REMOVAL OF EMERGING ORGANIC POLLUTANT FROM AQUEOUS SYSTEM

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Abstract

This work investigated comparative adsorption of Hydroquinone (HQ) using both a non-functionalised polystyrene divinylbenzene cross-linked Macronet (MN200) and commercial Granular Activated Carbon (GAC). The results demonstrate that HQ adsorption follows a pseudo-second order kinetic process, governed by particle diffusion for both sorbents. The uptake capacity was greater for MN200 compared to GAC, as was the rate of adsorption; which is ascribed to differences in the surface areas and inherent surface chemistries of the sorbents. The Freundlich model described HQ adsorption more appropriately, compared to the Langmuir equation, suggesting that HQ adsorption is a physical process with moderate favourability for both sorbents. Less than 30% of HQ was leached from either sorbent, even after 80 h.

Keywords

Hydroquinone, adsorption, polymeric resin, activated carbon, mechanism

Introduction

Phenolic compounds are one of the most common contaminants found in wastewater (Ayranci and Duman, 2005) and they have unpleasant odours even at a low concentration. Phenolic derivatives are toxic and carcinogenic, and their presence in aqueous systems causes negative effects for flora and fauna. (Dabrowski et al., 2005). Hence, phenol is listed as a priority pollutant by USEPA (USEPA). Hydroquinone (HQ) is a phenolic compound with two hydroxyl groups attached to the aromatic ring in the *para* position. HQ is used extensively in industry to manufacture pesticides, rubbers and medicines, as well as being used in skin whitening products. Although there is no evidence proving that HQ is carcinogenic to humans, it is known to cause vomiting, nausea, tinnitus and is toxic to the kidneys and stomach (Li et al., 2013, Suresh et al., 2011). Hence, the removal of HQ from anthropogenic water supplies is deemed necessary.

Different techniques, such as catalytic oxidation, electrochemical degradation and extraction, have been used to remove HQ from aqueous systems. However, these methods are unfavourable due to their associated high operating costs and low efficiencies. Adsorption, which incurs low cost, is an alternative to remove HQ from water (Li et al., 2013) with a variety of sorbents, e.g. carbon (Mohamed et al., 2006), bentonite (Yildiz et al., 2005) and silica (Fu et al., 2011), trialled for HQ adsorption; among those tested, activated carbon is the most common sorbent used for water treatment due to its specific surface area, and textural and chemical properties (Suresh et al., 2011). Contrastingly, polymeric sorbents are also widely used and have shown promise for water remediation due to their surface areas, controllable pore structures and simple regeneration (Valderrama et al., 2010). Previous studies reported that mesoporous resin XAD-4 and the microporous hyper-cross-linked sorbent NDA150 were successfully in removing HQ from aqueous systems (Zhu et al., 2013); however, macroporous polymeric resins have not been previously reported for HQ removal.

In this study, macroporous non-functionalised polystyrene divinylbenzene cross-linked Macronet MN200 was used to investigate HQ removal from aqueous phase and the performance compared to commercial Granular Activated Carbon (GAC). The kinetics, adsorption equilibria and leaching tendencies for both sorbents are presented to understand the interactions and mechanism of HQ adsorption. The effects of acidic functional surface groups of sorbent are also discussed.

Methodology

Stock solutions of Hydroquinone (HQ) were prepared at required concentrations, using pure deionised water. 0.04 g of each of dried MN200 and GAC (particles sized from 150 to 212 μm) were added to separate 150 mL quantities of HQ solution in batch reactors. The batch reactors were shaken at 225 rpm using an orbital shaker. At selected intervals, 0.3 mL aliquots were withdrawn from each solution and mixed with 0.3 mL of 25 mg L^{-1} dimethyl phthalate (internal standard) before analysis using Gas Chromatography – Flame Ionisation Detector (GC-FID). The GC programme used to quantify the HQ concentrations has previously been reported in the literature (Yu and Wu, 2012). For kinetic studies, the HQ concentration was adjusted to 40 mg L^{-1}; while initial HQ concentrations were prepared from 40 to 70 mg L^{-1} for the equilibria studies. Finally, 80 mgL^{-1} HQ solutions were used to investigate the leaching tendencies of the sorbents.

Results and discussion

In this study, HQ was removed from aqueous systems via adsorption using a macroporous polymeric resin MN200 and a microporous GAC; the textural properties of both sorbents have been reported in a previous study (Tao and Fletcher, 2013). Pseudo-first order, pseudo-second order and Elovich models (Figure 1 (a) and (b)) were applied to determine the kinetics of HQ sorption and the results demonstrate that the adsorption of HQ can be described using a pseudo-second order equation for both MN200 and GAC, with the kinetic parameters obtained shown in Table 1. The adsorption of aromatics onto MN200 involves van der Waals forces and the hydrophobicity of sorbent drives solute molecules from the aqueous system to the surface of the sorbent (Valderrama et al., 2010). In contrast, adsorption of aromatic compounds onto GAC is driven by dispersion forces between HQ benzene ring π-electrons and the basal planes of GAC (Valderrama et al., 2010, Suresh et al., 2011, Mohamed et al., 2006), as well as hydrogen bonding (Li et al., 2013, Suresh et al., 2011); electrostatic repulsion and attraction may contribute if ions are present (Valderrama et al., 2010).

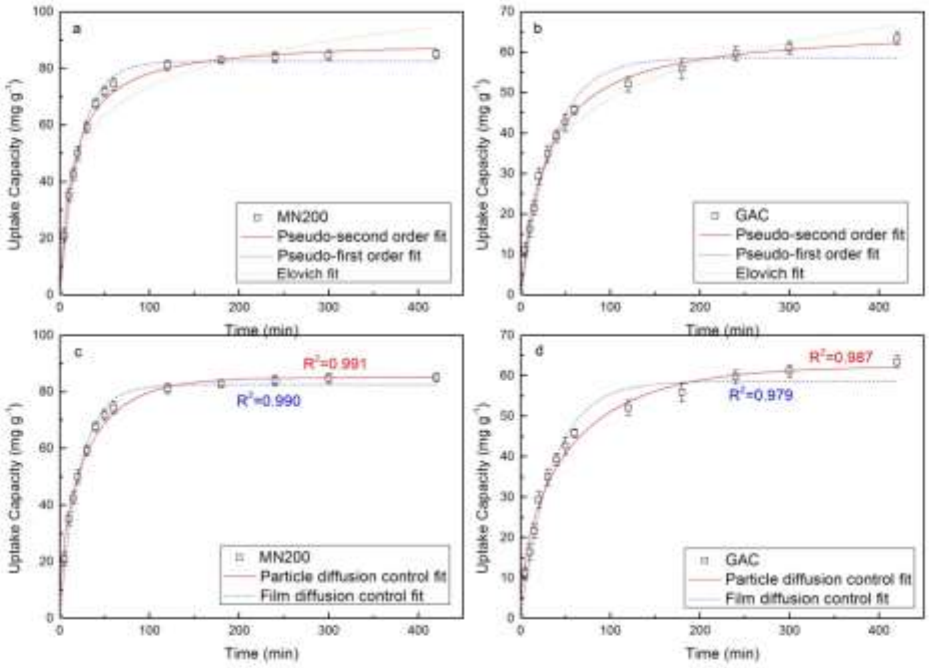

Figure 1: **Kinetic data for HQ adsorption, fitted using a pseudo-first order (dash line), a pseudo-second order (solid line) and Elovich (dot line) models for (a) MN200 and (b) GAC, where:**

Pseudo-first order equation: $q_t = q_e(1 - e^{-k_1 t})$,
Pseudo-second order equation: $q_t = (k_2 t q_e^2)/(1 + k_2 t q_e)$,
Elovich equation: $q_t = \left(\frac{1}{b}\right)\ln(ab) + \left(\frac{1}{b}\right)\ln(t)$,
q = uptake capacity, k = rate constant, a = desorption constant and b = initial adsorption rate (Valderrama et al., 2010),
HQ uptake capacities fitted using HPDM, showing particle diffusion (solid line) and film diffusion (dash line) control for (c) MN200 and (d) GAC, where:

Particle diffusion control equation: $\frac{q_t}{q_e} = \sqrt{1 - \exp(\frac{-2\pi^2 D_e}{r^2}t)}$,
Film diffusion control equation: $\frac{q_t}{q_e} = 1 - \exp(-\frac{3DC}{rC_r}t)$,
D = diffusion coefficient, r = sorbent's radius, C = NB concentration,
errors shown are for repeat runs (n = 2).

It was found that HQ uptake was higher for MN200 compared to GAC (Table 1), which may be due to the higher surface area for MN200 compared to GAC providing more active sorption sites for HQ molecules. Furthermore, MN200 exhibits faster adsorption rates compared to GAC, indicating that HQ adsorption is hindered by increased acidic group functionalisation of the sorbent. Formation of water cluster networks via hydrogen bonding between sorbent acidic functionalities and water molecules is thought to prevent HQ molecules from entering the sorbent microporosity (Dabrowski et al., 2005), additionally reducing HQ uptake for the acid functionalised sorbent despite the large surface area. The presence of oxygen containing functional groups on GAC is considered to reduce the electron density of the basal planes, hence, weakening the π-π dispersive interactions between the adsorbate and sorbent (Mohamed et al., 2006).

Table 1: Kinetic parameters of MN200 and GAC fitted using a pseudo-first order, a pseudo-second order and Elovich models

Adsorbent	MN200	GAC
Pseudo-first order		
q_e (mg g^{-1})	82.53	58.66
k_1 (min^{-1})	0.04	0.03
R^2	0.990	0.979
Pseudo-second order		
q_e (mg g^{-1})	90.25	66.34
k_2 (g mg^{-1} min^{-1})($x10^{-4}$)	7.22	5.37
R^2	0.996	0.996
Elovich		
a (mg g^{-1} min^{-1})	21.69	0.08
b (g mg^{-1})	0.07	0.08
R^2	0.946	0.987

Adsorption processes involve the three steps of (1) film diffusion, (2) particle diffusion and (3) actual adsorption. Film diffusion occurs when solute migrates from bulk solution to the sorbent surface, followed by diffusion into pores and intraparticle diffusion, which is known as particle diffusion. The final step, which occurs very quickly is the actual adsorption step; hence, the overall rate of adsorption is controlled by either film or particle diffusion, and the slowest step is called the rate limiting step (Faust, 1987). The Homogeneous Particle Diffusion Model (HPDM) was applied to determine the rate limiting step (Valderrama et al., 2010), with the overall rates of HQ adsorption onto both MN200 and GAC fond to be limited by particle diffusion (Figure 1 (c) and (d)). An intraparticle diffusion model (Figure 2 (a)) was adopted to further confirm HQ adsorption is dominated by particle diffusion. The adsorption is only limited by particle diffusion if there is only a linear slope passed through origin. However, it was found that there was more than one slope for both sorbent indicated that rates of HQ adsorption were governed by multi-steps. The first linear slopes represent the film diffusion, while the second linear slopes indicate the particle diffusion and the third slopes represent diffusion of solutes into micropores of sorbent (Tao and Fletcher, 2013). The film diffusion occurs relative fast (initial stage of adsorption); hence, the rates of HQ adsorption onto both sorbents were controlled by particle diffusion.

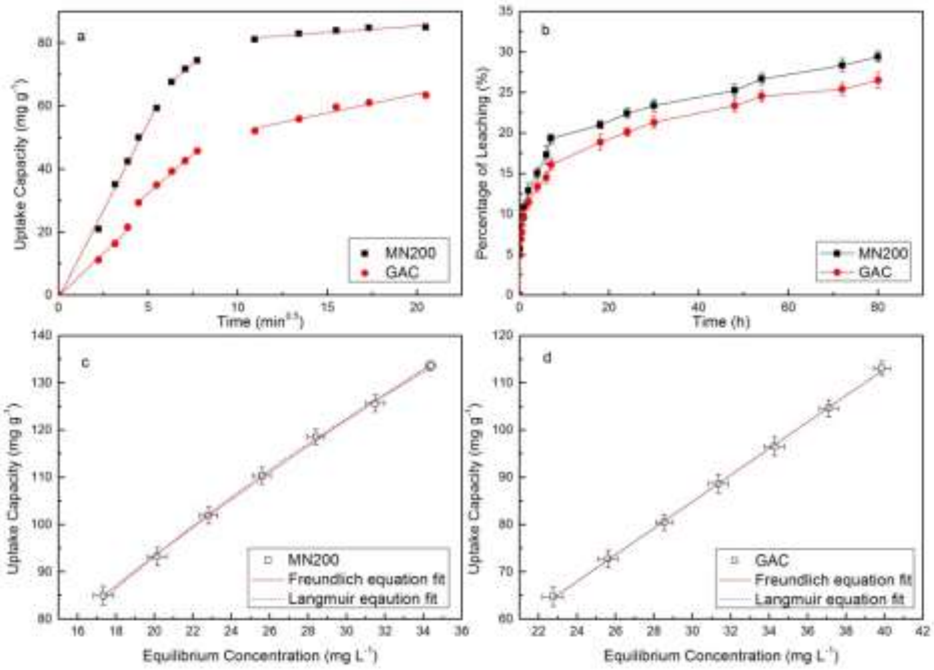

Figure 2: (a) Intraparticle diffusion kinetic fits for HQ adsorption by MN200 (squares) and GAC (circles) , where:
$q_t = k_i t^{0.5} + I$
k_i = intraparticle diffusion rate constant (mg/(g min)) and *I* = boundary layer (mg/g),
(b) Percentage of adsorbed HQ leached from MN200 (squares) and GAC (circles),
HQ uptake capacities fitted using Freundlich (solid line) and Langmuir (dash line) equations for (c) MN200 and (d) GAC, where:
Freudlich equation: $q_e = K_f C_e^{\frac{1}{n}}$
C_e (mg L^{-1}) and q_e (mg g^{-1}) are equilibrium concentration and uptake capacity, respectively. K_f (mg g^{-1} (L mg^{-1})$^{1/n}$) is the Freundlich adsorption constant and *n* represents a constant related to the adsorption affinity;
Langmuir equation: $q_e = \frac{q_m K_L C_e}{(1+K_L C_e)}$
K_L (L mg^{-1}) is the Langmuir adsorption constant and q_m (mg g^{-1}) is the monolayer adsorption capacity of the sorbent (Chen et al., 2011); errors shown are for repeat runs (n = 2).

The experiments for leaching tendencies were conducted by adding deionised water to fully HQ loaded sorbent particles and the results (Figure 2 (b)) demonstrate that 29% and 26% of HQ was leached from M200 and GAC, respectively, over 80 h. More HQ leached from MN200 as it is easier for the molecules to leach from the wider macroporosity of MN200 compared to the predominantly microporous GAC. Furthermore, it was found that the leaching rates for both sorbents were higher in the initial stages (first 7 h) during which time 19% and 16% of HQ was leached from MN200 and GAC, respectively. After which the leaching rates for both sorbents reduced dramatically.

Table 2: **Isotherm parameters obtained by fitting Freundlich and Langmuir equations to the data of HQ adsorption onto MN200 and GAC**

Adsorbent	MN200	GAC
Freundlich		
K_f (mg g^{-1} (L $mg^{-1})^{1/n}$)	12.79	2.90
n	1.51	1.01
R^2	0.9991	0.9996
Langmuir		
q_m (mg g^{-1})	326.66	14692.83
K_L (L mg^{-1}) ($x10^{-4}$)	199.9	1.93
R^2	0.9987	0.9995

The Freundlich and Langmuir models were applied to the equilibria data obtained for HQ adsorption onto MN200 and GAC (Figure 2 (c) and (d)) with the parameters obtained sown in Table 2. The results demonstrate that the Freundlich equation fitted the data more closely (higher R^2 values) for both sorbents compared to Langmuir regression. The Freundlich adsorption constant, K_F, gives an indication of adsorption capacity, i.e. the higher K_F , the higher the capacity (Tao and Fletcher, 2013). It can be seen that K_F is higher for MN200 than GAC, hence, the HQ uptake is expected to be higher for MN200, which is consistent with the kinetic studies. The value of n indicates adsorption favourability; adsorption is favourable for $2 < n < 10$, moderately favourable for $1 < n < 2$ and unfavourable for $n < 1$ (Tao and Fletcher, 2013). The results show that HQ adsorption onto MN200 and GAC is moderately favourable. Moreover, for $n > 1$, the adsorption is physical while chemical processes have $n < 1$ (Lin et al., 2009), indicating both sorbents are involved in physical processes with HQ.

Conclusion

Hydroquinone (HQ) was successfully removed from aqueous systems via adsorption using non-functionalised polystyrene divinylbenzene cross-linked Macronet MN200 and commercial Granular Activated Carbon (GAC). The results demonstrate that HQ adsorption onto both sorbents is limited by particle diffusion. MN200 exhibits higher HQ uptake and faster rate of adsorption compared to GAC due to its higher surface area. Moreover, the formation of water clusters, via hydrogen bonding between the acidic functional groups on the surface of GAC and water molecules, inhibits HQ molecules from entering the porosity of GAC. Adsorption equilibria data was fitted most closely by the Freundlich equation, and adsorption of HQ was shown to be moderately favourable and a physical process for both sorbents. Moreover, leaching tendencies were low with less than 30% leached over 80 h for both sorbents.

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