips	$q_e = \frac{K_s C_e^n}{1 + a_s C_e^n}$	–	[32]
Redlich-Peterson	$q_e = \frac{K_{RP} C_e}{1 + a_{RP} C_e^n}$	–	[33]
Dubinin–Radushkevich	$q_e = q_0 \exp(-K_{DR} \varepsilon^2)$	$\ln(q_e) = \ln(q_0) - K_{DR} \varepsilon^2$	[34]
Toth	$q_e = \frac{K_{TO} C_e}{(\alpha_{TO} + C_e)^{1/n}}$	–	[35]
Khan	$q_e = \frac{q_0 K_K C_e}{(1 + K_K C_e)^n}$	–	[36]

Table 6
Calculated parameters calculated by nonlinear regression

Model	Calculated parameters			S_D	R^2
Temperature = 30°C					
Freundlich	K_F = 4.248	n = 1.666	–	1.8903	0.9969
Langmuir	K_L = 0.007	q_0 = 172.0	–	5.0907	0.9797
BET	$K_{BET,1}$ = 0.017	$K_{BET,2}$ = 0.001	q_0 = 150.0	5.0907	0.9797
Temkin	K_{TE} = 0.160	a_{TE} = 26.95	–	9.4876	0.9137
Sips	K_S = 4.249	a_S = 0	n = 0.600	1.8903	0.9969
Redlich-Peterson	K_{RP} = 231.1	a_{RP} = 53.64	n = 0.402	1.8962	0.9969
Dubinin–Radushkevich	K_{DR} = 1,496	q_0 = 97.59	–	15.731	0.8475
Toth	K_{TO} = 396.2	a_{TO} = 11.70	n = 0.479	3.5128	0.9895
Khan	K_K = 1.983	q_0 = 2.894	n = 0.404	1.9285	0.9967
Temperature = 60°C					
Freundlich	K_F = 2.079	n = 1.465	–	1.6834	0.9970
Langmuir	K_L = 0.004	q_0 = 183.7	–	1.8063	0.9967
BET	$K_{BET,1}$ = 0.009	$K_{BET,2}$ = 0.001	q_0 = 150.0	1.8063	0.9967
Temkin	K_{TE} = 0.067	a_{TE} = 30.42	–	7.0143	0.9466
Sips	K_S = 1.373	a_S = 0.004	n = 0.812	1.3436	0.9981
Redlich-Peterson	K_{RP} = 218.8	a_{RP} = 104.7	n = 0.318	1.6815	0.9970
Dubinin–Radushkevich	K_{DR} = 2,625	q_0 = 89.14	–	10.354	0.9074
Toth	K_T = 397.2	a_T = 31.19	n = 0.433	1.3629	0.9981
Khan	K_K = 0.028	q_0 = 31.81	n = 0.433	1.2614	0.9984

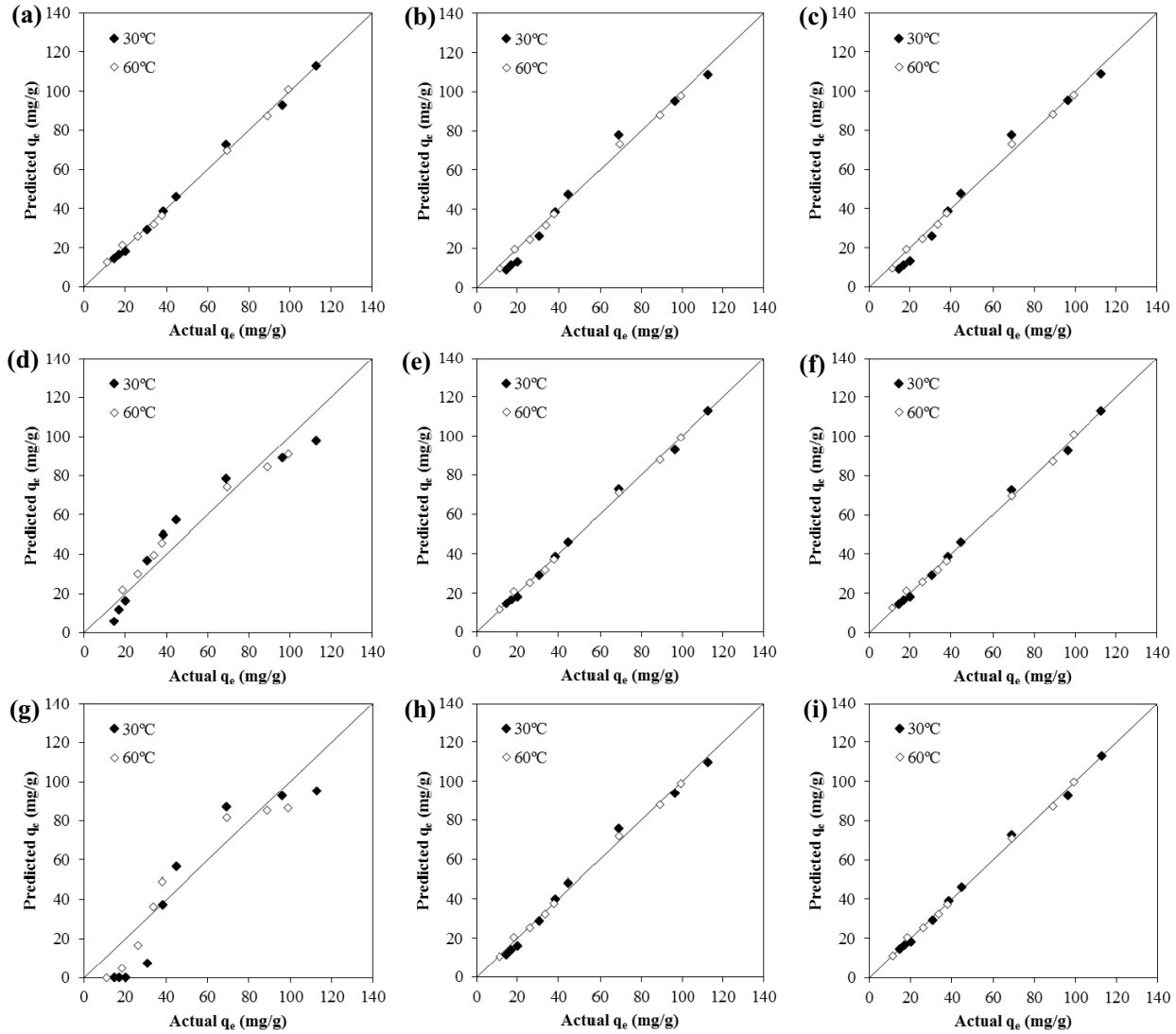

Fig. 5. Plot of predicted vs. actual values of adsorption capacity for the Freundlich (a), Langmuir (b), BET (c), Temkin (d), Sips (e), Redlich-Peterson (f), Dubinin–Radushkevich (g), Toth (h), and Khan (i) isotherm models through nonlinear regression.

it is worth noting that the greatest deviation of Sips from the capacity predicted by the Freundlich model is no more than 5%. Considering the experimental error existing in the measurements, it is doubtful that it can be decided whether Freundlich or Sips is the better fit with any kind of statistical significance. In that case, Freundlich presents the advantage of simplicity, having only 2 parameters.

3.5. Desorption and resin recovery

According to the manufacturing specifications, polymeric resin DOWEX OPTIPORE™ L493 can be regenerated by either steam at low pressures or condensate. In this project, desorption was carried out with water at boiling point (100°C) in batch conditions. The desorption experiments first carried out consisted of repeated cycles of adsorption/desorption on the same catalyst mass in the same conditions: adsorption (100 mL, 30°C, 500 ppm of phenol, 250 rpm, 0.25 g of resin) and desorption (100 mL, 100°C, ultrapure water, 250 rpm, 0.25 g of resin). The results showed an initial loss of capacity after the first regeneration cycle compared with fresh resin (22%), with a regeneration of 78%. Subsequent cycles have yielded a capacity loss of 1%–3%, which has been mostly attributed to an observed loss of catalyst mass during manipulation due to low volumes of resin involved. In practice, this indicates that there was no further significant loss after the first regeneration cycle (Fig. 6). This indicates that of the solute initially adsorbed, a fraction has remained adsorbed after regeneration in these conditions but that such an effect is not cumulative. Such a limitation could be attributed to several factors, such as limited accessibility of some adsorption sites, irreversible adsorption, or the adsorption equilibrium in the current regeneration conditions.

Experiments were carried out with a different number of regeneration steps, in which the water used for regeneration was changed for clean water to displace the adsorption

Table 7
Regeneration efficiency of DOWEX OPTIPORE™ L493 at 100°C

Sample no.	Regeneration cycle	Regeneration steps	q_e (mg/g)	R (%)
1	New catalyst	–	102.7	100
1	1	1	80.7	79
1	2	1	77.6	76
1	3	1	76.2	74
2	New catalyst	–	106.8	100
2	1	1	94.1	88
2	2	2	98.1	92
2	3	3	103.6	97

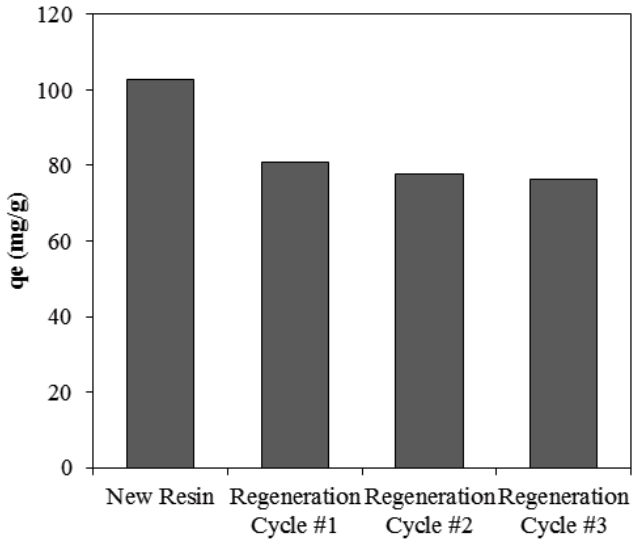

Fig. 6. Evolution of adsorbent capacity after several cycles of adsorption (30°C) and desorption (100°C).

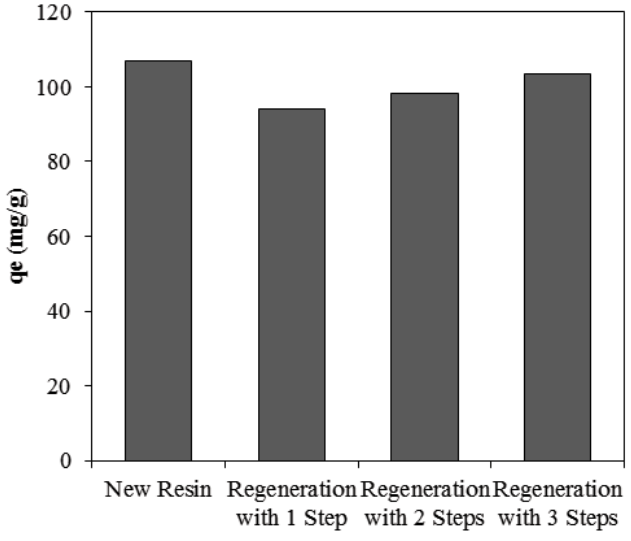

Fig. 7. Evolution of adsorbent capacity after several cycles of adsorption/desorption with an increased number of steps.

equilibrium further. The results show that with an increased number of regeneration steps, the regeneration increases (Table 7). With 3 consecutive regeneration steps, a 97% regeneration was obtained (Fig. 7). This indicates that an optimization for the minimum volume of water and maximum recovery in regeneration could be achieved. However, it is a difficult proposition to carry out in laboratory-scale batch conditions. With continuous and low flow rates, however, it should be possible to optimize the regeneration procedure in order to produce minimum waste.

The values of capacity vs. concentration obtained during these experiments for the desorption process at 100°C have been plotted alongside the adsorption isotherms at 30°C and 60°C. The parameters of the Freundlich model equation have been tentatively fitted to this set of data (Fig. 8). The data produce a flat low profile at 100°C, indicating a high degree of phenol desorption.

The use of steam might also provide good results for the purpose of phenol desorption, in light of the present data. Such a proposition would have the theoretical advantage of desorption at an even higher temperature (up to 120°C, as

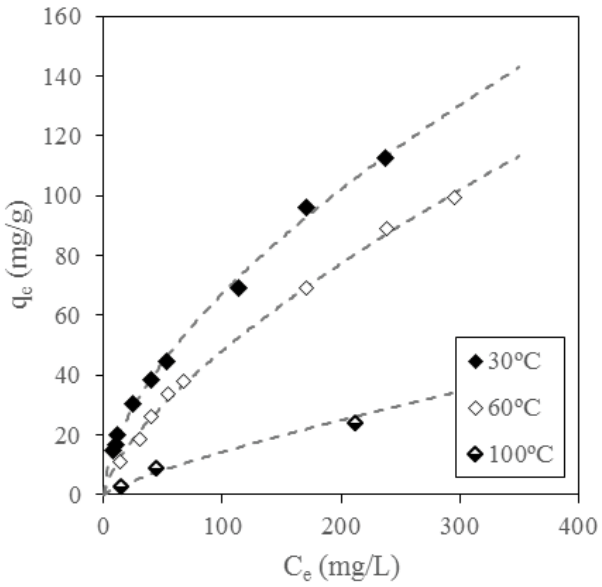

Fig. 8. Desorption isotherm at 100°C, alongside adsorption isotherms at 30°C and 60°C.

Table 8
Compilation of common adsorbent capacity at C_e = 200 mg/L

Adsorbent	C_e range (mg/L)	Temperature (°C)	q_e (mg/g)	Reference
AMBERLITE™ IRA-420	100–1,700	30	28	[37]
AMBERLITE™ XAD-4	151–900	30	42	[38]
	100–2,500	25	25	[39]
AMBERLITE™ XAD-7	100–2,500	25	28	
AMBERLITE™ XAD-16	100–900	30	16	[40]
DOWEX OPTIPORE™ L493	5–250	30	98	–[a]
Macronet MN200	5–500	21	65	[41]
AuRIX 100	5–500	21	58	
Activated carbon	–	30	144	–[a]
Organoclays	1–550	25	4.7–30	[42]
Zeolites	9–1,500	30	0.8–22	[43]

[a]Experimental value

per resin material limitations), which would require lesser volumes of condensate water and less waste generation. However, further testing would be necessary in order to validate this proposition.

3.6. Benchmarking against existing adsorbents

The capacity for phenol removal of the resin studied in this paper has been compared with other commercial resins and common adsorbents according to current literature sources (Table 8). It can be seen that DOWEX OPTIPORE™ L493 has a very high capacity compared with common resin market standards for organic removal. It is reportedly an average of 60%–75% higher than standard organic removal resins such as AMBERLITE™ IRA-420 and the AMBERLITE™ XAD Series. This higher capacity is in no small part to be attributed to the higher BET surface area of the DOWEX OPTIPORE™ L493 resin (1,100 m^2/g) in front of AMBERLITE™ XAD-4 (750 m^2/g), AMBERLITE™ XAD-7 (450 m^2/g), and AMBERLITE™ XAD-16 (800 m^2/g). This resin also has a far larger loading capacity than other common adsorbents like zeolites and organoclays materials, although the wide array of existing products makes a completely exhaustive literature-based comparison difficult. It does not have a higher adsorption capacity than activated carbon. This literature-based information was confirmed through experimental testing in the laboratory, with the same method used to determine the capacity for DOWEX OPTIPORE™ L493. However, in spite of the apparent advantages of a higher loading capacity, activated carbon presents an array of difficulties for regeneration that make it an expensive adsorbent to use. To regenerate activated carbon in situ, it is necessary to either use environmentally unfriendly organic solvents. Regenerating activated carbon through water desorption and temperature requires implementation of very demanding conditions that would demand a system designed to withstand temperatures and pressures that are unnecessary for regular operation (190°C and 25 bar) [24].

4. Conclusions

The properties of DOWEX OPTIPORE™ L493 Adsorbent have been tested for phenol removal, showing good performance and high efficiency of removal (≥95%) treating streams of medium-high concentration (up to 250 ppm) and high flow rates (up to 60 BV/h). Furthermore, this resin appears to be selective toward phenol adsorption and relatively unaffected by competitive adsorption of organics in a complex matrix such as that of real wastewater samples. The study of adsorption isotherms has shown that adsorption capacity increases as the concentration of phenol in the mobile phase does within the range that has been studied (10–250 mg/L). Additionally, the experimental data have shown that adsorption is favored at lower temperatures (<30°C), where the equilibrium capacity is higher. As loading capacity is considerably decreased at high temperatures, where desorption is favored in the equilibrium, condensate at 100°C can be used in order to regenerate the adsorbent. Optimization of the batch regeneration conditions has shown that the adsorption of phenol on the resin is fully reversible, and adequate displacement of the adsorption equilibrium has produced recoveries as good as 97%. Contrasting this results with existing literature has shown that DOWEX OPTIPORE™ L493 Adsorbent has a remarkably high capacity compared with other commercial polymer resins, as well as other staple adsorbents such as organoclays and zeolites. And, although it has lower capacity than activated carbon, the prospects of this resin for easy in situ regeneration strategies show great potential as an alternative adsorbent for phenol removal purposes.

Symbols

a_{RP} — Redlich-Peterson isotherm constant, L/mg
a_S — Sips isotherm constant, L/mg
a_{TE} — Temkin isotherm constant, mg/g
a_{TO} — Toth isotherm constant, L/mg

C_0 — Adsorbate initial concentration, mg/L
C_e — Adsorbate equilibrium concentration, mg/L
C_{in} — Adsorbate concentration at the inlet, mg/L
C_{out} — Adsorbate concentration at the outlet, mg/L
E — Removal efficiency, %
$K_{BET,1}$ — BET isotherm constant for adsorption for the first layer, L/mg
$K_{BET,2}$ — BET isotherm constant for adsorption for upper layers, L/mg
K_{DR} — Dubinin–Radushkevich isotherm constant, mol^2/J^2
K_F — Freundlich isotherm constant, $[(mg/g)/(mg/L)^n]$
K_K — Khan isotherm constant, L/mg
K_L — Langmuir isotherm constant, L/mg
K_{RP} — Redlich-Peterson isotherm constant, L/g
K_S — Sips isotherm constant, L/g
K_{TE} — Temkin isotherm equilibrium binding constant, L/mg
K_{TO} — Toth isotherm constant, mg/g
M — Mass of resin, g
m_e — Adsorbate concentration in the adsorbent at equilibrium, mg
n — Isotherm model exponent
q_0 — Maximum theoretical capacity, mg/g
q_e — Adsorption capacity at equilibrium, mg/g
$q_{e,0}$ — Adsorption capacity at equilibrium of fresh resin, mg/g
$q_{e,r}$ — Adsorption capacity at equilibrium of recovered resin, mg/g
R — Recovery efficiency, %
ε — Dubinin–Radushkevich isotherm constant, J/mol

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