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Immobilization of phenol in cement-based solidified/stabilized hazardous wastes using regenerated activated carbon: role of carbon

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Abstract

The use of regenerated activated carbon as an immobilizing additive for phenol in solidification/stabilization (S/S) processes was investigated. The adsorption capacity of regenerated carbon was compared to that of the virgin form and was found to be very close. The effects of pH and Ca(OH)₂ concentration within the S/S monolith on the adsorption process were also examined. Kinetic tests were performed to evaluate the adsorption of phenol on different forms of F400 carbon, including the regenerated form. Kinetic tests were performed in aqueous solutions as well as in liquid–sand mixtures. In both cases, it was found that phenol adsorption on F400 carbon was fairly fast. More than 60% of the equilibrium adsorption amount could be achieved within the first hour for aqueous solutions. For sand-solution kinetics, it was found that 1% carbon (based on dry sand weight) was capable of achieving more than 95% removal of the initial amount of phenol present in solution (1000 and 5000 ppm). Fourier transform infrared (FT-IR) spectroscopy and X-ray mapping tests indicated a homogenous mixing of the carbon into the cement matrix. The carbon was also found to enhance the hydration of cement, which was retarded by the existence of phenol. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Solidification/stabilization; Phenol; Organics; Activated carbon; Regenerated activated carbon

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1. Introduction

Solidification/stabilization (S/S) has been recognized as an efficient and safe process for the treatment and disposal of a wide spectrum of hazardous waste materials. Stabilization can be defined as a process employing additives (reagents) to reduce the hazardous nature of waste by minimizing the rate of contaminant migration into the environment. Solidification, on the other hand, can be described as a process by which sufficient quantities of a solidifying agent are added to the hazardous materials to result in a solidified mass [1]. A number of binders are used to achieve the solidification of waste. The most common ones are Portland cement, lime/flyash and other pozzolanic materials.

S/S technology, which has been known for more than 15 years, has gained recognition from USEPA as an accepted technology [2]. Moreover, since it is relatively inexpensive, the S/S process is among the first options for contaminated site treatment, when applicable.

S/S technology was initially developed for inorganic waste, especially metals. The solidification process, which includes the use of Ordinary Portland Cement (OPC) in most applications, was found to enhance the immobilization of metals by forming insoluble metal salts, which are precipitated within the solid monolith. This mechanism yields a significant reduction in the leaching of these metals. On the other hand, most organic materials do not react with the inorganic binders, due to large differences between hydrophobicity and polarity of the organic contaminants and the inorganic binders [3]. This leads, in many cases, to hazardous organic contaminants being inefficiently immobilized within the solid matrix, and significant leaching of many of these contaminants has been detected [4]. Since there are very few sites that are contaminated with purely inorganic waste, it is important to adapt the S/S technology for organic waste as well. One approach proposes using sorbent additives in the solidified matrix to enhance the immobilization of organic compounds. These include clays, natural materials (such as peat moss, zeolites, etc.) and activated carbon [1]. Among these, activated carbon has a tremendous capacity for the adsorption of a wide spectrum of organic compounds. However, the high cost of activated carbon inhibits its use in large amounts in the S/S processes.

Large amounts of spent activated carbon are currently being disposed without further utilization. Part of the reason for this is that food processing industries and other users prefer to use virgin activated carbon for health-related reasons. Taking into consideration that regenerated carbon costs less than 25% of the virgin form, if regenerated carbon proves to be efficient in immobilizing hazardous organics in cement-based S/S processes, this process can be used more effectively to handle organic waste. Moreover, spent activated carbon will be removed from the waste stream. Economic benefits in the form of a new market for regenerated activated carbon will also be an additional advantage.

In this study, the use of regenerated activated carbon as an additive in the S/S cement-based process was investigated. In particular, this paper reports on aspects relating to the immobilization of phenol. Equilibrium and kinetic behavior of phenol adsorption on virgin and regenerated activated carbon are compared. The behavior of

activated carbon under conditions similar to those occurring during the solidification process is evaluated.

2. Background

2.1. Immobilization of organics by S/S

Unlike metals, organics do not usually precipitate within the solidified monolith. However, the mechanism of immobilization of organics within the solidified waste is not yet clear. It has been proposed that organics are mostly sorbed or trapped in pores within the solid matrix [5]. Tittlebaum et al. [6] reported that *p*-bromophenol was located in grains, the insides of which were cement, with the organics located on the grain surfaces. *p*-Bromophenol was also reported to exist in the calcium–silicate–hydrate (C–S–H) gel, in a heterogeneous fashion [6]. Immobilization by trapping in the pores makes organics more susceptible to leaching. This is particularly true for volatile and semi-volatile materials [4]. The leachability of organics from the pores is primarily dependent on their diffusivity and solubility in the pore fluid. The existence of organics in the solidified waste has also been reported to affect the S/S process by retarding the setting of the cement [3].

2.2. Activated carbon as an additive in S/S

Activated carbon has been known, for a very long time, for its adsorption capacity for a wide spectrum of organic materials. Its high surface area (around $1000 \text{ m}^2 \text{ g}^{-1}$) enables the adsorption of large amounts of organic material on a small amount of carbon.

Conner [7] reported that activated carbon could be an effective additive in S/S processes when organic contaminants are targeted. In fact, some S/S vendors use activated carbon in small amounts to improve the immobilization of hazardous organics in the solidified waste [4]. However, the amounts used are very small due to the relatively high cost of activated carbon. In another study [8], the addition of activated carbon to the S/S process was found to eliminate the leaching of aniline, acenaphthene, benzene, trichloroethylene and bis(2-chloroethyl)ether from solidified waste.

The adsorption of many organic compounds, including phenol, on activated carbon is known to be sensitive to pH [9,10], ionic strength of the solution [11–13], and temperature. It is expected, therefore, that changes in pH and the release of ions accompanying the cement hydration process will have an impact on the adsorption of organics on activated carbon within the cement matrix. The hydration of cement is also expected to coat and encapsulate a fraction of the carbon particulate, reducing the accessibility of the organics to the carbon surface. Kinetic studies are therefore essential to estimate the extent of adsorption expected during the solidification process.

3. Experimental

3.1. Materials

Two forms of activated carbon were used in this study: F400 virgin activated carbon and F400 regenerated activated carbon, both supplied by Calgon Carbon (Pittsburgh, PA, USA). These will be referred to as F400-V and F400-R, respectively. A powdered form of the F400-R was prepared by grinding the F400-R to particle size less than 50 μm . This form will be referred to as F400-R-PAC. No other conditioning of the carbon was performed.

A Micromeritics Gemini 2360 (Norcross, USA) BET instrument with N_2 was used to measure the surface area of the carbons. These were found to be 943 and 966 $\text{m}^2 \text{g}^{-1}$ for F400-V and F400-R, respectively.

Type I OPC was used in experiments involving cement. In experiments involving sand, cube test sand (CT 190A-ELE International, Lake Bluff, IL, USA) was used.

All chemicals used in this study, including phenol and salts, were purchased in analytical grade, and no further purification was performed.

3.2. Adsorption isotherm measurements

Equilibrium adsorption isotherms were measured at pH values of 3.5, 7, 9.5 and 12 for both virgin and reactivated carbons. The following buffer solutions were used to control the pH of the solutions: 0.05 M KCl/HCl for pH 3.5; 0.05 M KCl/NaOH for pH 9.5 and 12; and 0.05 M $\text{Na}_2\text{HPO}_4/\text{H}_3\text{PO}_4$ for pH 7.

Equilibrium isotherms for phenol were determined using the bottle point method following the ASTM standard procedure (ASTM D3860-89a). Pre-weighed amounts of carbon (ranging from 20 to 300 mg) were placed in 50 ml bottles with two blank (without carbon) solution bottles to test for evaporation. Each point on the isotherm is the average of three bottle measurements. The adsorption solutions were prepared by dissolving phenol in the buffer solution. The bottles were then filled with 50 ml of solution, leaving no headspace, to minimize evaporation, and covered with parafilm and caps. They were placed on a G24 Environmental Incubator shaker (New Brunswick Scientific, Edison, NJ, USA) and agitated at 270 rpm for a period of 48 h for the F400-R-PAC carbon and 14 days for the F400-V and F400-R carbons. The time for equilibration was determined in preliminary experiments. After equilibration, an UV spectrophotometer (Shimadzu, UV160U) was used to measure the phenol concentration in the solution. A wavelength of 270 nm was used. The amount adsorbed on the carbon was then calculated from a mass balance.

In experiments for the effect of calcium hydroxide, this salt was added to the buffer solution at the required concentration prior to mixing with phenol.

3.3. Adsorption rate measurements

Two types of kinetic studies were performed: one with activated carbon in aqueous solutions of phenol, and the other with a mixture of carbon and sand in phenol solution.

In the studies involving no sand, 24 mg samples of carbon were placed in a number of 50 ml bottles. Fifteen milliliters of 0.25 mg ml^{-1} phenol solution buffered at pH 7 were then added to each bottle. The bottles were placed on the shaker and agitated at

260 rpm. Two bottles were withdrawn from the shaker at known times, and the concentration of phenol in the solution in these bottles was measured using UV spectrophotometry. The amount adsorbed was calculated by a mass balance, and the average of the two-bottle measurements was used to obtain a kinetic data point.

For kinetic studies involving sand, about 1 kg of sand was placed in a 1-liter jar. The sand was then spiked with a known volume (to produce a sand to liquid ratio of 5:1) of phenol solution (1000 or 5000 mg l⁻¹ phenol solutions) and allowed to age for 4–5 days, with a minimum headspace in the jars and with periodic end-over-end mixing. The amount of phenol adsorbed by the sand after this period was tested and found to be negligible (less than 1%). Activated carbon was then added in amounts of 1% or 2% (weight percent with respect to dry sand weight), and mixed completely with the sand. Samples were taken from the supernatant solution on top of the sand–carbon mixture at known times, filtered through a 0.22- μ m filter, and analyzed using UV spectrophotometry. The amount adsorbed was calculated from a mass balance.

3.4. Measurements on cement encapsulated carbon

The effects of cement coating on both adsorption and desorption of phenol from regenerated activated carbon were tested. For adsorption, 24 mg of granular F400-R carbon were sprayed with water, then rolled over the fine cement powders, which had been previously separated with 100 mesh screen, to form a uniform coating. These cement-coated carbon particles were sprayed with water and rolled over a water film until the cement was completely wet. The uniformity of the coating was later tested using optical microscopy (Nikon H-III optical microscope) by mounting these coated carbon granules in cold epoxy resin, polishing with SiC polishing paper, and then examining them optically. The coated granules were placed in a 100% humidity chamber at room temperature to allow the cement to hydrate. After hydration, the granules were placed in a bottle containing 15 ml of 250 mg l⁻¹ phenol solution buffered at pH 7. The bottle was shaken for 2 h at 270 rpm. A sample of the solution was then removed, and the concentration of phenol remaining in solution was determined using UV spectrophotometry. From a mass balance, the amount adsorbed on the encapsulated carbon was determined.

To study the effects of cement encapsulation on the desorption of phenol, phenol was allowed to adsorb on 24 mg granular F400-R until equilibrium in aqueous solution. The amount adsorbed was approximately 90 mg phenol per gram of carbon. Carbon granules were then removed from the solution and coated quickly with cement using the procedure described above. Following hydration for a known time in a 100% humidity chamber, the coated carbon was placed in a bottle containing 15 ml of pH 7 buffer solution. The bottle was then placed in a shaker for 8 h at 270 rpm. The amount desorbed was determined using UV spectrophotometry, as described earlier.

3.5. Fourier transform infrared (FT-IR) spectroscopy and X-ray mapping of solidified waste

To investigate the effects of carbon on the hydration of phenol-containing cement pastes and the distribution of constituents, FT-IR spectroscopy and X-ray mapping with

scanning electron microscopy (SEM) were used, respectively. Cement specimens were prepared using Type I OPC. The water/cement ratio used in the study was 0.5. The water source was the phenol solution (1000 and 5000 mg l⁻¹) which was spiked to the sand. The sand/cement ratio was approximately 2.0. Regenerated powdered activated carbon, 0% or 2% (with respect to dry sand weight), was added to the sand/cement slurry to study the effect of carbon in the presence of phenol on the hydration behavior of the cement pastes. Cement pastes were cast into 2 in. (diameter) by 4 in. (length) PVC cylinders and cured for 7 days. Fine powders for FT-IR analysis were obtained by grinding, and were sieved with a 200-mesh screen. IR analysis was carried out on a Bio-Rad FTS 40 spectrophotometer in the wavelength range of 400–4000 cm⁻¹ using the KBr disc technique. The specimens for X-ray mapping with SEM were fractured, and their fractured surfaces were coated with gold to prevent charging. X-ray mapping was performed on a Hitachi field emission scanning electron microscopy (FESEM) with 20 kV of accelerating voltage and 15 mm of working distance.

4. Results and discussion

4.1. Adsorption capacity

It is important to ensure that the thermally regenerated F400 carbon has a reasonable capacity compared to its virgin form for its use to be justified. Adsorption isotherms for phenol, for both the virgin carbon, F400-V, and the regenerated carbon, F400-R, were obtained at different pH values. Fig. 1 shows the isotherms at pH 7 and 12 at room temperature.

At pH 12, the isotherms of F400-V and F400-R are essentially identical. At pH 7, F400-R has a slightly lower capacity, but the difference is insignificant for application in S/S. Similar results were obtained at pH 3.5 and 9.5, indicating that F400-R will provide a large economic advantage without a significant capacity penalty. It is also worth noting that F400-R shows a high capacity for phenol (≈ 100 mg g⁻¹) in the concentration range studied. This is encouraging, since it suggests that only small quantities of carbon will be required as an additive in the S/S mix, which is economically desirable. The amount of carbon required to effectively adsorb phenol in an S/S mix has been studied and will be discussed in more detail later in this paper.

4.2. Effects of pH and Ca(OH)₂

Cement-based S/S systems produce large amounts of Ca(OH)₂ during hydration which precipitates in the cement pores, creating a significant source of alkalinity and a high pore water pH (about pH 12) [14]. It is expected, therefore, that in the S/S process, adsorption on carbon will start in the neutral, or slightly acidic, environment of the contaminated soil when carbon is initially mixed in, and continue in an increasingly alkaline environment as hydration progresses. This assumes that the cement pore fluid has free access to the carbon pores during the entire solidification process.

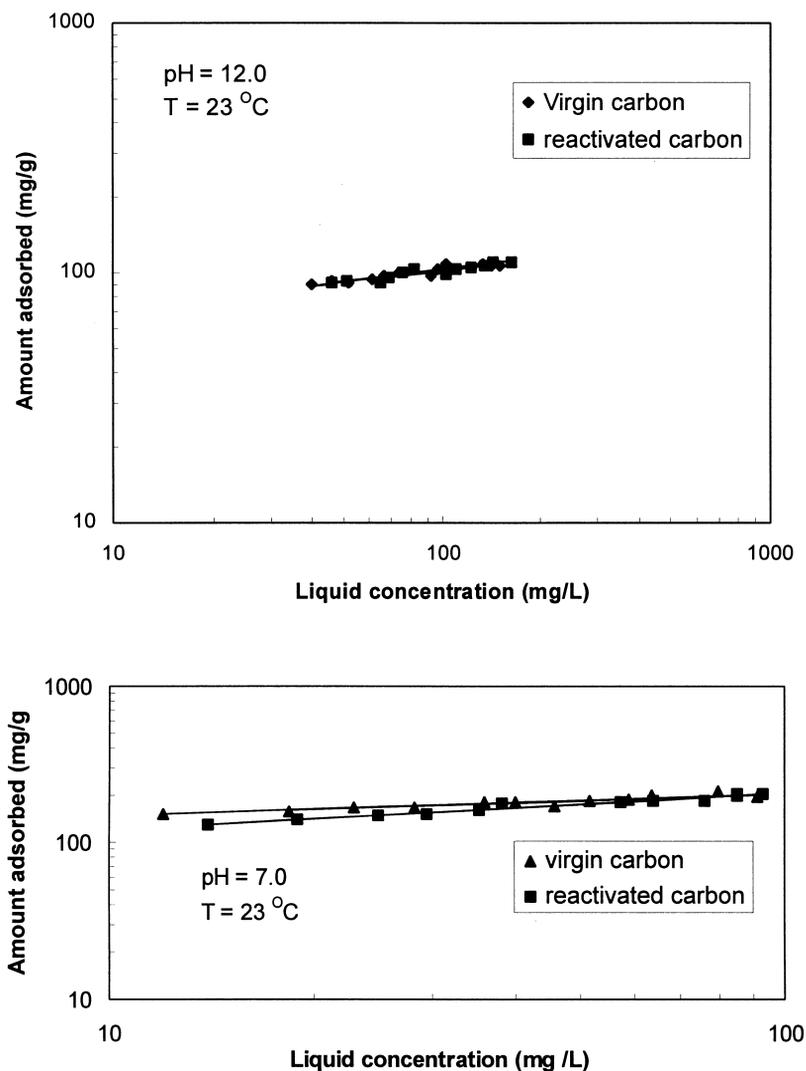


Fig. 1. Comparison of adsorption capacity of virgin and reactivated carbon for phenol.

It is reported in the literature that pH influences the adsorption capacity of dissociating compounds (such as phenol) on activated carbon [9,10]. F400-R does show a strong sensitivity to pH, as can be seen in Fig. 2. The adsorption capacity for phenol increases from pH 3.5 to 7, remains approximately constant from pH 7 to 9.5, and then decreases significantly as the pH is increased to 12. This behavior can be explained on the basis of the charge characteristics of phenol and the carbon surface.

Phenol, which has a pK_a value of 9.99 [15], exists mainly in the negatively charged phenolate form at pH values above 10. The carbon surface, due to its acidity, will also be negatively charged at high pH [16]. Consequently, repulsive electrostatic interactions

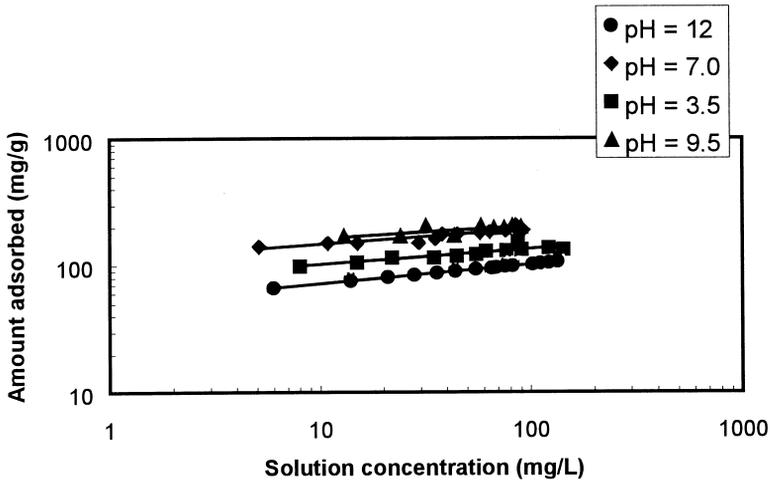


Fig. 2. Effect of pH on adsorption of phenol on F400-R.

between the carbon surface and phenol and between adsorbed phenolate ions cause a reduction in adsorption capacity. Additionally, water adsorption on the carbon is enhanced by the dissociation of heterogeneous carboxylic oxygen groups at high pH, blocking pores and reducing the effective surface area of carbon [12].

While F400-R has a lower capacity for phenol at high pH, this reduction is not likely to be significant for S/S for two reasons. First, the adsorption capacity at pH 12, though lower than at pH 7.0, is still very high. Thus, the amount of carbon required is likely to be small. Secondly, it is expected that cement will encapsulate carbon particles well before the pH in the carbon pores reaches 12. As will be shown later, once the carbon particle is encapsulated, mass transport into or out of the carbon pores is effectively stopped. Thus, it is likely that the pH in the carbon pores will be lower than 12 and the adsorption capacity correspondingly higher.

As was mentioned earlier, $\text{Ca}(\text{OH})_2$ is liberated during the hydration of cement. Since it is reported in the literature that positive salt ions, such as Ca^{2+} , affect the adsorption capacity of activated carbon for many organics [11–13], the effect of this ion on the adsorption of phenol on F400-R was determined. Fig. 3 shows three isotherms obtained for phenol at $\text{Ca}(\text{OH})_2$ concentrations of 3, 6 and 10 mg l^{-1} . These three concentrations were chosen based on limitations imposed by the low solubility of $\text{Ca}(\text{OH})_2$ at high pH (less than 15 mg l^{-1}). It is observed that $\text{Ca}(\text{OH})_2$ has no effect on adsorption capacity. In general, the presence of cations in solution has been observed to increase adsorption capacity of phenol at $\text{pH} > \text{p}K_a$ [10]. This is explained on the basis of charge between adsorbed ions and neutralization of surface charge. The lack of a similar effect with Ca^{2+} ions in this study is postulated to be due to the low concentration of these ions in solution due to the low solubility of $\text{Ca}(\text{OH})_2$ at high pH. However, $\text{Ca}(\text{OH})_2$ is present in large amounts as a precipitate within the cement matrix, as will be seen later. This precipitate can play a significant role in the immobilization of phenol in the S/S matrix.

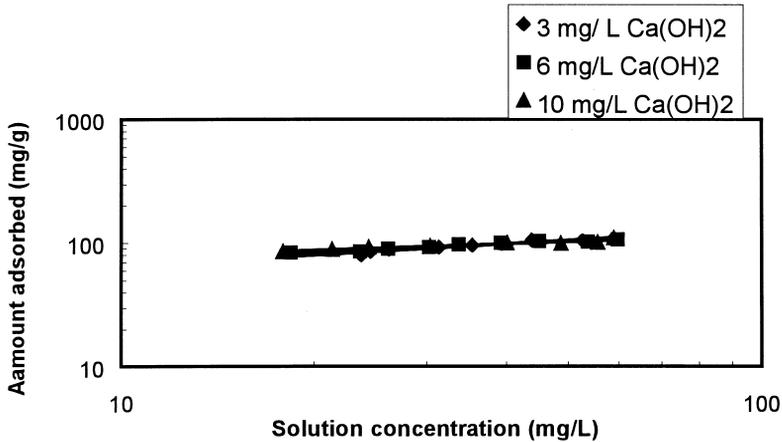


Fig. 3. Effect of Ca(OH)_2 on phenol adsorption on F400-R.

4.3. Effect of hydration time

Since activated carbon in the S/S process will be adsorbing in a solidifying cement matrix, it is expected that the adsorption rate will be affected by the presence of the cement. The cement is likely to coat the particles and block access to the internal pore structure of carbon. Thus, as the cement hardens, mass transport into the pores will be progressively hindered. The effectiveness of the carbon will therefore hinge on the rate of adsorption relative to the hydration rate.

Shown in Fig. 4 is the rate of adsorption of phenol on F400-R coated with cement as a function of the hydration time of the coating. The rate is reported relative to the rate in uncoated carbon at the same conditions. Clearly, encapsulation has a very strong retarding effect. For all hydration times exceeding 10 h, less than 4% of the phenol amount adsorbed on uncoated carbon was adsorbed on the cement-coated carbon. The

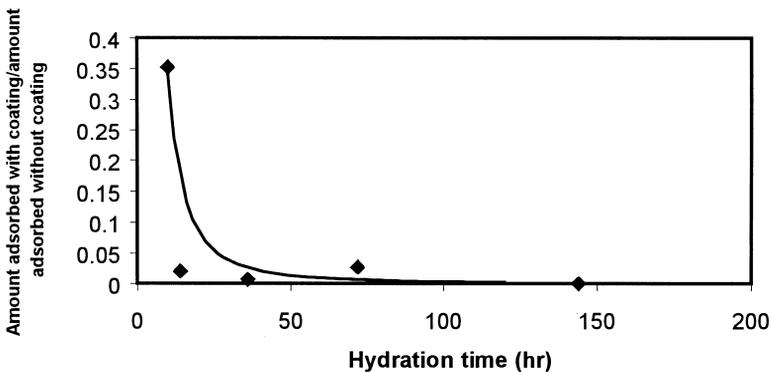


Fig. 4. Effect of cement hydration time on the adsorption of phenol on F400-R carbon.

reason for this behavior can be understood from the mechanism of hydration of cement. When Portland cement is contacted with water to initiate the hydration, calcium ions are rapidly leached from the cement granules to form a local concentrated solution of mainly calcium hydroxide, leaving behind silica-rich cement grains. The aqueous calcium hydroxide is thought to react with silicic acids on the surface of cement granules to form a gelatinous semi-permeable membrane of calcium silicate hydrate around the cement particles, which then extends to connect granules together [14]. It is postulated that, as the hydration proceeds, there is a build-up of the gel-membrane outside the carbon pores, and this forms a barrier against the diffusion of phenol into the particle.

The results in Fig. 4 lead to the conclusion that it is essential to ensure that a sufficient amount of adsorption has taken place in considerably less than 10 h after mixing, to maximize the effectiveness of carbon. Alternatively, it may be necessary to mix the carbon with the contaminated soil prior to adding the cement.

Since encapsulation of the carbon particles has been shown to severely hinder adsorption, it is to be expected that desorption will be equally affected. This is indeed the case, as can be seen in Fig. 5. This figure shows the amount of phenol desorbed from coated F400-R in 8 h relative to desorption from non-coated F400-R as a function of hydration time. It is observed that, for the range of hydration time tested, 8 to 64 h, the amount of phenol leached from the coated carbon is less than 2% of the amount leached when the carbon was left uncoated. Moreover, as the hydration time exceeded 14 h, the amount desorbed was almost zero. This indicates that, once in the solidified waste form, activated carbon particles will retain most of the adsorbed phenols on their surface.

4.4. Rate of phenol adsorption

As was stated earlier, for the carbon to be effective in S/S of organics, it is essential that the rate of adsorption be sufficiently high to ensure capture of the organics prior to pore blockage by cement. Fig. 6 presents kinetic data for phenol adsorption from aqueous solution at pH 7 on three activated carbons: F400-V, F400-R and F400-R-PAC.

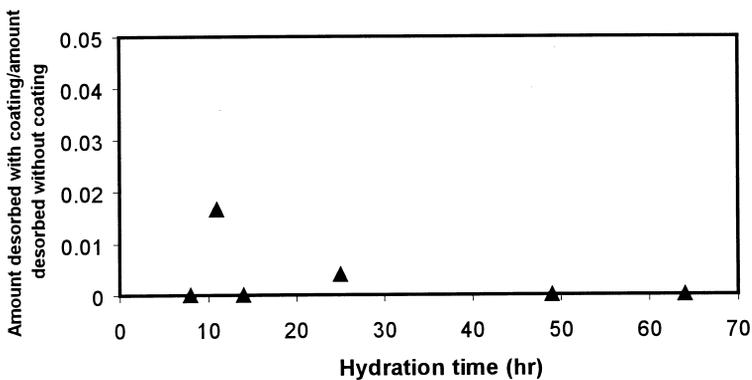


Fig. 5. Effect of cement hydration time on the desorption of phenol from F400-R carbon.

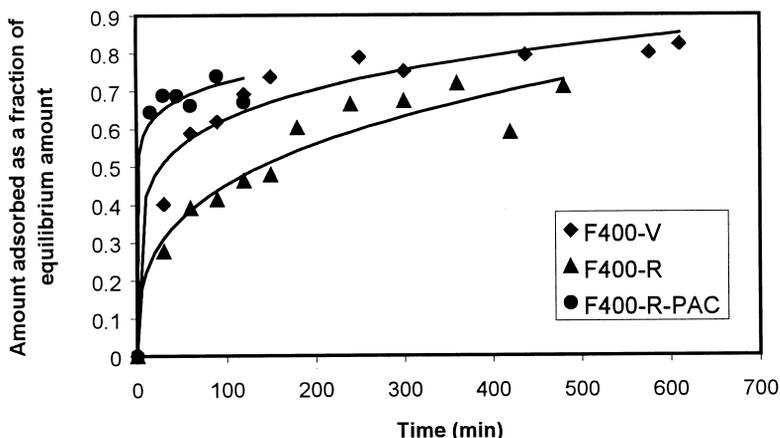


Fig. 6. Rate of phenol adsorption on F400 carbon.

The amount adsorbed is expressed as a fraction of the maximum (equilibrium) amount achievable. For all three carbons, there exists an initial high adsorption rate, corresponding to the highest driving force for mass transfer. This phase extends approximately to 20 min for F400-R-PAC, 80 min for F400-V, and 170 min for F400-R. During this initial period, about 50–65% of the equilibrium adsorption takes place. The shorter this period, the more feasible is the carbon for S/S.

On comparing the kinetic curves for the three carbons, it can be seen that the virgin form, F400-V, has a higher rate than the regenerated form, F400-R. This appears to indicate a different pore structure. It is thought that carbon pores get partially clogged after the carbon is exhausted. The regeneration process might not result in a full recovery of the original pore structure, resulting in a lower diffusivity of the adsorbate molecules in F400-R.

The powder form, F400-R-PAC, shows a much higher initial rate of adsorption than either granular carbons. In a little over 1 h, about 70% of the equilibrium capacity is

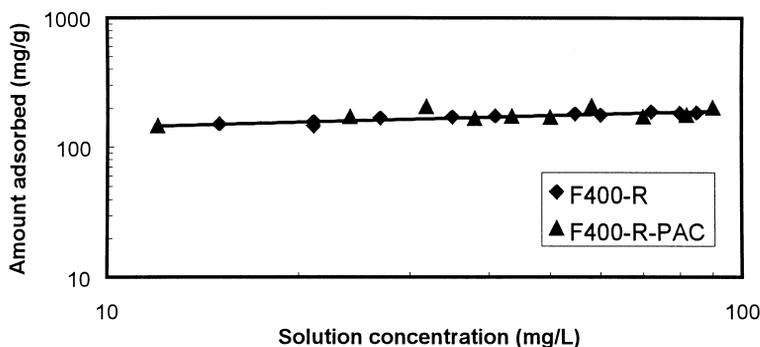


Fig. 7. Comparison of adsorption equilibrium isotherms of F400-R and F400-R-PAC.

achieved. This result is encouraging. Since it takes cement considerably longer than 1 h to effectively encapsulate the carbon, the high initial rate of adsorption of F400-R-PAC indicates that it will be possible to mix the carbon with the cement and soil in one step. Also, recognizing that the capacity of the carbon is very high, 70% of equilibrium capacity represents a high operating capacity. Thus, the total amount of carbon required is likely to be small. It should be noted that the equilibrium capacity of F400-R-PAC is identical to that of F400-R, as can be seen in Fig. 7. An additional advantage of the powder form is that it can be more evenly distributed throughout the waste form and will result in a more homogeneous solidified waste than the granular carbon.

The adsorption rate on F400-R-PAC was also measured in the presence of sand in order to establish how sand affects kinetics, and to determine the relative quantity of carbon that is required for effective removal of the phenol. Shown in Fig. 8 are kinetic curves for two initial phenol concentrations (1000 and 5000 ppm) and two carbon loadings (1% and 2% weight carbon/weight dry sand). In these experiments, the sand

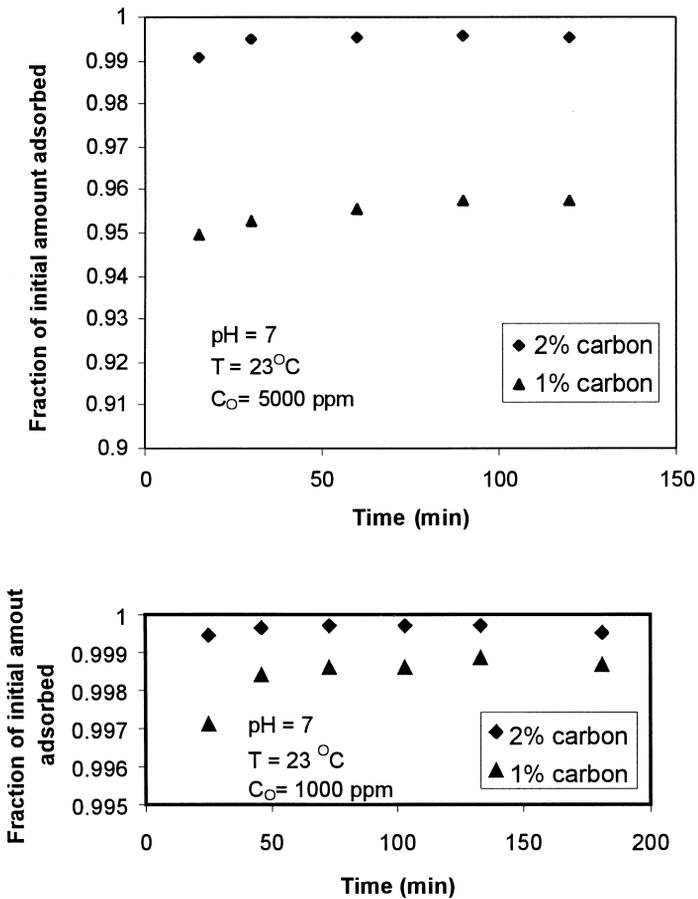


Fig. 8. Adsorption rate of phenol on F400-R-PAC in carbon–sand mixture.

was spiked with the appropriate amount of phenol and then mixed with the carbon, as described in Section 3. For all cases measured, it was observed that 95% or more of the initial amount of phenol was adsorbed within the first 20 min of contact. This is a very good rate relative to the rate of hydration. Also, the presence of sand does not appear to hinder the rate of adsorption.

Following a rapid initial rate, the kinetic curve plateaus out after about 50–60 min. This is similar to what was observed in the absence of sand (Fig. 6), and indicates that the high initial rate is followed by a slow approach to equilibrium. Clearly, however, from the results in Fig. 8, because of the high capacity of F400-R-PAC, a very high percentage of phenol is removed from solution when the plateau is reached.

As would be expected, the fraction of phenol removed is dependent on the initial concentration of phenol. At a 1% loading and an initial phenol concentration of 5000 ppm, 95% of the phenol is removed within 20 min, while in the case of the 1000 ppm initial phenol concentration, it is over 99%. This indicates that the quantity of carbon that has to be added needs to be optimized for the initial loading, based on economics and the requirements for removal. It should be noted that because of the slow approach to equilibrium, the quantity of carbon that has to be added is considerably higher than what would be calculated using isotherm data. However, as can be seen in Fig. 8, the relative amount required is only a small percentage of the amount of sand to be treated, which is promising for practical applications.

4.5. X-ray mapping results — homogeneity of carbon distribution

Figs. 9 and 10 show the results of the X-ray mapping test performed on a solidified cement sample containing carbon. Carbon (F400-R-PAC), calcium and silicon distributions are displayed on these figures, in addition to the magnified picture of the surface. The magnifications in Figs. 9 and 10 are $100\times$ and $4000\times$, respectively.

To monitor the distribution of the carbon particles coming from the added carbon, the background noise from the cement carbon (mainly in the form of carbonate) was manipulated and minimized in Figs. 9 and 10. The white dots in the carbon distribution picture are the activated carbon particles within the cement matrix. Carbon was detected with both magnifications ($100\times$ and $4000\times$). This reflects a wide size distribution of the carbon particles. It is concluded from Figs. 9 and 10 that activated carbon is compatible with the other constituents of the cement matrix, and that its distribution within the sample is fairly homogeneous. No aggregates or clusters of carbon are observed. This is favorable with respect to the mass transfer of organic pollutants to the carbon particles.

The silicon distribution is also shown in Figs. 9 and 10. The large clusters of silicon seen at $100\times$ are sand particles. The source for the rest of silicon is cement. A large amount of calcium is also observed all over the sample, except in regions occupied by sand particles. This is mainly due to the liberation of calcium hydroxide, occurring during the cement hydration process. It is expected, however, that most of the calcium hydroxide exist in a precipitated form, due to its low solubility at high pH. The soluble portion of the calcium ions was found not to affect the adsorption of phenol on the carbon, as mentioned earlier.

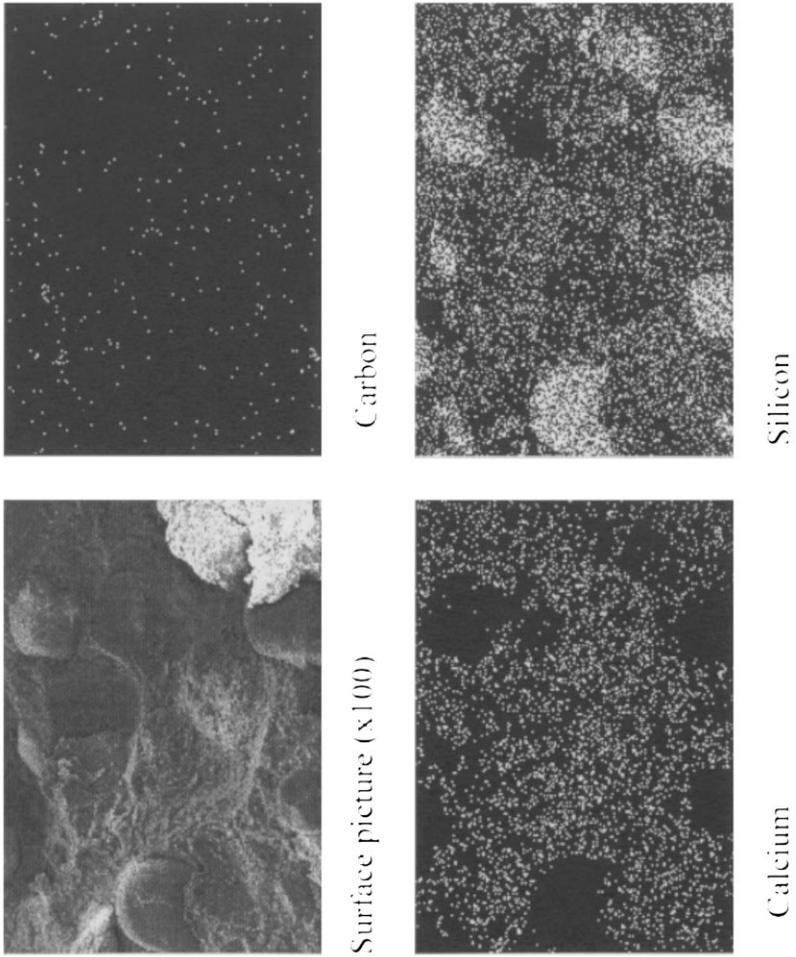
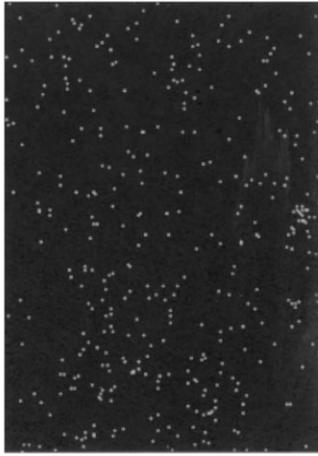
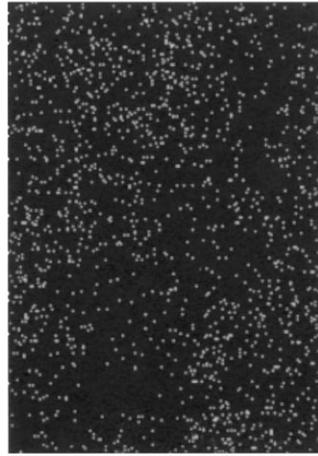


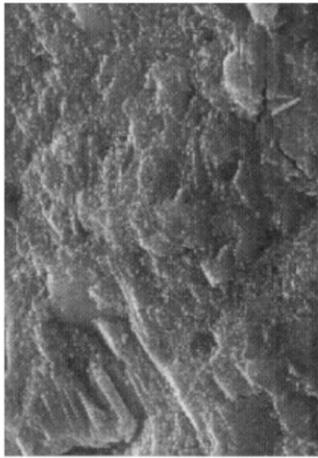
Fig. 9. X-ray mapping of solidified sample; 100× magnification.



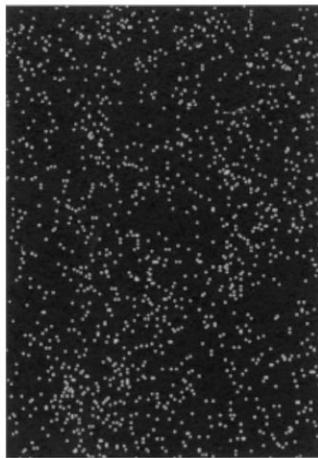
Carbon



Silicon



Surface picture (x4000)



Calcium

Fig. 10. X-ray mapping of solidified sample; 4000 × magnification.

4.6. Effect of added activated carbon on the hydration of cement

The indirect effect of added carbon on the hydration of cement was investigated using FT-IR vibrational spectroscopy. The results of this test are shown in Fig. 11 for a control sample (0% phenol and 0% carbon), two initial concentrations of phenol (1000 and 5000 mg l⁻¹) and two loadings of activated carbon (0% and 2% of dry sand weight). An anti-symmetric stretching ν_3 band centered at 990 cm⁻¹, an out-of-plane bending of ν_4 band centered at 520 cm⁻¹, and an in-plane-bending of ν_2 band centered at 460 cm⁻¹, all indicate the presence of an SiO₄⁴⁻ tetrahedral bonding in all samples. An SO₄²⁻ band located at 1113 cm⁻¹ and a carbonate band at 1420 cm⁻¹ were also observed. Lower intensities for the ν_3 , ν_4 , and ν_2 bands were observed as the concentration of phenol decreased. Shukla et al. [17] suggest that the diminution in the absorption around

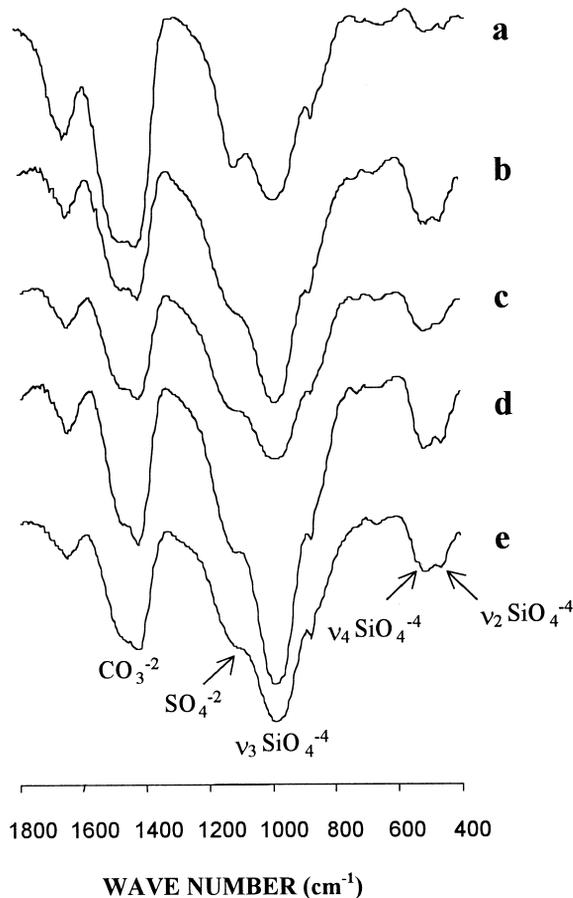


Fig. 11. FT-IR spectra of Portland type I cement: (a) control sample (0% phenol, 0% activated carbon), (b) 1000 mg l⁻¹ phenol and 0% activated carbon, (c) 1000 mg l⁻¹ phenol and 2% activated carbon, (d) 5000 mg l⁻¹ phenol and 0% activated carbon, (e) 5000 mg l⁻¹ phenol and 2% activated carbon.

800–1000 cm^{-1} is caused by the reaction of the clinker phases. It is also generally accepted [18,19] that the intensities of the bending modes ν_2 and ν_4 are dependent upon the degree of hydration in the OPC and that a high degree of polymerization lowers the intensity of these peaks. The existence of phenol will retard the hydration of cement as observed in this work and elsewhere [3].

The intensities of all peaks (ν_3 , ν_4 and ν_2 of SiO_4^{4-} bond) were lower in the cases with 2% activated carbon in the OPC than with 0% carbon, in both the 1000 and 5000 mg l^{-1} samples. This indicates that the added activated carbon adsorbs most of the phenol and consequently enhances the cement hydration. This is a significant advantage of adding activated carbon to the S/S mixtures. From Fig. 11, it is observed that the addition of carbon to the S/S mixtures decreases the intensities of the carbonate peak centered at 1420 cm^{-1} . This is evident by comparing spectra b and c with 0% and 2%, respectively, and likewise spectra d and e. However, with increasing concentrations of phenol, the carbonate peak intensity increases again. A similar trend was previously observed [20] in an S/S system, where the formation of amorphous $\text{Ca}(\text{OH})_2$ on the clinker phases increased with phenol concentration and decreased with added carbon, indicating that the mechanisms for the formation of CaCO_3 and $\text{Ca}(\text{OH})_2$ were closely linked. From this observation, it can be deduced that the enhanced polymerization of the silicate in the control sample is due to the carbonate reaction with C–S–H, while CH reacted preferably with the CO_2 in the phenol-containing samples [18].

5. Conclusions

Reactivated carbon has been shown to be a promising additive for S/S of phenol. This additive has both the capacity and kinetic characteristics that are economically desirable. The capacity of the virgin and the less expensive reactivated forms of the activated carbon were found to be comparable. Additionally, the capacity of the reactivated carbon was not influenced by the calcium hydroxide present. Consequently, only a small quantity of reactivated carbon was found to be necessary to effectively immobilize the phenol. With regard to kinetic characteristics, in the powdered form, the reactivated carbon was found to rapidly adsorb phenol, which implies that a simple one-step mixing process for soil, cement and carbon can be used. It was also established that activated carbon encapsulated by cement effectively retained the phenol, minimizing the possibility of leaching of this component.

The results obtained with phenol are extremely encouraging and strongly suggest the utility of reactivated carbon as an additive for effective S/S of other organics.

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