Influence of soil components on adsorption–desorption of hazardous organics-development of low cost technology for reclamation of hazardous waste dumpsites

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Abstract

The waste disposal practices on land frequently lead to the deposition of hazardous waste at geologically/hydrogeologically unsuitable locations, resulting in surface and groundwater contamination. The movement of chemicals through soil is not only dependent on the physical, chemical and biological properties of the waste but also on the characteristics of the soil of the disposal site. In this paper the authors report their results on the influence of soil components on adsorption–desorption of certain industrially widely used hazardous organics like phenol, *p*-nitrophenol, 4-chloro-2-nitrophenol and 2,4-dichlorophenol on typical soils of Patancheru industrial area (Hyderabad, AP, India). The data on nature of organics, soil organic matters, clay, free iron and aluminum oxides of soils are known to influence the adsorption–desorption process are presented. There was reduction up to 67.5% (organic matter removed), 53.8% (clay removed) and 24.2% (iron and aluminum oxides removed) in the adsorption capacity of the soils when compared to untreated soils indicating the role played by these soil components in adsorption process. Desorption isotherms of soil adsorbed hazardous organics exhibited hysteresis at higher initial concentration indicating the degree of irreversibility of adsorption–desorption process. Mixed microbial cultures were developed which can degrade the hazardous organics to complete mineralisation by utilizing them as sole source of carbon and their corresponding biokinetic constants were evaluated. Preparation of dumpsites with suitable soil surface having high holding capacity for organics and their in situ biodegradation by mixing with specific microbial cultures can be exploited as a cost effective technology for reclamation of hazardous waste dumpsites.
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1. Introduction

Hazardous organic contaminants are frequently part of hazardous waste disposed on land and the study of waste-site interaction is the key to assess the fate of land-disposed hazardous waste. Adsorption of organics to soil directly or indirectly controls the fate of organics, including movement in soil, degradation (chemical or biological) and subsequent leaching to groundwater. A large volume of information concerning various aspects of adsorption is available [1–3]. On the other hand, much less attention has been paid to desorption as compared to adsorption. Plant uptake, biodegradation and transport largely depend on the adsorption–desorption equilibrium. Desorption of hazardous organic compound is also critical in determining the organic behavior in runoff stream, their mixing in watershed [4] and ground water pollution. Factors which influence the extent of adsorption of organics by soils are numerous and complicated. A typical soil environment represents solid, liquid and gaseous phases [5]. The solid phase includes minerals and organic matter which is responsible for adsorption and retaining the hazardous compounds where they can be degraded, the liquid phase constitutes water, dissolved salts and gases like nitro-

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gen, oxygen, carbon dioxide constitute the gaseous phase. It has been observed that the adsorption potential depends mainly on the content of the organic matter, clay, inorganic crystalline and amorphous oxides of Fe, Al, Si in soils apart from other physico-chemical properties like pH, texture and cation exchange capacity. Contaminants which are sorbed tend to be held against leaching and the higher the adsorption potential for a soil, the lower the risk of ground water contamination [6]. Different sorbent materials are also being proposed for controlled release formulations to minimize the impact of hazardous chemicals released in soils [7,8].

The extensive use of phenol and its derivatives in industrial processes over the past decades has led to widespread pollution of the environment by these toxic compounds [9,10]. The total hazardous waste generation in Andhra Pradesh (India) is estimated as 6884 TPM (tons per month) out of which around 190.3 TPM constitutes phenolic wastes disposed mainly by petrochemicals, pharmaceuticals and polymer industries [11]. Phenol concentrations ranging from several hundreds to 10,000 mg/l have been reported in industrial wastewaters [12]. It is obvious that without proper treatment, industrial wastewaters and hazardous wastes are an important source of anthropogenic phenols, which contribute to water and soil pollution. Biological treatment processes are playing an increasingly important role in pollution prevention and hazardous waste-site remediation projects. Bioremediation is the productive use of microbial cultures to remove or detoxify contaminants that have found their way into the environment [13]. Degradation of the hazardous compounds is the result of the activities of the indigenous microbial populations present in the soil. There are three principally different routes [14] that result in bacteria (or other microbes) capable of degradation of a certain compound or group of compounds at a certain site:

1. The indigenous microflora has been exposed to the organic contaminant, long enough for genetic evolution to create a capacity to degrade the contaminant. This type of evolution takes place constantly but is relatively slow. As a consequence the microbial community possesses the degradative pathways, but may be inefficient because of low cell number or low activity level.
2. The indigenous microbial flora, which is adapted to the local conditions is exposed to a contaminating organic compound. The bacteria acquire genes and degradative pathways from bacterial cells immigrating from elsewhere. Transfer of genetic material can take place through conjugation, transduction or transformation.
3. The above evolution is also relatively slow but can be enhanced by supplying gene clusters. If no natural gene clusters are available, these may be constructed. Laboratory strains can be used as donors, either to transfer the capacity to 'wild type' strains newly isolated from the site or by introducing the donors into the site and letting gene transfer to occur.

Biological treatment using microbial cultures has been studied by several researchers [15–19] where the results showed a good removal efficiency of hazardous organics. Humic soils provide a suitable habitat for a wide range of organisms and by enriching the soils with suitable mixed culture systems the hazardous organics can be degraded to complete mineralisation which can be exploited as a cost effective technology for reclamation of hazardous waste dumpsites and polluted ground waters. The results of our investigations on these aspects are presented in this paper.

2. Methods

2.1. Soils

Samples were collected from the top 15–20 cm of the soil. A V-shaped hole was dug and sliced from the three sides and this sample was placed in a bucket. This core represented an individual sample and 15 such individual samples following a random sampling pattern were collected and a composite sample was made by mixing the 15 samples, which was representative of the entire area selected.

In a similar way soils were collected from three different areas namely Muttangi, Isnapur and Bolarum of the Patancheru industrial area of Hyderabad (AP, India).

After collection of the soil samples, the lumps were broken and stones removed. The soil was completely mixed and stored in polythene bags and brought to the laboratory for analysis. The soils were air-dried under shade, sieved through 2 mm sieve and used for the studies.

2.2. Equipment

ECIL/GS 5703 UV–vis Spectrophotometer was used for the spectrometric analysis and ICP-MS was used for heavy metal analyses.

2.3. Reagents

Analytical grade chemicals were used for the preparation of the standards and reagents. Spectroscopic grade chemicals and solvents were used for instrumental analysis. All the standards, reagent solutions and samples were stored in polyethylene containers previously cleaned with 4 M HNO_3 and rinsed with deionised water.

2.4. Characterization of the soils

Four replicates of each of the sieved soil samples were characterized according to different parameters: pH, electrical conductivity, cation exchange capacity, iron and aluminum oxides, mechanical composition, chlorides, sulphates, total nitrogen and total phosphorous. These parameters were determined by standard analytical methods

[20]. The quantity of the various macro elements was ascertained by atomic absorption in the case of calcium and magnesium and atomic emission in the case of sodium and potassium.

2.5. Concentration of elements

The pseudo-total concentration of the metals was estimated after digestion of the samples with aqua regia [21,22]. Five grams of soil was weighed into a 500 ml round-bottomed flask and 7.5 ml concentrated HCl and 2.5 ml concentrated HNO_3 per gram of dry matter were added. The attack was allowed to proceed for 16 h at room temperature and then for 2 h in open reflux condition at 180 °C. After digestion the solution was filtered into a 100 ml flask and the filter paper and residue were rinsed several times with several ml of warm (50 °C) 2 M nitric acid, making the solution up to the mark with the same acid solution.

2.6. Soil treatment

2.6.1. Destruction of organic matter

Organic matter was destroyed using H_2O_2 (30%). To 50 g soil 100 ml of water was added followed by addition of 10 ml of H_2O_2. After effervescence ceased one more dose of H_2O_2 was added. This process was repeated until effervescence ceased once for all. The soil was later dried and preserved for adsorption studies.

2.6.2. Destruction of clay

The clay content was separated from the soils by using the International pipette method [23].

2.6.3. Removal of iron and aluminum oxides

The iron and aluminum oxides were removed by following the citrate–bicarbonate–dithionite (CBD) procedure [24]. The soil was dried and used for further studies.

2.7. Adsorption studies

The adsorption studies on whole soils, organic matter destroyed soils (H_2O_2 treated), clay separated soils (International pipette method) and CBD treated soils were carried out by equilibrating 3 g of soil with 50 ml of hazardous organic with concentration ranging from 5 mg/l to 50 mg/l in 1×10^{-2} M $CaCl_2$ at 37 ± 1 °C for 24 h. Identical soil blanks minus the organic compound were also maintained in every case. The suspensions were centrifuged at 5000 rpm for 15 min. A 10 ml aliquot of the supernatant was taken in a 250 ml, separating funnel and extracted with ethylacetate. The amount adsorbed was determined by analyzing the equilibrium concentration of organic compounds by measuring the absorbancy at their respective λ (max) and calculating the difference between final and initial concentration after correcting for soil blanks.

2.8. Desorption studies

Five grams of soil sample was taken and treated with 20 ml of the organic compounds (5–25 mg/l) in 0.01 M $CaCl_2$ [25]. After shaking for 24 h at 37 ± 1 °C the slurry was centrifuged and 5 ml of supernatant was taken out and its absorbency at respective λ (max) was measured. To the remaining slurry containing 15 ml solution and soil, 5 ml of $CaCl_2$ (0.01 M) was added again and incubated for 24 h and centrifuged to determine the equilibrium concentration. The process was repeated for 5 consequent days. Identical soil blanks were maintained simultaneously and the net absorbency of equilibrium concentration at each stage was obtained by subtraction of the absorbency of blanks.

2.9. Biodegradation studies

Five grams of soil was suspended in 50 ml of nutrient broth (Hi Media®) and incubated at 37 °C for 48 h. Five millilitres was then transferred from the incubated suspension into 50 ml of minimal medium [26] amended with different concentration ranges of phenolic compounds as the sole source of carbon. The flasks were then incubated at 37 °C till full enrichments were obtained. Aliquots were transferred every week from cultures to fresh medium. Subcultures were streaked on minimal salt agar plates containing phenolics as sole carbon and nitrogen source. Growth was determined by measuring the turbidity and the concentration of the phenolics was estimated in the extract by measuring the absorbance on UV spectrophotometer at their respective λ (max). To prove complete mineralisation of the hazardous organics in the culture fluid the bacterial cells were removed by centrifugation at 7000 rpm for 20 min [27]. The supernatant was extracted with ether, evaporated to dryness in a stream of air and the extract dissolved in methanol. Preparative thin layer chromatography (TLC) was prepared on pre-coated TLC plates with silica gel GF254. Chromatograms were developed in the solvent system, petroleum ether:ethyl acetate (9:1).

3. Results and discussion

3.1. Characterization of the soils and hazardous organics

Table 1 shows the different physicochemical parameters obtained during the characterization of the three types of soils. As can be seen soil B is having maximum organic matter, mineral oxide (Fe and Al) content and soil A has maximum clay content.
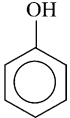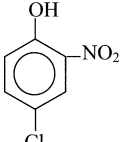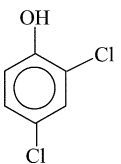
The characteristics of the hazardous organics selected for the present study are given in Table 2.

Table 1
Physicochemical analysis of 2 mm soils of Patancheru industrial area

Sampling area	Isnapur	Muttangi	Bolarum
Sample code	I	M	B
pH	7.6	7.5	7.7
Electrical conductivity (dS/m)	3.3	0.1	0.5
Cation exchange capacity ($cmol(P^+)/kg^{-1}$)	19.1	16.5	14.3
Iron oxides (%)	2.56	1.81	6.6
Aluminum oxides (%)	10.7	8.65	11.1
Permeability, C m/s (10^6)	4.23	6.81	6.71
Hydraulic conductivity, (10^{-4}) (C m/s)	4.1	6.7	6.6
Organic carbon (%)	1.5	0.93	2.4
Mechanical composition (%)			
Coarse sand	0.2	80.0	1.17
Fine sand	56.9	5.6	78.4
Silt	14.6	5.3	10
Clay	28.3	7	10
Texture	Loam	Sandy loam	Loamy sand
Chlorides (mg/g)	0.07	0.379	8.6
Sulphates (mg/g)	0.19	0.15	11.9
Calcium (mg/g)	0.327	0.8	0.3
Magnesium (mg/g)	0.002	0.469	0.021
Sodium (mg/g)	0.013	0.04	0.07
Potassium (mg/g)	0.0064	0.145	7.8
Nitrogen (mg/g)	0.005	0.056	0.9
Phosphorous (mg/g)	0.001	0.01	0.5
Barium (mg/kg)	120.6	0.1	0.5
Cobalt (mg/kg)	2.4	<dl	0.6
Chromium (kg/g)	3.3	<dl	1.9
Copper (mg/kg)	1.4	<dl	20.4
Manganese (mg/kg)	<dl	<dl	10.1
Lead (mg/kg)	34.6	<dl	5.24
Zinc (mg/kg)	21.2	0.1	7.3
Nickel (mg/kg)	3.0	<dl	<dl

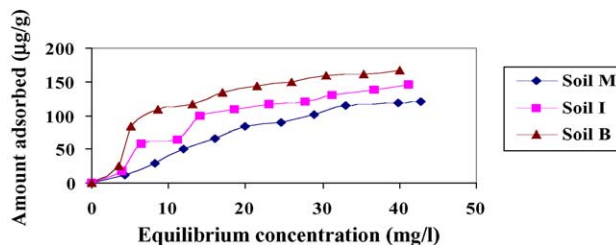<dl: Below detectable limit (<0.1 mg/kg)

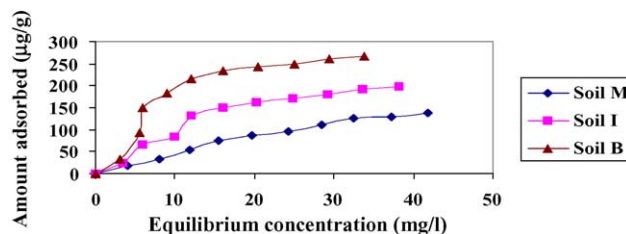Fig. 1. Adsorption isotherm of phenol on 2 mm soils.

Fig. 2. Adsorption isotherm of *p*-nitrophenol on 2 mm soils.

3.2. Adsorption studies

The adsorption isotherms for the three soils are presented in Figs. 1–4. Adsorption of the hazardous organics increased with the initial concentration of the organic compounds and this phenomenon is quite common in the adsorption studies [28]. The isotherms are of the S type according to the classifications by Giles et al. [29]. The S-shaped isotherms illustrate that the more organic compound is already adsorbed on the soil, the easier it is for additional molecules to become fixed, probably through hydrophobic interactions.

Table 2
Characteristics of the persistent hazardous organics selected for the study

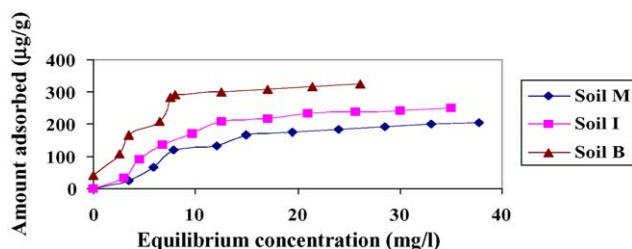| Hazardous organic	Structure	Molecular formula	Molecular weight	Melting point	λ(max) (nm)	Toxicity (LD_{50}) (Rat)
Phenol		C_6H_5OH	94.11	40.9	220.5	0.5–5 g/kg
p-Nitrophenol		$C_6H_5NO_3$	139.11	113	384	50–500 mg/kg
4-Chloro-2-nitrophenol		$C_6H_4Cl NO_3$	173.56	88	236	50–500 mg/kg
2,4-Dichlorophenol		$C_6H_4 Cl_2$	163	45	232.5	50–500 mg/kg

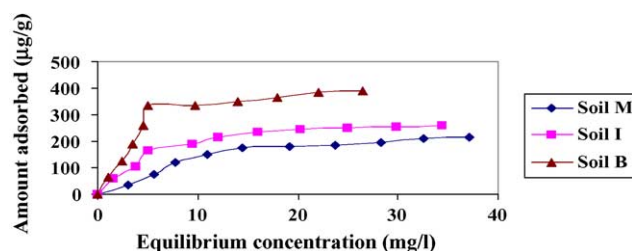Fig. 3. Adsorption isotherm of 4-chloro-2-nitrophenol on 2 mm soils.

Fig. 4. Adsorption isotherm of 2,4-dichlorophenol on 2 mm soils.

The adsorption data fit well to Freundlich equation: $Q_e = K_f C_e^{1/n}$ (Q_e = amount adsorbed per unit mass of adsorbent (mg/kg), C_e = equilibrium concentration (mg/l)) as evident from the values of correlation coefficient (R^2) that range from 0.74 to 0.97. The constant K_f is related to the strength of binding and depends on temperature and $1/n$ indicates the degree of linearity between solution equilibrium concentration and adsorption [30,31] and is usually less than one. Freundlich constants K_f and $1/n$ are determined from a logarithmic transformation of $\log Q_e = \log K_f + (1/n) \times \log C_e$.

2,4-Dichlorophenol and 4-chloro-2-nitrophenol exhibit high K_f values (Table 3) because of their high hydrophobicity (high K_{OW} and low solubility) compared to p-nitrophenol followed by phenol having low K_{OW} and high solubility. Compounds with high K_{OW} are considered relatively hydrophobic and tend to have large adsorption [32]. The adsorption coefficients showed correlation with the organic carbon present in the soils. Soil B showed the highest K_f valued due to high

Table 3
Freundlich constants for adsorption of the hazardous organics on 2 mm soils

Soil	Compound	Amount adsorbed, Q_e (μg/g)	K_f (μg/g)	$1/n$
M	Phenol	120	2.8	0.5
	p-Nitrophenol	138.3	3.5	1
	4-Chloro-2-nitrophenol	205	12.5	0.75
	2,4-Dichlorophenol	215	15.8	0.6
I	Phenol	145	6.3	0.8
	p-Nitrophenol	198.3	15.8	0.83
	4-Chloro-2-nitrophenol	250	31.6	1
	2,4-Dichlorophenol	260	46.2	0.9
B	Phenol	166.6	7.9	1
	p-Nitrophenol	268.3	35.4	0.9
	4-Chloro-2-nitrophenol	326.6	50.1	0.8
	2,4-Dichlorophenol	391.6	63	0.9

organic carbon content compared to other soils signifying the importance of organic carbon in adsorption of hazardous organics [33]. Thus soil containing more organic carbon can become an excellent sorbent for poorly soluble organic species. The values of $1/n$, which reflect the intensity of adsorption, were less than unity because only a small portion of the theoretically available soil surface is available for adsorption [34].

3.3. Effect of soil organic matter on adsorption of hazardous organics

The organic matter destroyed soils showed a significant reduction (67.5%) in their adsorption capacities when compared to untreated soils indicating that organic carbon plays an important role in the adsorption of these hazardous organics (Table 4). Several workers have carried out adsorption studies on soils and proved that the presence of organic matter in the soil was the most important factor affecting adsorption [35,36]. This indicates that the soil organic matter plays an important role in adsorption of hazardous organics hence affecting the bioavailability towards biodegradation.

3.4. Adsorption of hazardous organics on clay

Adsorption studies were conducted on clay destructed soils. The clay was separated from the soils ensuring that there was minimum destruction of the chemical nature by using the International pipette method. Adsorption of the hazardous organics was studied at two different concentrations via 5 mg/l and 25 mg/l on the three soils. The results indicated that there was variable decrease in adsorption with a maximum value of 53.8% on clay destructed soils showing the role played by clay in adsorption of hazardous organics (Table 5). The results were in accordance with those obtained by Hermosin and Cornejo [37,38] and Cox et al. [39,40] where the authors showed that clay fraction was responsible for sorption of many soil-applied pesticides.

3.5. Effect of free iron and aluminum oxides on adsorption

The presence of non-crystalline to poorly crystalline iron and aluminum oxides has been shown to be important in adsorption of hazardous organics [41,42]. These minerals are characterized by having pH dependent charges [43]. In the CBD treatment of soils due to reduction of iron(III) to iron(II) the cation exchange capacity increases, which help in increasing the sorption of ionic or highly polar compounds, while the levels of free iron and aluminum oxides decrease which result in decrease in the adsorption of non-ionic organics [44]. Hence, an attempt was made to study the effect of these soil substituents in the adsorption of hazardous organics. Free iron and aluminum oxides were destroyed using CBD procedure and the adsorption of phenol, p-nitrophenol, 4-chloro-2-nitrophenol, 2,4-dichlorophenol was studied at two different

Table 4
Effect of organic matter on adsorption of the hazardous organics

Soil	Compound	2 mm sieved soils				H$_2$O$_2$ treated soils				% reduction	
		5 ppm		25 ppm		5 ppm		25 ppm		5 ppm	25 ppm
		C_e	Q_e	C_e	Q_e	C_e	Q_e	C_e	Q_e		
M	Phenol	4.3	11.6	20	80.3	4.5	8.3	21.7	55	28.4	31.5
	p-Nitrophenol	4.0	16.6	19.7	88.3	4.3	11.6	21.5	58.3	30.1	33.9
	4-Chloro-2-nitrophenol	3.5	25	15	166.6	4	16.6	18.8	103.3	33	37.9
	2,4-Dichlorophenol	3.0	33.3	14.5	175	3.1	21.6	18.5	108.3	35.1	38.1
I	Phenol	4	16.6	18.5	108.3	4.4	10	21.2	63.3	39.7	41.5
	p-Nitrophenol	3.5	25	16	150	4.3	11.6	21	66.6	53	55
	4-Chloro-2-nitrophenol	3	33.3	12.5	208.3	4.1	15	19	100	45	51.9
	2,4-Dichlorophenol	1.5	58.3	12	216.6	3.4	26.6	19.6	90	54.3	58.4
B	Phenol	3.5	25	17	133.3	4.3	11.6	21.5	58.3	53.6	56
	p-Nitrophenol	3	33.3	12	216.6	4.2	13.3	20	83.3	60	61.5
	4-Chloro-2-nitrophenol	2.5	41.6	8	283.3	4	16.6	18.5	108.3	60	61.7
	2,4-Dichlorophenol	1	66.6	5	333.3	3.6	23.3	18.5	108.3	65	67.5

C_e: equilibrium concentration (mg/l), Q_e: amount adsorbed (μg/g).

Table 5
Effect of clay on adsorption of the hazardous organics

Soil	Compound	2 mm sieved soils				Clay destructed soils				% reduction	
		5 ppm		25 ppm		5 ppm		25 ppm		5 ppm	25 ppm
		C_e	Q_e	C_e	Q_e	C_e	Q_e	C_e	Q_e		
M	Phenol	4.3	11.6	20	80.3	4.5	8.33	21.6	56.6	28.4	29.5
	p-Nitrophenol	4.0	16.6	19.7	88.3	4.2	13.3	21	66.6	19.8	24.5
	4-Chloro-2-nitrophenol	3.5	25	15	166.6	3.8	20	17.5	125	20	24.9
	2,4-Dichlorophenol	3.0	33.3	14.5	175	3.5	25	18	116.6	24.9	33.3
I	Phenol	4	16.6	18.5	108.3	4.4	10	21.2	63.3	39.7	41.5
	p-Nitrophenol	3.5	25	16	150	4.2	13.3	20.5	75	46.8	50
	4-Chloro-2-nitrophenol	3	33.3	12.5	208.3	3.9	18.3	19	100	45	51
	2,4-Dichlorophenol	1.5	58.3	12	216.6	3.1	31.66	19	100	45	53.8
B	Phenol	3.5	25	17	133.3	4	16.6	20	83.3	33.3	37.5
	p-Nitrophenol	3	33.3	12	216.6	3.6	23.3	17	133.3	30	38.4
	4-Chloro-2-nitrophenol	2.5	41.6	8	283.3	3.3	28.6	14.5	175	32	41.3
	2,4-Dichlorophenol	1	66.6	5	333.3	2.5	41.6	13.6	190	37.5	42.9

C_e: equilibrium concentration (mg/l), Q_e: amount adsorbed (μg/g).

Table 6
Effect of oxides of iron and aluminum on adsorption of hazardous organics

Soil	Compound	2 mm sieved soils				CBD treated soils				% reduction	
		5 ppm		25 ppm		5 ppm		25 ppm		5 ppm	25 ppm
		C_e	Q_e	C_e	Q_e	C_e	Q_e	C_e	Q_e		
M	Phenol	4.3	11.6	20	80.3	4.4	10	21.1	65	13.7	19
	p-Nitrophenol	4.0	16.6	19.7	88.3	4.2	13.3	20.8	70	19.8	20.7
	4-Chloro-2-nitrophenol	3.5	25	15	166.6	3.8	20	16.5	141.6	15	19.9
	2,4-Dichlorophenol	3.0	33.3	14.5	175	3.4	26.6	17	133.3	20.1	23
I	Phenol	4	16.6	18.5	108.3	4.1	15	19.3	95	9.6	12.2
	p-Nitrophenol	3.5	25	16	150	3.7	21.6	17.5	125	13.6	16.6
	4-Chloro-2-nitrophenol	3	33.3	12	208.3	3.2	30	14.5	175	9	15.9
	2,4-Dichlorophenol	1.5	58.3	12	216.6	2.1	48.3	14.5	175	17.1	19.2
B	Phenol	3.5	25	17	133.3	3.8	20	18.8	103.3	20	22.5
	p-Nitrophenol	3	33.3	12	216.6	3.4	26.6	15	166.6	20.1	23
	4-Chloro-2-nitrophenol	2.5	41.6	8	283.3	3	33.3	12	216.6	19.9	23.5
	2,4-Dichlorophenol	1	66.6	5	333.3	1.9	51.6	10	250	22.5	24.2

C_e: equilibrium concentration (mg/l), Q_e: amount adsorbed (μg/g).

Table 7
Desorption data

Soil	Initial concentration	Cumulative percentage desorbed (%)			
		Phenol	*p*-Nitrophenol	4-Chloro-2-nitrophenol	2,4-Dichlorophenol
M	5 ppm	71.5	69.8	66.4	49.8
I		60.2	53.2	45	34.3
B		53.2	49.8	31.9	32.4
M	10 ppm	70.6	64.8	62.7	47
I		57.1	52.5	43.6	32.2
B		51.9	47.2	31.8	29.2
M	15 ppm	70	62.4	61.0	44.4
I		56.3	51.9	43.9	30.9
B		50.7	44.4	30.9	25.2
M	20 ppm	67	60	58.7	41
I		54.2	51.2	40.7	29.5
B		51.4	43.6	28.8	22.5
M	25 ppm	63.9	56	50	39
I		50.7	51	38.4	30.7
B		48.7	43	23.5	21

concentrations via 5 mg/l and 25 mg/l on the three soils. There was decrease in adsorption up to 24.2% on CBD treated soils showing the role of iron and aluminum oxides in adsorption (Table 6). The percentage reduction in adsorption in CBD treated soils over untreated soil was found to be highest in the soil B where iron and aluminum oxides percent was also the highest among the three soils taken for study. The decrease in percent of hazardous organics adsorbed by soils after removal of organic matter; iron and aluminum oxides indicated that both these soil constituents enhance the adsorption of the selected hazardous organics on soils. Similar results were obtained by He et al. [45], when sulphate adsorption was carried out on different soils. The results indicated that the sulphate adsorption on aluminum oxide was five times more than observed for kaolinite (clay) mineral.

3.6. Desorption of hazardous organics from soils

The desorption data for the hazardous organics are presented in Table 7. The desorption varied from 21% to 71.5% in the three soils. This variation may be due to heterogeneity involved in different soils with sorption sites that vary widely in type and energy of bonding. Further with increasing amount of adsorbed organics, not only the surface sites are occupied but also the hazardous organics may find its way into soil micro-pores caused by clay and structurally complex polymer network. Thus rediffusion of organics into soil solution becomes hindered due to porosity of the soil followed by the unfavorable energetic conditions.

Total desorption revealed that adsorption of the hazardous organics is almost irreversible. The effect is called hysteresis. The causes for hysteresis are not well understood. In some cases hysteresis may be partially due to degradation of the compound during equilibrium and also by physical and/or chemical properties of soil solution system. Similar observa-

tion were made by Zhang et al. [46] and Saltzman et al. [47]. This indicates that native soil organic matter and clay content play an important role in adsorption–desorption of hazardous organics from soil solution.

3.7. Biodegradation of hazardous organics

Mixed culture systems were developed from the soil M and were found to degrade phenol, *p*-nitrophenol, 4-chloro-2-nitrophenol and 2,4-dichlorophenol. These mixed cultures were able to utilize the respective organic compounds as sole source of carbon. This was inferred from the growth of mixed culture systems followed by increase in absorbency at 600 nm during the degradation of target hazardous organics followed by the decrease in absorbency at the respective λ (max) (Figs. 5–8). TLC data revealed complete disappear-
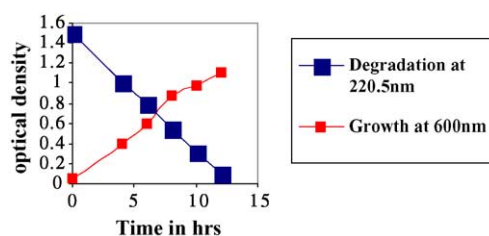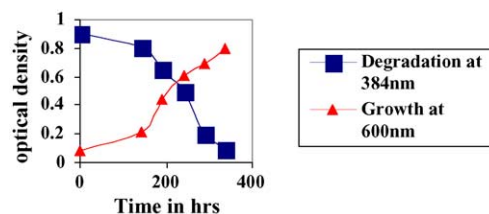
Fig. 5. Degradation of phenol.
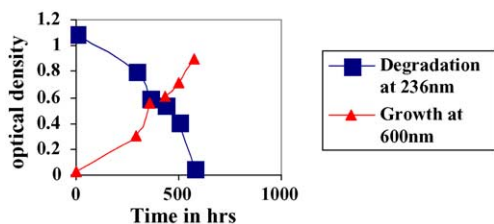
Fig. 6. Degradation of *p*-nitrophenol.

Fig. 7. Degradation of 4-chloro-2-nitrophenol.

Fig. 8. Degradation of 2,4-dichlorophenol.
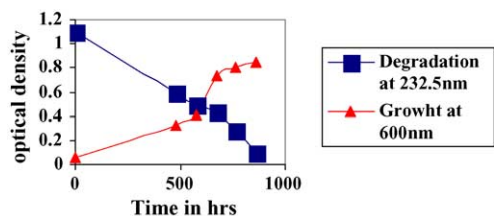
Table 8
Biokinetic constants

Compound	Time (h)	q_{max} (mg/g VSS/day)	K_s (mg/l)
Phenol	12	5.564	1496
p-Nitrophenol	336	4.184	153
4-Chloro-2-nitrophenol	576	2.767	42.45
2,4-Dichlorophenol	864	1.602	19.94

ance of the target spots after the degradation time indicating mineralisation of the substrate to carbon dioxide and water.

Using the Michelis–Menten $(q = q_{max} \ S/(K_s + S))$ relationship, the biokinetic constants like the maximum specific substrate utilization rate (q_{max}), Michelis–Menten inhibition constant (K_s) and the time required for complete degradation of hazardous organics were calculated (Table 8). In the present study phenol was readily degraded and the addition of substituents to phenol tended to inhibit biodegradation. The order of degradation for the hazardous organics was phenol > p-nitrophenol > 4-chloro-2-nitrophenol > 2,4-dichlorophenol. The dominant organism, which was capable of degradation was isolated and identified as *Pseudomonas*.

4. Conclusions

The present study clearly indicates that soil constituents like organic matter, clay, iron and aluminum oxides increase the adsorption capacity of soils thereby prevent the leaching of hazardous organics into the groundwater. Microorganisms capable of using phenolic compounds as the sole source of carbon and nitrogen were isolated from the soils and were examined for their ability to mineralize phenol, p-nitrophenol, 4-chloro-2-nitrophenol and 2,4-dichlorophenol. There are reports available on microorganisms degrading phenols [48–52] but the isolates used in the present study were able to degrade phenolic compounds having both chloro

and nitro groups. The ability of the isolated microorganism to utilize a wide variety of hazardous organic compounds makes it a good candidate for use in the biodegradation of hazardous waste dumpsites or industrial sludges containing these compounds.

Application of naturally occurring organic matter (humic substances identified as resins, waxes, fats, proteins, pigments, carbohydrates and polymeric organic acids) to the top soil of dumpsites can retard the movement of organic pollutants from the soil and enriching such soils with appropriate microbial cultures can result in degradation of the hazardous organics to complete mineralisation. This can be exploited as a cost effective technology for the reclamation of contaminated soils and ground waters.

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