ADSORPTION OF SOME TOXIC SUBSTANCES BY WASTE COMPONENTS

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(Received March 7, 1978)

Summary

The adsorption of cadmium, arsenate and trichloroethylene from solutions in 5,000 vpm aqueous acetic acid by polyethylene, textile, paper and lower greensand has been studied. Solutions were buffered to pH values of 5, 7 or 9 using sodium hydroxide and the adsorption process was found to be largely complete within 1 hour in most cases. The absorption of cadmium and arsenate conformed to a Langmuir isotherm with saturation concentrations in the adsorbant of several thousand ppm for cadmium and several hundred ppm for arsenate. The adsorption of trichloroethylene generally conformed to a linear Freundlich isotherm with a solution of adsorbant concentration ratio of ca. 1:10 for paper, ca. 1:55 for textile, and ca. 1:150 for polyethylene. The pH of the solutions had a pronounced effect on the adsorption of arsenate but only a relatively small effect on the adsorption of cadmium or trichloroethylene.

A number of experimental studies [1—4] have been carried out to assess the effects of leaching and adsorption on the concentrations of hazardous waste components likely to arise in leachates. In one of these [4] the adsorption of phenol, *p*-cresol and 2,6-xylenol by domestic waste was studied in some detail. The adsorption of these compounds proved to be largely reversible conforming to a Freundlich isotherm of the form:

$$C_s = KC^n \tag{1}$$

where C_s is the concentration in the solid substrate, C is the concentration in the leachate and K and n are constants. Values for K and n were determined respectively as 0.035 and 1.43 for phenol, 1.107 and 1.03 for *p*-cresol and 2.913 and 0.96 for 2,6-xylenol. These results indicated that adsorption by domestic waste is unlikely to play a major role in the removal of phenolic compounds from leachates, although it would tend to delay the arrival of high concentrations of phenols at the base of the landfill. The experimental work described in this note sets out to examine the adsorption of an inorganic cation, an inorganic anion and a halogenated solvent by various components of domestic waste, and to assess the importance of leachate pH in controlling

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TABLE 1

Adsorption of cadmium

Substrate refuse component	pH	te (hours)	Q (w/w, ppm)	b (Langmuir)	Langmuir reversibility	K (Freundlich)	Limit C_s**	Freundlich reversibility
Polyethylene	5	1¼	6,500	0.0121	I	110	2,200	I
	7	1	8,000	0.0080	I	50	2,500	I
Textile	5	1¼	7,000	0.0127	P	100	2,000	P
	7	1	7,000	0.0140	P	80	2,300	I
Paper	5	2¾	8,500	0.0171	P	240	2,400	R
	7	4¼	8,500	0.0347	P	70	4,200	I
Lower Greensand	5	21	7,000	0.298	P	500	5,000	R
	7	4¾	(15,000)*	0.0739	I	500	5,000	I

Key: te   time for 90% of adsorption at 24 hours to be reached in equilibration experiments
Q saturation concentration for cadmium in substrate
b Langmuir parameter in $C_s = QbC/(1 + bC)$
K Freundlich constant for linear region $C_s = KC$
R Reversible adsorption observed
I Irreversible adsorption observed
P Partially reversible adsorption observed

* Q value not obtainable from isotherm data. Estimated value used to calculate b.
**Value of C_s at the end of the linear region for which K applies.

adsorption behaviour. The experimental results may then form a basis for more general comments on the capacity of wastes to attenuate the release of hazardous substances from landfill by adsorping them from leachates.

The substances selected for study were cadmium (inorganic cation), arsenate (inorganic anion) and trichloroethylene (halogenated solvent). Unprinted newspaper, 50/50 Dacron/cotton sheet and 1.6 mm thick polyethylene sheet, all in the form of 5 cm squares, were used as representative waste components. Lower Greensand from Uffington, Oxon. was also included to give data for the inorganic ions which could be compared with the results from lysimeter experiments [5]. An aqueous solution containing 5,000 vpm acetic acid was used as a simple leachate model and this was buffered to pH values of 3, 7 or 9 using sodium hydroxide. The time required to establish adsorption equilibrium was determined by contacting a 200 ml aliquot of solution containing 1,000 mg/l of the test substance with 10 g of the substrate (refuse component) at 30°C. The concentration of the test substance was then monitored as a function of time by withdrawing aliquots for analysis*.

Adsorption and desorption isotherms were measured at 30°C using the following procedure to determine points on the isotherm. A 100 ml aliquot of solution containing a measured concentration of the test substance was left for 24 h at 30°C to equilibrate with a 10 g sample of substrate. After this time the free liquid was decanted, submitted for analysis and replaced with an equal volume of uncontaminated 5,000 vpm acetic acid solution at the appropriate pH. After a further 24 h at 30°C the concentration of the test substance in solution was determined by analysis. The concentrations in the substrate were calculated by a mass balance method.

The data obtained for the adsorption of cadmium ions are summarised in Table 1. Generally the adsorption process approached equilibrium within a few hours and, at low values of C_s conformed reasonably well with a linear Freundlich isotherm of the form:

$$C_s = KC \tag{2}$$

However, the full adsorption process could only be described adequately by a Langmuir adsorption isotherm of the form:

$$C_s = QbC/(1 + bC) \tag{3}$$

where b is a constant related to the binding energy of solute to substrate and Q is the ultimate adsorption capacity of substrate for solute (i.e. the maximum value attained by C_s). The precipitation of cadmium hydroxide precluded isotherm measurements at pH 9, although it was noted that the buffering capacity of paper for solutions of this pH effected some solubilisation of cadmium from the hydroxide floc over a period of hours. The adsorption

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*Trichloroethylene was determined by gas chromatography, care being taken to avoid evaporative losses during handling. Cadmium and arsenic analyses were carried out by Analytical Services Section, Chemical Analysis Group, Environmental and Medical Sciences Division, Harwell Laboratory.

process appeared to be largely irreversible and the desorption data did not give a good fit to either Freundlich or Langmuir isotherms. Values of Q were generally in the range 6,500 to 8,500 ppm (w/w) except for Lower Greensand which proved to be an extremely effective adsorbant for cadmium at pH 7. There were no major differences between the adsorption properties of the refuse components, although paper was a better adsorbant than polyethylene or textile. Slightly higher adsorption was found at pH 7 than pH 5, but with the exception of sand, no large differences were apparent between the two pH conditions other than changes in the extent to which the adsorption process was reversible.

The data obtained for arsenic adsorption are summarised in Table 2. The times taken for the adsorption to approach equilibrium were highly variable but generally less than 20 hours. The isotherms obtained did not conform to a linear Freundlich isotherm eqn. 2 over any significant concentration range but were reasonably well described by the Langmuir eqn. 3. Taken overall paper and sand appeared to be the best adsorbants for arsenate although the reversibility of adsorption increased at higher pH. Adsorption of arsenate by polyethylene and textile was highly pH dependant with the process being

TABLE 2

Adsorption of arsenate

Substrate refuse component	pH	te (hours)	Q (w/w, ppm, arsenic)	b (Langmuir)	Langmuir reversibility
Polyethylene	5	¼	150	0.234	I
	7	ca. 15	90	0.100	P
	9	ca. 19	25	0.0408	P
Textile	5	¾	160	0.0537	P
	7	ca. 11	130	0.0889	P
	9	4	80	0.0333	R
Paper	5	1½	(300)*	0.0374	P
	7	3½	220	0.0045	R
	9	ca. 3	(500)*	0.0156	R
Lower Greensand	5	ca. 12½	(300)*	0.108	I
	7	6½	230	1.660	P
	9	2	(500)*	0.0390	P

Key: te time for 90% of 24 hour adsorption to be reached
 Q saturation concentration for arsenate (as arsenic) in substrate
 b Langmuir parameter in $C_s = Qbc/(1 + bc)$
 K, n Freundlich parameters in $C_s = KC^n$
 R Reversible adsorption observed
 I Irreversible adsorption observed
 P Partially reversible adsorption observed
*Estimated value used to calculate b.

slightly more reversible in the case of textile. At higher pH the extent of adsorption by these two materials decreased markedly indicating that adsorption as H_3AsO_4 or $H_2AsO_4^-$ was preferred over adsorption of $HAsO_4^{2-}$ or AsO_4^{3-} ions which predominate in solution [6] at pH 9. This is clearly reflected in the Q values for polyethylene and textile and the b values for polyethylene.

The adsorption of trichloroethylene by refuse components proved to be the simplest to describe and the experimental results are summarised in Table 3. The adsorption process generally approached equilibrium within a few hours, was at least partially reversible and, with one exception, conformed well with a linear Freundlich isotherm eqn. 2. The extent of adsorption varied slightly with pH, larger K_A values being found at higher pH for polyethylene and textile. Values of K_A for polyethylene were 2 to 5 times higher than for textile and some 8 to 20 times higher than for paper. The saturation concentration

TABLE 3

Adsorption of trichloroethylene

Substrate refuse component	pH	te (hours)	K_A			K_D			Freundlich reversibility
Polyethylene	5	3	116			214			P
	7	2½	153			153			R
	9	2½	174			174			R
Textile	5	ca. 12	37			60			P
	7	2	57.5			86.5			P
	9	5	66.5			98.5			P
Paper	5	2¼	14.5			14.5			R
	7	1¼	7.5			7.5			R
	9	4¼	Non-linear relationship as follows:						P
Paper C (v/v, ppm)	9	Adsorption	C	18	125	190			
			C_s	629	2,574	8,151			
C_s (v/w, ppm)	9	Desorption	C	14	65	87			
			C_s	369	1,465	7,145			

Key: te   time for 90% of 6 hour adsorption to be reached, or 90% of 20 hour adsorption if at pH 5

K_A Freundlich constant for adsorption line $C_s = K_A C$

K_D Freundlich constant for desorption line $C_s = K_D C$

R   Reversible adsorption observed

I   Irreversible adsorption observed

P   Partially reversible adsorption observed

for trichloroethylene in polyethylene appears to be in excess of 10,000 ppm
v/w, or 15,000 ppm w/w, while the saturation concentration in textile appears
to be in excess of 8,000—10,000 ppm v/w. The results with paper were more
variable and pH dependent. At pH 5 the saturation concentration appeared to
exceed 5,000 vpm, at pH 7 3,000 vpm and at pH 9 8,000 vpm.

The results of these experiments, taken as a whole, indicate that if the
contact times between leachates and refuse are only a few minutes, adsorption
processes may not occur to any appreciable extent. Provided contact times
of a day or more prevail, fairly full use of adsorption capacity is possible.
Cadmium appears to be adsorbed quite strongly by refuse components and
is only partially desorbed. The process is only slightly pH dependant with
better adsorption occurring at higher pH. The reverse appears to be true for
arsenate where more extensive adsorption occurs at lower pH. Compared to
cadmium the capacity of refuse components for adsorbing arsenate is rather
limited. Refuse components containing plastics have a significant adsorption
capacity for trichloroethylene.

Domestic waste is approximately half paper and cardboard by weight and
about 1/20th plastic items. On the basis of this study it would seem that
domestic waste has a significant and potentially useful capacity for adsorbing
and retaining heavy metal cations such as cadmium. However, it seems un-
likely to exhibit any useful adsorption capacity for anions such as arsenate.
The results obtained for the adsorption of cadmium and arsenate by Lower
Greensand are in accord with the observed retention of heavy metals, and
elution of anions, in the lysimeter experiment at Uffington [5]. The ad-
sorption capacity of domestic waste for halosolvents such as trichloroethylene
seems quite significant, and this property might prove useful in landfill
operations if the combination of evaporation and adsorption maintains
leachate halosolvent concentrations at acceptable levels [7].

Combining information on the bulk properties of domestic refuse and the
adsorption isotherms of waste components, it may prove possible to use a
chemical engineering approach to design a landfill as a packed bed absorber
for liquid wastes. Specification of leachate quality may then allow optimum
use of the site capacity for adsorbing and retaining the components of liquid
wastes.

Acknowledgement

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