

Use of Surface Modified Silica gel factory Waste for Removal of 2,4-D Pesticide from Agricultural Wastewater: A case study

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Received 16 Aug. 2011;

Revised 19 June 2012;

Accepted 26 June 2012

ABSTRACT: The silica gel waste (SGW), after its collection from a local factory (Kolkata, India) was modified with cationic surfactant and was utilized as an adsorbing media for the removal of 2,4-dichlorophenoxyacetic acid (2,4-D) from agricultural runoff of a tea garden. Characterization of base adsorbent and modified adsorbent was carried out. The efficacy of the adsorbent was evaluated through both batch and fixed bed mode. Kinetics and isotherm study were conducted and the parameters were compared with 2,4-D bearing distilled water samples. The values of diffusion coefficients were determined. Presence of electrolyte and solution pH was found to affect the performance of the adsorbent significantly. The removal efficiency of surfactant modified silica gel waste (MSGW) in case of wastewater was found to be lower than the 2,4-D bearing distilled water sample. The data of column run was analyzed using Logit model. Batch desorption study was carried out using ethanol and acetone. The studies revealed surfactant coated SGW to be an efficient adsorbing media for 2,4-D removal.

Key words: Adsorption, Herbicide, waste, Agricultural runoff

INTRODUCTION

The large-scale application of pesticides in agriculture field and forestry, fast growing of agrochemical industries worldwide and the domestic activity of controlling pastes cause various pesticides and herbicides entering into the surface and ground water resources (Ghaderi *et al.*, 2012). These render serious pesticide pollution in the water resources (Nasrabadi *et al.*, 2011; Mhadhbi and Boumaiza, 2012). The leaching runoff and industrial discharges are responsible for this contamination in surface water (Gupta *et al.*, 2006; Ahsan and DelValls, 2011; Assassi *et al.*, 2011). One of the widely used herbicides in the world is 2,4-dichlorophenoxyacetic acid (2,4-D). It is considered as moderately toxic and potentially carcinogenic (Chao *et al.*, 2008). Due to its low pKa value (2.73), it exists predominantly in anionic form which can badly affect the aquatic life and hamper the ecosystem and at the same time the poor biodegradability makes 2,4-D environmentally stable (Carter 2000). As a consequence, it has been frequently detected in water bodies in various regions of the world. The removal of pesticides from water has thus become

one of the major environmental concerns these days (Hammed *et al.*, 2009).

The various treatment technologies such as chemical oxidation (Chu *et al.*, 2004), photo-degradation (Topalov *et al.*, 2001; Kundu *et al.*, 2005), miceller flocculation (Poras and Talens, 1999), biological process (He and Wareham, 2009; Elefsiniotis and Li, 2008) and sorption techniques (Xi *et al.*, 2010, Salman and Hammed 2010; Hammed *et al.*, 2009; Chao *et al.*, 2009; Chao *et al.*, 2008; Gupta *et al.*, 2006; Goyné *et al.*, 2004; Aksu and Kebasakal; 2005 & 2004; Prado and Airodi, 2001; Alam *et al.*, 2000; Akcay and Yurdakoc, 2000) are available for removal of 2,4-D from water environment. Among these methods adsorption has been proven to be an effective and attractive mechanism (Hameed *et al.*, 2009; Aksu and Kebasakal, 2010). Recently, adsorption of 2,4-D has been carried out using various surfactant modified metal oxides because the use of surfactant bearing sludge (surfactant exhausted sorbent) has become one of the cost-effective alternatives for organic pollutant removal from wastewater (Xi *et al.*, 2010; Akcay and

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Yurdakoc, 2000). The ionic surfactants form monolayer or bilayer structures on the charged metal oxide surface depending on surfactant concentration (Somasundaran and Fuerstenau, 1966). The surfactant layers pose the ability to solubilize different organic molecules within its structure. Again, during the last decade, initiative has been taken by the many researchers to use the industrial wastes as an adsorbing media for wastewater treatment. Such use of waste would not only reduce its disposal problem but also would reduce the discharge of liquid waste in the environment. Therefore use of such waste as metal oxide would be useful. Silica gel is a material that is well known for its high thermal and chemical stability, good selectivity, swelling resistance, possibility of repeated use and economic viability (Donia *et al.*, 2009). So the waste generated from a silica gel factory could be used as metal oxide. Moreover, in a recent study carried out by the present authors, it was observed that the waste generated from a local silica gel factory was effective in adsorptive removal of the cationic surfactant from wastewater (Koner *et al.*, 2011). With this in view, the present study aims at further investigation of the potential of that waste, after its use as a sorbent for cationic surfactant (CS), for the removal of 2,4-D from real wastewater collected from an agricultural runoff of a tea garden.

MATERIALS & METHODS

Orange II (Hi-Media, India), cetyltrimethylammonium bromide (CTAB) (Hi-Media, India), technical grade 2,4-D (98% pure) (Merck, Germany) and chloroform (Merck, India) were used as received. All other chemicals used in this study were of high purity and used without further purification. All the chemicals were of analytical reagent grade. An electrical balance (CP 225D, Sartorius GMBH) was used for weighing. Digital pH meter (PB-11, Sartorius GMBH) was used for pH measurements. A spectrophotometer (UV 1800, Rayleigh, Beijing) was used for absorbance measurement. For SEM and EDX analysis, JEOLJSM5800 scanning electron microscope was used. The silica gel waste was supplied by local factory located at Kolkata, India. After receipt of the material it was thoroughly washed with tap water followed by distilled water to remove the foreign substances and dried at 100°C. It was then sieved and about 70% of the total material lied in the particle size between 150 and 300 µm and that was used for the study. The final material after its washing and sieving was measured to be around 65% of the collected waste. The silica gel waste (SGW) was then treated with CTAB, a representative of CS to form micelle like structure on their surfaces and thus surfactant-modified silica gel waste (SMSGW) was prepared. This material was then

for 2,4-D removal from water environment. Spectrophotometric method was used for the determination of CS in the concentration range 0-12 mg/l (Few and Ottewil, 1956). Orange II (0.4×10^{-3} M) chemically known as p-(β-naphthol-azo) benzene sulfonic acid as ion pairing agent with CS was used and chloroform was used as an extraction solvent from the solution and the same was taken for absorbance measurement at 485 nm wavelength. 2,4-D was quantified by spectrophotometric method in the concentration range of 0-35 mg/l at 230 nm wavelength. The real wastewater containing 2,4-D was collected from surface runoff of a tea garden situated in Jalpaiguri district, West Bengal, India. To control the weeds of the tea garden, 2,4-D herbicide is applied in the form of 2,4-D sodium salt (80% w/w) which is commercially known as SALIX salt. After application of SALIX salt in the garden, there was a heavy storm of duration 25 min and the runoff was collected from one of the field channels of the garden during the storm. The characteristics of the wastewater are presented in Table 1. The concentration of 2,4-D in the wastewater was measured to be 32.90 mg/l. After collection, the wastewater was passed through ordinary filter paper in order to remove the suspended particles and then it was taken for the study.

Table 1. Characteristics of real wastewater (agricultural runoff) collected from tea garden

Parameter	Values
2,4-D	32.9 mg/l
pH	8.5±0.1
Turbidity	213 NTU
Total dissolved solids	136 mg/l
Total suspended solids	256 mg/l
Conductivity	148.8 µS/cm
Total hardness	44 mg/l as CaCO ₃
COD	37 mg/l

The kinetic experiments were carried with a fixed SMSGW dose of 8 g/l at 30°C taking the wastewater and the same was compared using synthetic samples of 2,4-D prepared in distilled water at the same initial concentration and the samples were shaken in a mechanical shaker at an agitation speed of 150 rpm. The shaking time was varied from 0 to 30 min. The equilibrium time was found to be 20 min and was used for further studies. 2,4-D bearing real wastewater generally contains various dissolved salts which may interfere the performance of the adsorbent. Therefore, it is required to investigate the effect of various interfering substances on the 2,4-D removal process. Thus, experiments were carried out to see the effects of various electrolytes and dissolved salts like sodium

chloride, sodium sulphate, calcium chloride, magnesium sulphate (0.01N and 0.02N). Effect of pH (in the range 1.47 - 10.88) was also studied. For these studies the initial 2,4-D concentration spiked in distilled water was taken as 50 mg/l and the adsorbent dose was 10 g/l. The temperature and contact time and pH were 30°C, 20 min and 3.9±0.1 respectively. Batch desorption study was conducted using organic solvents. Four isotherm models, namely Freundlich, Langmuir, Temkin and Redlich-Peterson isotherm were also tested for their ability to describe the experimental results at the temperature of 30°C and the isotherm parameters obtained for wastewater were compared with distilled water spiked sample. Fixed bed column study was conducted using a column of 2.5 cm internal diameter and 100 cm length. The adsorbent was packed in the column between two layers of glass wool and the depth of bed was 20 cm. The study was conducted in the up flow mode with a volumetric flow rate 10 ml/min (~1.22 m³/m²/hr). The samples were collected at certain intervals and were analyzed for remaining 2,4-D concentration. In order to investigate the mechanism of solute adsorption onto the adsorbent, four kinetic models viz., first order reaction model (Benfield and Randall 1980) based on the solution concentration, pseudo-first order equation of Lagergren (1898) based on the solid capacity, second order reaction model based on the solution concentration (Benfield and Randall 1980) and pseudo-second order reaction model of Ho and McKay based on the solid phase sorption (Ho and McKay 1999) were analysed and a comparison of the best fit sorption mechanism was made. The linearized forms of different reaction models are shown below.

$$\text{First order: } \ln C_t = \ln C_o - k_1 t \quad (1)$$

$$\text{Pseudo first order: } \frac{dq_t}{dt} = k_{s1} (q_e - q_t) \quad (2)$$

$$\text{Second order: } \frac{1}{C_t} - \frac{1}{C_o} = k_2 t \quad (3)$$

$$\text{Pseudo second order: } \frac{t}{q_t} = \frac{1}{k_{s2} q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where,

C_t = solute concentration at any time t

C_o = solute concentration at time $t=0$

q_t = amount of solute adsorbed per unit weight of adsorbent at any time t

q_e = amount of solute adsorbed per unit weight of adsorbent at equilibrium

k_1 = first order reaction rate constant

k_{s1} = pseudo-first order reaction rate constant

k_2 = second order reaction rate constant

k_{s2} = pseudo-second order reaction rate constant

The experimental reaction kinetic data were analysed using the above four kinetic model.

RESULTS & DISCUSSION

Before preparation of SMSGW, it is important to find the maximum adsorption capacity and the initial CS concentration at which it would occur. In the present study, CTAB was used as a representative of CS. Therefore, the adsorption isotherm study was carried out in the initial CTAB concentration range of 0-20000 mg/l. The adsorbent dose was kept fixed at 30 g/l. The contact time was taken as 30 min since this was the equilibrium contact time. The temperature and pH were 30^o C and 6.9±0.1 respectively. From this isotherm study, the maximum adsorption capacity was found to be 0.188 mmol/g (68.62 mg/g) and it occurred when initial concentration of CTAB was 7500 mg/l. This condition was used for the preparation of SMSGW. Therefore, 180 g SGW (at a dose of 30 g/l) was shaken for one hour with 6 litres of CTAB solution having concentration of 7500 mg/l. After shaking, the supernatant was discarded and the SGW was washed thoroughly initially with tap water and finally with distilled water and then dried at 60°C for 24 hours. Thus the SGW was converted to SMSGW.

The characterization of the base adsorbent was carried out after proper washing and sieving of the collected waste. Table 2 summarizes the different properties of the base adsorbent (SGW) and modified adsorbent (SMSGW) such as size, bulk density, pH point of zero charge (pH_{pzc}), BET surface area and pore volume. The surface morphology of the adsorbent was obtained from the Scanning Electron Microscopy (SEM) studies and the elemental composition from Energy Dispersive X-ray (EDX) analyses. The SEM photograph showed that the adsorbent particles are of ill defined shapes having irregular surfaces. It was also noted that after surfactant modification the surface of SGW became smooth (Fig. 1) and lowered the surface area. EDX analysis is a useful tool for identification of the kinds of elements contained in the solid specimen within short analysis period. The EDX analysis showed that the SGW contained 96% silica.

Kinetics studies were conducted to find out the equilibrium contact time for 2,4-D uptake from real wastewater as well as distilled water spiked sample by SMSGW. An adsorbent dose of 8 g/l and the shaking time ranging from 0 to 30 min was used to conduct the kinetic study. Fig. 2 shows the results of effect of

Table 2. Characteristics of SGW and SMSGW

Parameter	SGW	SMSGW
Particle size (μm)	150 - 300	150 - 300
Bulk density (g/cc)	0.615	0.624
pH_{pzc}	2	10.2
BET surface area (m^2/g)	264.6	194.4
Pore volume (ml/g)	0.66	0.38

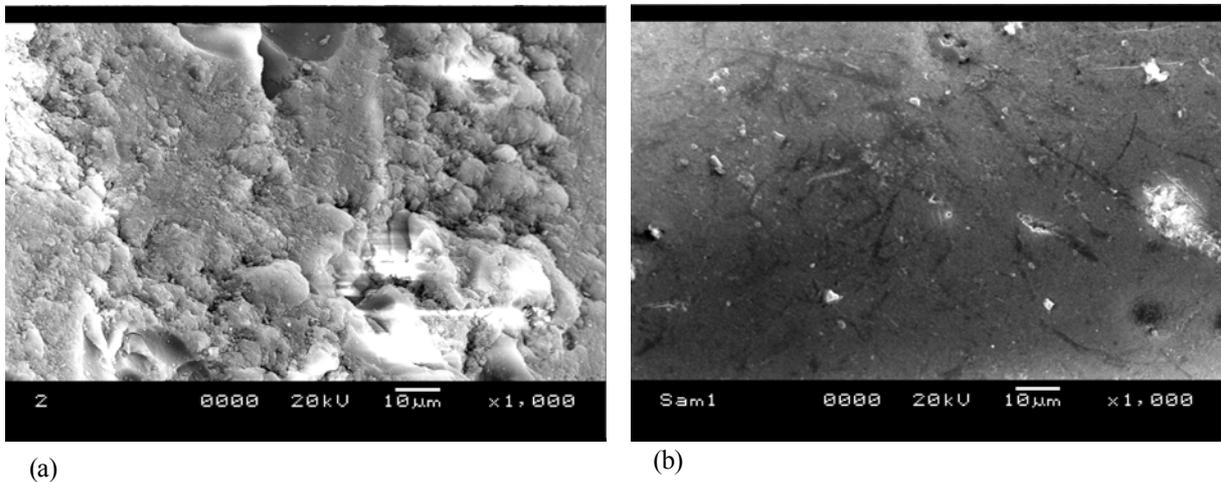


Fig. 1. SEM image of (a) SGW and (b) SMSGW

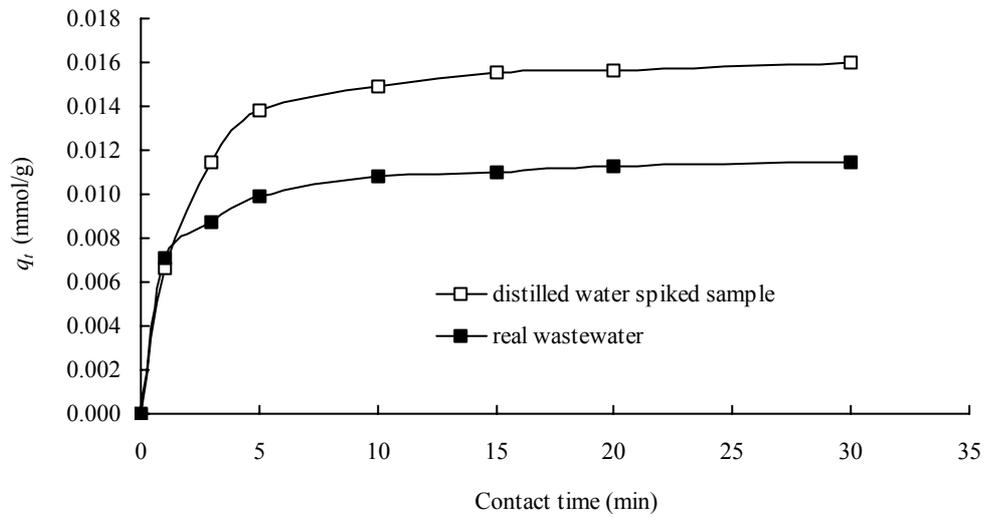


Fig. 2. Effect of contact time on 2,4-D uptake by SMSGW

contact time. The rate of adsorption is very rapid initially. From the figure it is shown that in 15 min the equilibrium reached. But a contact time of 20 min considered to be sure that full equilibrium was reached. Similar trend was also observed in case of 2,4-D-spiked in distilled water sample. But in case of distilled water spiked sample the removal efficiency was better than wastewater due to presence of various electrolytes and probably higher pH of the wastewater.

The equilibrium contact time, so found, indicated very quick reaction compare to other studies like 90 min (Gupta *et al.*, 2006), 450 min (Hameed *et al.*, 2009) and 7 days (Aksu and Kebasakal, 2004). The practical application of this adsorbent in continuous mode in the field will be easier since it would facilitate to reduce the reactor volume due to such lower value of equilibrium contact period.

The rate of sorption was determined by testing the four reaction kinetics models as described earlier. After analyzing the four models, it was found that the pseudo-second order model (Fig. 3) fitted best among all the models indicating the rate limit step to be chemisorption or chemical adsorption (Ho and McKay 1999). The equations, equilibrium uptake capacity, reaction rate constant and the determining coefficients

(R^2) of the pseudo-second order model are shown in Table 3. The value of reaction constant was found to be 0.4425 g/mg-min for real wastewater and 0.2067 g/mg-min distilled water spiked sample. The reaction constant, so found, could be used for the design of different types of batch reactors generally used in the field.

The diffusion coefficients for the present study were determined using first order reaction kinetics data. Assuming spherical geometry of the sorbents, the first order rate constant, K_1 obtained from first order kinetics profiles can be correlated to the pore diffusion and film diffusion coefficients (Helfferich, 1962).

$$t_{1/2} = 0.030 \frac{r_0^2}{D_p} \quad (5)$$

$$t_{1/2} = 0.23 \frac{r_0 \delta \bar{C}}{D_f C} \quad (6)$$

Where,

- t_{1/2} = half time
- r₀ = radius of adsorbent particle = 0.0225 cm
- D_p = pore diffusion coefficient (cm²/sec)
- D_f = film diffusion coefficient (cm²/sec)

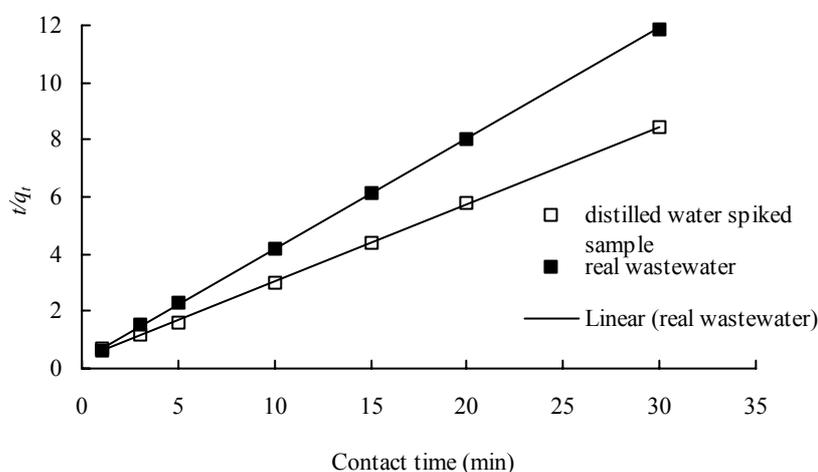


Fig. 3. Linear plot of pseudo-second order reaction kinetic model

Table 3. Equations and R^2 values of the linear fit lines of pseudo-second order reaction models for the removal of 2,4-D by SMSGW

Sample type	Equation of linear fit line	Reaction rate constant (g/mg ² min)	R^2
Real wastewater	$\frac{t}{q_t} = 0.3365 + 0.3854 t$	0.4425	0.9999
Distilled water spiked	$\frac{t}{q_t} = 0.3529 + 0.2701 t$	0.2067	0.9998

\bar{C} = concentration of adsorbate on the adsorbent = 27.68 mg/l

C = concentration of adsorbate in solution = 5.22 mg/l

δ = film thickness (cm)

$t_{1/2}$ can be calculated using the relation (Asher et al., 1990)

$$t_{1/2} = -\frac{[\ln(0.5)]}{K_1} \quad (7)$$

The value of K_1 in case of real wastewater was found to be 0.0225 min⁻¹. Using the value of K_1 , the values of $t_{1/2}$ were calculated and it was found to be 1848.39 sec. Assuming spherical geometry of the sorbents, $\delta = 0.001$ cm (Helfferich, 1962) and using calculated values of $t_{1/2}$ the film diffusion coefficients, D_f and pore diffusion coefficients, D_p for real wastewater were calculated and these were 1.48×10^{-8} cm²/sec and 8.21×10^{-9} cm²/sec respectively. Now according to Michelson (1975) for film diffusion to be the rate limiting step in sorption, the value of film diffusion coefficient (D_f) should be between 10^{-6} to 10^{-8} cm²/s, where as for pore diffusion to be rate limiting, the pore diffusion coefficient (D_p) should be in the range of 10^{-11} to 10^{-13} cm²/s. In the present study, the value of D_f was found to be near to 10^{-8} that indicated that there is also a possibility for the film diffusion to be the rate limiting step.

The effect of pH and electrolytes were studied taking initial 2,4-D concentration of 50 mg/l (spiked in distilled water sample). The adsorbent dose was 10 g/l. From the Fig. 4, it is shown that with increase of pH, the capacity of 2,4-D uptake by SMSGW decreased since at higher pH the surface of SMSGW ($pH_{pzc} = 10.2$) became more negative and therefore resulted

lower affinity of the adsorption of anionic 2,4-D molecules (Gupta et al., 2006; Chao et al., 2009; Hamed et al., 2009). But for the present case, as the desorption of CTAB from the surface of SMSGW occurred at lower pH, the adsorption of 2,4-D at lower pH also found to decrease (Koner et al., 2011). The result for effect of electrolytes is plotted in Fig. 5. There was a reduction in removal efficiency in presence of these salts. This was due to competition of coexistence of anions on positively charged surface. Chao et al. (2009) have studied that the negative effect of anions on 2,4-D removal was in the order of $SO_4^{2-} > Cl^-$. Similar result was obtained in this case also. It was also interesting to see that in presence of $CaCl_2$ and $MgSO_4$, the removal efficiency was slightly increased compare to the removal efficiency in presence of $NaCl$ and Na_2SO_4 respectively. This was probably due to presence of multivalent cations that increased the positive charge of SMSGW.

A proper contact between the adsorbate and adsorbent is necessary for any adsorption process. The concentration gradient at the adsorbent surface is maximum initially. However, with time adsorbate species start migrating to the adsorbent surface and concentration gradient starts decreasing. After some time concentration gradient becomes negligible and there is no net transfer onto the adsorbent. This establishes the dynamic equilibrium between adsorbate present in solid and liquid phase. The adsorption isotherm defines this equilibrium state. Several models have been developed to define the adsorption isotherm. Among them four widely used models such as Freundlich model (Freundlich 1906), Langmuir model (Langmuir 1918), Temkin model (Temkin and Pyzhev, 1940) and Redlich-Peterson model (Redlich and Peterson 1959) have been studied in the present study.

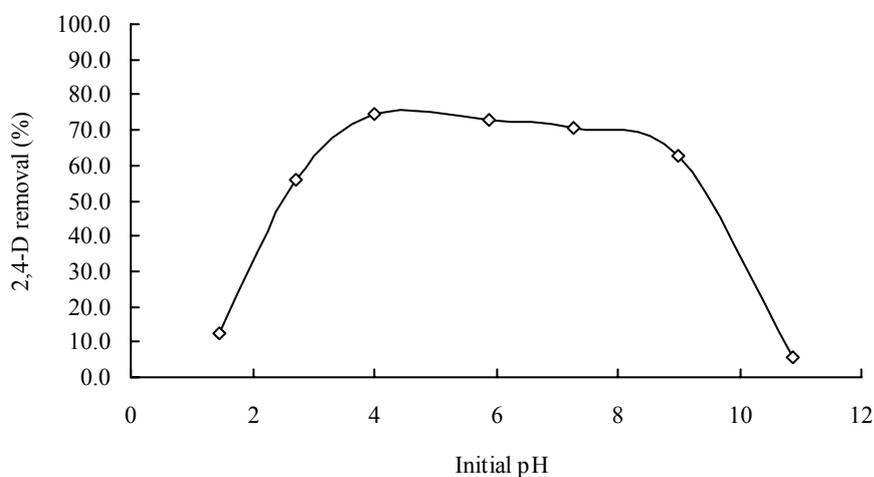


Fig. 4. Effect of initial pH on 2,4-D uptake by SMSGW

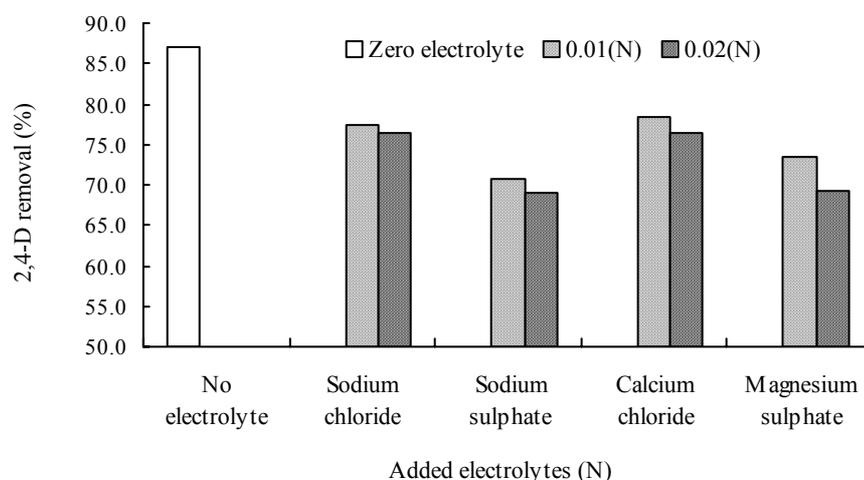


Fig. 5. Effect of electrolytes on 2,4-D uptake by SMSGW

The Freundlich equation is an empirical expression that encompasses the heterogeneity of the adsorbent surface and the exponential distribution of sites and their energies. The expression for Freundlich model is given in equation 8.

$$q_e = k_f C_e^{\frac{1}{n}} \quad (8)$$

Where,

k_f = Freundlich constant related to adsorption capacity

$\frac{1}{n}$ = adsorption intensity

q_e = amount of adsorbate on adsorbent at equilibrium (mg/g)

C_e = equilibrium concentration (mg/l)

The linear form of Freundlich isotherm model is represented below.

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (9)$$

Langmuir isotherm model is known as idealized monolayer model. The basic assumptions of Langmuir model (i) a fixed number of accessible sites having equal energy (homogenous surface) and (ii) reversibility of the adsorption process. When the rate of adsorption becomes equal to the rate of desorption of molecules from the surface, equilibrium is reached. Langmuir isotherm model may be expressed as

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (10)$$

Where,

q_m = maximum adsorption capacity (mg/g)

K_L = constant related to energy of the sorption system (l/mg)

The linearized form of the Langmuir isotherm model is presented below.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L} \frac{1}{C_e} \quad (11)$$

Temkin isotherm considered the effect of indirect adsorbate adsorbent interactions on adsorption. Temkin isotherm also represents the binding heterogeneity with a simple expression, which has predictive power over a wide range of concentration. Temkin isotherm can be represented as

$$q_e = \frac{RT}{b} \ln(K_T C_e) \quad (12)$$

Where, R is universal gas constant, T is absolute temperature (K) and b and K_T are models constants. It can be linearized as

$$q_e = B_1 \ln(K_T) + B_1 \ln(C_e) \quad (13)$$

Where, $B_1 = \frac{RT}{b}$ related to heat of adsorption and

K_T is the equilibrium binding energy constant (l/mg) corresponding to the maximum binding energy.

The Redlich-Peterson isotherm model incorporated three parameters and can be applied either in homogeneous and heterogeneous systems. Jossens et al. (1978) included the basic concepts of Freundlich and Langmuir isotherms to make a single equation and expressed as

$$q_e = \frac{K_R C_e}{1 + a_R C_e^\beta} \quad (14)$$

This equation can be linearized as

$$\ln\left(K_R \frac{C_e}{q_e} - 1\right) = \ln(a_R) + \beta \ln(C_e) \quad (15)$$

Where, K_R and a_R are the model constants and β is the exponent which has the value between 0 to 1. Depending on the value of exponent β either in Langmuir or Henry's law of isotherm. A trial and error optimization technique was adopted to solve the above equation using MATLAB. Table 4 represents the constants of the above four isotherm models for both wastewater and distilled water spiked samples respectively. From the R^2 values of determining coefficients (R^2) it is seen that Redlich-Peterson model fitted best in comparison to other models for the real wastewater. Similar result obtained in case distilled water spiked sample also. The maximum adsorption capacity obtained from Langmuir isotherm was 17.73 mg/g (0.08 mmol/g) at 30°C, which was found to be lower than the distilled water spiked sample (33.9 mg/g or 0.153 mmol/g). Such lower value of adsorption capacity and higher value of optimum adsorbent dose than distilled water spiked sample was due to the presence of dissolved salts in the wastewater. Moreover, the solubility of 2,4-D sodium salt (45000 mg/l at 25°C) in water is 50 times of 2,4-D acid (900 mg/l at 25°C). This higher solubility of the 2,4-D salt resulted lower affinity towards adsorption.

The capacity obtained for uptaking pesticides (for distilled water spiked sample) was found to be greater than other sorbents like dioctadecyl dimethylammonium bromide-modified polysagrite (Xi *et al.*, 2010), blast furnace sludge and dust (Gupta *et al.*, 2006), activated used tyres (Hamadi *et al.*, 2004), oil shale ash (Al-

Quodah *et al.*, 2007), bituminous shell (Ayar *et al.*, 2008), 3-trimethoxysilylpropylamine anchored silica gel (Prado and Airodi, 2001) and waste rubber granules (Alam *et al.*, 2000). Though this capacity was lower compare to carbonaceous adsorbents derived from date stone (Hameed *et al.*, 2009) and fertilizer waste (Gupta *et al.*, 2006), granular and powdered activated carbon (Salman and Hamed, 2010; Aksu and Kebasakal 2004 & 2005) and layered double hydroxides (Chao *et al.*, 2008; Chao *et al.*, 2009). The important part, however, in case of 2,4-D removal by SMSGW was the utilization of exhausted waste after removal of CS, which is known to be an environmental pollutant and resistant to biodegradation. The use of an industrial waste for CS removal and further use of exhausted waste for 2,4-D removal made the process not only cost-effective but also it caused waste minimization.

It is also very important to be mentioned that the uptake capacity of SMSGW could be increased, if the adsorption of CTAB on the surface of SGW was carried out in presence of electrolytes and with pH adjustment during the preparation of SMSGW, since the presence of electrolytes and higher pH was found to enhance the surfactant coverage on the surface of silica particles (Koner *et al.*, 2011). So in actual application in the field there is no possibility to achieve the adsorption capacity of SMSGW lower than the capacity obtained here. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L (Hall *et al.*, 1966), which is given by

$$R_L = \frac{1}{1 + C_o K_L} \quad (16)$$

Table 4. Isotherm constants for 2,4-D removal from real wastewater and distilled water spiked samples by SMSGW at 30°C

Freundlich constants				
Sample type	K_f [(mg/g)(l/mg) ^{1/n}]		1/n	R^2
Real wastewater	0.258		0.856	0.9780
Distilled water spiked	1.67		0.657	0.9629
Langmuir constants				
Sample type	q_m (mg/g)	K_L (l/mg)	R_L	R^2
Real wastewater	17.73 (0.08 mmol/g)	0.011	0.734	0.9797
Distilled water spiked	33.90 (0.153 mmol/g)	0.032	0.381	0.9767
Temkin constants				
Sample type	K_T (l/mg)		B_T	R^2
Real wastewater	0.228		2.231	0.9527
Distilled water spiked	0.518		5.306	0.9973
Redlich-Peterson constants				
Sample type	K_R (l/mg)	a_R	β	R^2
Real wastewater	0.416	0.751	0.2260	1.0000
Distilled water spiked	1.656	0.188	0.7460	1.0000

Where, C_0 is the initial concentration of 2,4-D (mg/l) and K_L (l/mg) is Langmuir constant. The value of R_L indicated nature of adsorption; irreversible ($R_L = 0$), favourable ($0 < R_L < 1$) and unfavourable ($R_L = 1$). The value of R_L (Table 4) indicated favourable adsorption. The breakthrough curve for 2,4-D using SMSGW for the column run is shown in Fig. 6. The breakthrough time (corresponding to $C/C_0 = 0.1$) and exhaust time (corresponding to $C/C_0 = 0.9$) were found to be 12 and 25 hours respectively. The corresponding volumes of treated wastewater were 7.2 and 15 l respectively. The properties of adsorption zone or mass transfer zone were calculated using the column data (Adak, 2006). Height of adsorption zone was found to be 16.45 cm and the rate of adsorption zone movement through the bed was 1.26 cm/h. The percentage of the total column saturated at breakthrough was found to be 42%.

The fixed bed column was designed by Logit method (Oulman 1980). The logit equation can be written as:

$$\ln \left[\frac{C/C_0}{1 - C/C_0} \right] = -\frac{KNX}{V} + KC_0t \quad (17)$$

- Where,
 C = Solute concentration at any time t
 C_0 = Initial solute concentration
 V = Approach velocity
 X = Bed depth
 K = Adsorption rate constant
 N = Adsorption capacity coefficient

Rearranging Eq. 17

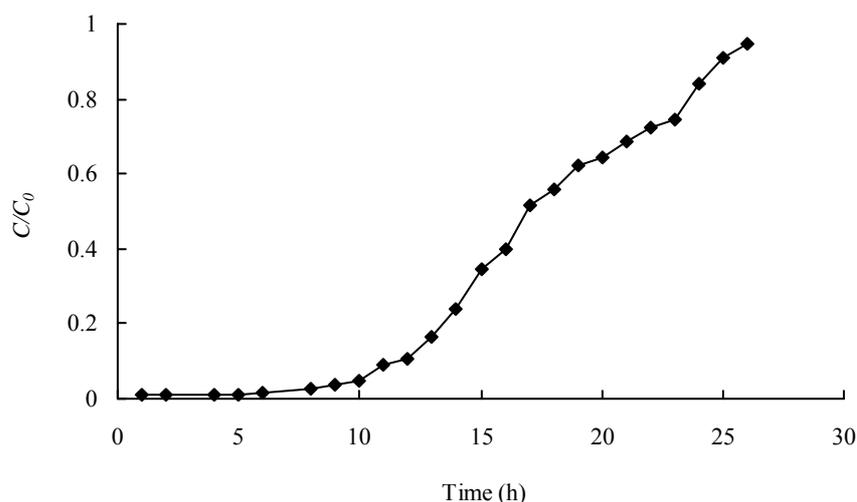


Fig. 6. Breakthrough curve for 2,4-D uptake from wastewater by SMSGW

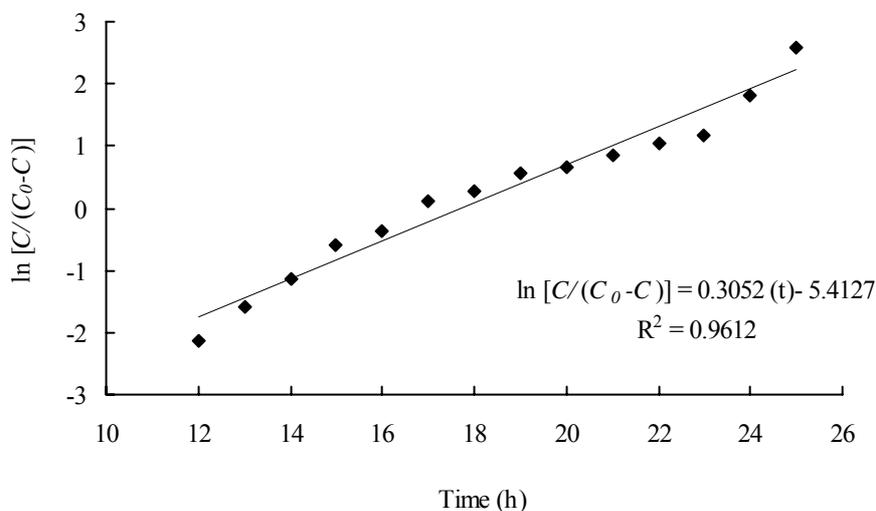


Fig. 7. Linearized form of Logit model

$$\ln\left[\frac{C}{C_o - C}\right] = -\frac{KNX}{V} + KC_o t \quad (18)$$

Plot of $\ln\left[\frac{C}{C_o - C}\right]$ vs. t gives a straight line with

slope KC_o and intercept $-\frac{KNX}{V}$ from which, value

of K and N could be calculated. Plot of vs. t is shown in Fig 7. The value of adsorption rate coefficient (K) and adsorption capacity coefficient (N) were obtained as 0.0095 l/mg.h and 3473 mg/l respectively. These values could be used for the design of adsorption columns.

2,4-D could be desorbed from exhausted SMSGW surface using ethanol and acetone. It was observed that in case of acetone and ethanol more than 80% and 75% desorption was achieved respectively. 10 g of exhausted SMSGW was taken in 50 ml of solvent (200 g/l) and then agitated at 150 rpm for 60 min at a temperature of 30 ± 2 C. The regenerated 2,4-D could be collected and reused. The organic solvent could be distilled off using a Soxhlet apparatus and the same solvent could be recycled for the same purpose.

CONCLUSION

SMSGW could effectively be used for the removal of 2,4-D from real wastewater. A very quick reaction was found to occur for the adsorption process. The removal efficiency and adsorption capacity was found to be lower for wastewater in comparison to distilled water. The uptake capacity of SMSGW decreased in presence of various electrolytes and at higher pH. Interestingly in a wide range of pH, the removal was not significantly affected. The value of diffusion coefficients indicated that the film diffusion might be the rate limiting step for real wastewater. The adsorption of 2,4-D followed the R-P isotherm model best compared to other isotherm models like Freundlich, Langmuir and Temkin isotherm model. The capacity obtained from Langmuir isotherm can be compared with many other adsorbents especially which are derived from industrial waste. Therefore, an industrial waste after its use for removal of surfactant could be reused for pesticide removal from water environment. Such effective use of a 'waste' made the process not only cost-effective but also environment-friendly.

ACKNOWLEDGEMENT

We are thankful to the SERC Division, Department of Science and Technology, New Delhi, India for the financial support for this work. We are also grateful to M/S Kalpataru Pvt. Ltd., Kolkata, India for supplying us the silica gel waste material and Mr. Alakesh Chandra Mandal of Indian Institute of Science, Bangalore, India for his kind help and valuable advice.

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