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EFFECT OF TEMPERATURE AND AGEING ON SEWAGE SLUDGE DECOMPOSITION, ORGANIC ACIDS TRANSFORMATION AND CADMIUM RELEASE

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Sewage sludge is being heaped in congested urban cities, and the safe disposal of this waste on to agricultural soils is becoming a serious environmental concern around the world. The present incubation study of 135 days duration aims at evaluating the effect of ageing and temperature on the release of cadmium (Cd) from the sewage sludge. The study was carried out at different temperatures (22 and 45°C) to estimate Cd availability and organic matter (OM) degradation in soils receiving sewage sludge at 0, 15 and 30 g kg^{-1} soil. Fourier Transform Infrared Spectroscopy (FTIR) analysis revealed that sludge addition and high temperature (45°C) caused obvious changes in fulvic acid spectra mainly at 1050-1250 cm^{-1} region. While humic acid spectra showed more humification and aromatic character with ageing, that are chemically and biologically more stable for Cd retention. Sequential extraction of Cd revealed a significant decrease in OM bound and reducible Cd fractions at the higher temperature (45°C). While residual and exchangeable Cd fractions increased with ageing, indicating that high temperature had a major influence on the availability and redistribution of different Cd forms. It is proposed that regular monitoring of sewage sludge amended soils is required for better assessment of Cd availability and OM contents in hot and dry regions.

Keywords: Humic acid, fulvic acid, incubation, spectroscopy, cadmium speciation.

INTRODUCTION

The insoluble solid residue left after wastewater treatment is referred as sewage sludge. Being economical and readily available, the best way of its disposal is through land application by considering its soil conditioning properties and beneficial effects on plant productivity (Murtaza *et al*., 2012). Sewage sludge is not only a rich source of OM, essential plant nutrients and microorganisms but also contains high concentration of potentially toxic heavy metals and organics, salts and pathogens depending upon the type and degree of treatment process. Consequently, there are various environmental as well as health risks associated with the soil-application of sewage sludge. Hence, a careful assessment of the characteristics of sewage sludge is required for its application on agricultural lands and in decreasing the public health risks (Guerrini *et al*., 2017).

Physical, chemical and physico-chemical characteristics of soil and sewage sludge derived OM primarily govern the mobility and bioavailability of heavy metals in soil environment. Despite documented importance of the OM, there are different views about the role of OM on metal mobility (McBride, 2003). Time bomb hypothesis states that when sewage sludge is applied, heavy metals availability is increased due to decomposition of labile and soluble humate complexes. But with ageing and OM stabilization, it results in recalcitrant humic and fulvic acid fractions which are responsible for metal retention inducing plateau response (Bolan *et al*., 2014).

Temperature exerts a strong impact on OM transformation as it enhances metal mobility, translocation and results in uptake by plants (Hooda and Alloway, 1993). However, the role of different ambient temperatures in the availability of heavy metals has not been widely documented, as sewage sludge derived humic and fulvic acids could precipitate with metals by forming outer/inner-sphere complexes (Antoniadis and Alloway, 2001).

Humic and fulvic acids induce changes in metal speciation through the formation of soluble and stable metal-humate complexes and consequently affect the bioavailability of metals including Cd. Muscolo *et al*. (2006) also specified that activities of humic substances were due to their varied chemical composition. So studying the structural differences of humic and fulvic acids through FTIR would enable us to understand the variation of their biological activities (Wu *et al*., 2016).

Cadmium is a major concern for human, animals and microbial activities due to its toxicity even at very low concentration (Huang *et al*., 2017). Compared to other trace metals, Cd is mostly found in soluble and exchangeable fraction due to its adsorption on labile humate complexes. More specifically, the bioavailability of Cd and its interaction with humic and fulvic acids contents of sewage sludge has not been widely studied (Murtaza *et al*., 2015). Accordingly, the present study was carried out to evaluate the effect of temperature on sewage sludge derived Cd via the transformation of humic and fulvic acids.

MATERIALS AND METHODS

The soil used in this study was collected from the farm area of University of Agriculture, Faisalabad (UAF), Pakistan (latitude 31.4181, longitude 73.0778). Aerobically processed sewage sludge was collected from I-9 sector wastewater treatment plant at Islamabad, Pakistan. The selected initial properties of soil and sewage sludge used in the experiment are presented in Table 1, while Cd fractions in soil and sludge samples are given in Table 2.

Table 1. Chemical properties of soil and sewage sludge at the start of experiment.

Parameter	Unit	Soil	Sewage sludge
Texture	-	Sandy loam	-
Saturation	%	31.13	
pH_s	-	7.10	7.40
EC_e	$dS\ m^{-1}$	2.09	4.40
SAR	$(mmol\ L^{-1})^{1/2}$	10.20	-
CEC	$cmol_c\ kg^{-1}$	8.40	59.10
Total K	$mg\ kg^{-1}$	110.00	240.00
Total N	%	0.07	0.49
Total P	$mg\ kg^{-1}$	9.50	2400.00
OC[a]	%	0.84	31.60
Humic acid[a]	$mg\ g^{-1}$	-	14.30
Fulvic acid[a]	"	-	6.50
Total metal			
Cd	$mg\ kg^{-1}$	0.39	5.13
Pb	"	4.87	74.85
Ni	"	2.23	53.30
Zn	"	51.40	182.50
Fe	"	1642.00	9567.00
Mn	"	161.00	341.00

[a]Calculated on OC (%) dry wt. basis

For incubation, 200 g soil was taken in plastic pots. Sewage sludge was applied at three rates (0, 15 and 30 g kg^{-1} soil) which is equivalent to 0, 15 and 30 Mg ha^{-1} soil (for 10 cm of upper soil layer). Two ambient temperatures (22 and 45°C) were maintained at 50% of water holding capacity (WHC) of soil through out the experiment. Pots were placed at 22°C in growth chamber located at Centre of Agricultural Biochemistry and Biotechnology (CABB), UAF and to achieve 45°C temperature; samples were placed in incubator located at Ayub Agricultural Research Institute (AARI), Faisalabad. Distilled water was added daily by weighing to maintain 50% WHC during the whole study period for 135 days. Treatments were replicated thrice and arranged in a three factor-factorial under completely randomized design (CRD). Soil samples were taken after 0, 45, 90 and 135 days for Cd speciation and to see OM transformations.

Extraction of humic and fulvic acids: Each time 30 g of soil sample was treated three times with distilled water to extract non-humic substances. Each sample was then extracted with 300 mL of 0.1 *M* NaOH solution to separate humic substances (Senesi et al., 1996). Extraction was repeated until a clear supernatant was obtained after centrifugation at 4000 rpm for 15 min and filtered through Whatman paper (125 mm). Humic acid was then precipitated out of the extracted solution with 1.5 *M* H_2SO_4 for 24 h at 4°C. The precipitated humic acid was separated from fulvic acid by centrifugation (10000 rpm for 20 min). The separated precipitates of humic acid were dissolved in 0.1 *M* NaOH. The separated samples of humic and fulvic acids were freeze-dried and stored for FTIR analysis. The contents of humic and fulvic acids were determined by $KMnO_4$ oxidation method (Amir et al., 2004).

FTIR analysis: The instrument used for determining infrared spectra was Perkin Elmer 1600 FTIR Spectrophotometer covering a wave range of 600-4000 cm^{-1} @ 16 nm s^{-1} by using pellets containing 2 mg freeze-dried humic and fulvic acids with 250 mg dry potassium bromide (Demyan et al., 2012).

Sequential extraction procedure: The European Community Bureau of Reference (BCR) is a modified form of Tessier et al. (1979), was followed to determine fractions of Cd (Ure et al., 1993). One gram of each soil sample was taken for the Cd fractionation. Each supernatant after each fractionation step was then analyzed on atomic absorption spectrophotometer (Model Thermo S-Series, USA). The extractants, experimental conditions and nominal forms of metals are presented in four steps.

i. Exchangeable fraction (F1). 40 mL of (0.11 *M*) CH_3COOH, shaking for 16 h and centrifuge.
ii. Reducible fraction (F2). 40 mL of (0.5 *M*) $NH_2OH{\cdot}HCl$ (pH 2), shaking for 16 h and centrifuge.
iii. Oxidizable fraction (F3). 10 mL of (8.8 *M*) H_2O_2 (pH 2-3), stayed for 1 h, then add 10 mL of (8.8 *M*) H_2O_2 and digested at 85°C for 2 h. Add 50 mL of (1 *M*)

Table 2. Speciation of Cd in soil and sewage sludge before the incubation (µg kg^{-1}).

	Total Cd	F1	F2	F3	F4	Total Fraction (TF) (F1+F2+F3+F4)	Recovery % $(\frac{TF}{Total\ Cd} \times 100)$
Soil	390	10	50	110	170	340	87.2
Sludge	5130	1430	940	770	1630	4770	92.9

F1=Exchangeable fraction, F2 =Reducible fraction, F3 = Oxidizable fraction, F4 = Residual fraction.

CH$_3$COONH$_4$ (pH adjusted at 2 with HNO$_3$), shaking for 16 h and centrifuge.

iv. Residual fraction (F4). 2 mL of 65% HNO$_3$ + 6 mL 37% HCl, digested at 120°C for 2 h.

Quality assurance: All the chemicals and solvents used were of analytical grade procured from Merck (Darmstadt, Germany). The reliability of all the analytical procedure was verified by including blanks with every set of sample digest. Humic substances were extracted and purified from soil according to the method employed by the International Humic Substances Society (Helmke et al., 1996).

RESULTS

Availability of Cd was assessed from distribution of its chemical forms in sewage sludge amended soils. It was observed upon sewage sludge addition, Cd fractions were significantly influenced at varying temperature with ageing. At the start of the experiment, exchangeable Cd fraction was about 2 µg kg^{-1} in un-amended soil and 23.45 and 44.9 µg kg^{-1} in soils amended with sewage sludge at 15 and 30 g kg^{-1} soil, respectively. After 135 days of incubation at 45°C, concentration of exchangeable Cd significantly ($p \leq 0.05$) increased from 23.45 to 28.86 µg kg^{-1} and 44.9 to 52.4 µg kg^{-1} in soil receiving sewage sludge @ 15 and 30 g kg^{-1} soil, respectively (Table 3). On the contrary, incubation at 22°C showed a non-significant change in the concentration of exchangeable Cd in soil receiving sewage sludge.

Reducible fraction of Cd was 22.1 µg kg^{-1} in un-amended soil while it was 33.6 and 45.13 µg kg^{-1} in amended soils with sewage sludge at 15 and 30 g kg^{-1} soil, respectively before the start of incubation. After 135 days of incubation at 45°C, reducible Cd fraction significantly ($p \leq 0.05$) decreased from 33.65 to 29.71 followed by 45.13 and 39.76 µg kg^{-1} in soil with sewage sludge applied at 0, 15 and 30 g kg^{-1} soil, respectively (Table 4). However, incubation at 22°C showed non-significant changes in reducible Cd of soil with and without sewage sludge.

The oxidizeable fraction is the most dynamic fraction because OM decomposition at high temperature (45°C) had major influence on this fraction. It was 10 µg kg^{-1} in un-amended soil at the start of incubation, while it was 24.1 and 38.2 µg kg^{-1} in soil amended with sewage sludge at 15 and 30 g kg^{-1} soil, respectively. After 135 days of incubation at 45°C, oxidizeable Cd fraction decreased significantly ($p \leq 0.05$) from 24.1 to 18.16 µg kg^{-1} and 38.2 to 32.05 µg kg^{-1} with sewage sludge at 15 and 30 g kg^{-1} soil, respectively (Table 5). On the contrary, incubation at 22°C showed non-significant changes in oxidizeable Cd fraction in soils amended with sewage sludge.

Residual Cd fraction was about 34 µg kg^{-1} in un-amended soil before the start of incubation, while it was 58.4 and 82.9 µg kg^{-1} in soil receiving sewage sludge at 15 and 30 g kg^{-1}, respectively. After 135 days of incubation at 45°C, concentration of residual Cd significantly ($p \leq 0.05$) increased from 58.45 to 59.91 µg kg^{-1} and 82.81 to 84.85 µg kg^{-1} in sewage sludge amended soil at 15 and 30 g kg^{-1} soil, respectively (Table 6). On the contrary, incubation at 22°C showed non-significant change in residual Cd fraction after incubation in sewage sludge amended soil. Significant changes ($p \leq 0.05$) were recorded for sewage sludge rate, time, and temperature interactions in all the Cd fractions.

Table 3. Effect of temperature and ageing on exchangeable Cd fraction (µg kg^{-1}).

	22°C			**45°C**		
	Sewage sludge rate (g kg^{-1} soil)					
Days	**0**	**15**	**30**	**0**	**15**	**30**
0	2.0±0.02lm	23.45±0.8j	44.9±1.1e	2.0±0.05m	23.45±0.1j	44.9±0.2e
45	2.11±0.01m	23.77±1.1ij	45.24±0.7e	2.15±0.1lm	25.55±0.3h	46.73±0.4c
90	2.2±0.05klm	24.20±0.5i	45.97±1.8d	2.55±0.2kl	27.44±0.3g	49.24±1.7b
135	2.38±0.06klm	25.24±0.7h	46.63±1.2c	2.60±0.09kl	28.86±0.4f	52.4±1.2a
LSD	Rate × Temp. × Days 0.4365**					

Mean ± S.E; Mean sharing different letter(s) in a column are statistically significant at $p \leq 0.05$; n=3

Table 4. Effect of temperature and ageing on reducible Cd fraction (µg kg^{-1}).

	22°C			**45°C**		
	Sewage sludge rate (g kg^{-1} soil)					
Days	**0**	**15**	**30**	**0**	**15**	**30**
0	22±0.1mn	33.5±0.1fg	45.1±0.1a	22.1±.02mn	33.6±0.1f	45.13±1.1a
45	21.9±.2mno	33.3±0.5gh	44.8±1.2a	21.7±.07no	32.7±0.9j	43.94±1.3c
90	21.63±0.1op	33.0±0.6hi	44.3±1.7b	21.3±0.1pq	31.2±0.2k	41.63±1.3d
135	21.37±0.1pq	32.8±0.6ij	44.0±0.5c	20.7±0.2qr	29.7±0.5l	39.76±0.3e
LSD	Rate × Temp. × Days 0.3173**					

Mean ± S.E; Mean sharing different letter(s) in a column are statistically significant at $p \leq 0.05$; n=3

Table 5. Effect of temperature and ageing on oxidizable Cd fraction (µg kg^{-1}).

	22°C			45°C		
	Sewage sludge rate (g kg^{-1} soil)					
Days	**0**	**15**	**30**	**0**	**15**	**30**
0	10±0.01k	24.1±0.1f	38.2±0.1a	10±0.01k	24.1±0.1f	38.2±0.1a
45	9.91±0.6kl	23.95±0.4f	37.95±0.5a	9.66±0.03kl	22.53±0.3h	36.51±0.3c
90	9.78±0.1kl	23.20±0.2g	37.34±0.1b	9.16±0.1mn	20.60±0.3i	34.65±0.4d
135	9.48±0.7lm	22.48±0.2h	36.44±0.3c	8.98± 0.1n	18.16±0.2j	32.05±0.2e
LSD	Rate × Temp. × Days 0.4464**					

Mean ± S.E; Mean sharing different letter(s) in a column are statistically significant at $p \leq 0.05$; n=3

Table 6. Effect of temperature and ageing on residual Cd fraction (µg kg^{-1}).

	22°C			45°C		
	Sewage sludge rate (g kg^{-1} soil)					
Days	**0**	**15**	**30**	**0**	**15**	**30**
0	34.0±0.2mo	58.45±0.2k	82.81±1.1f	34.0±0.1mo	58.4±0.1k	82.9±0.2f
45	34.3±0.2no	58.9±1.2jk	83.68±1.14e	34.9±0.1mn	59.1±0.7j	84.1±0.3de
90	34.8±0.1mn	59.19±0.5j	84.29±1.2d	35.3±0.1lm	60.5±0.3h	86.15±1.3b
135	34.9±0.2mn	59.91±0.5i	84.85±0.8c	35.7±0.3lm	62.3±0.4g	88.48±1.2a
LSD	Rate × Temp. × Days 0.5253**					

Mean ± S.E; Mean sharing different letter(s) in a column are statistically significant at $p \leq 0.05$; n=3

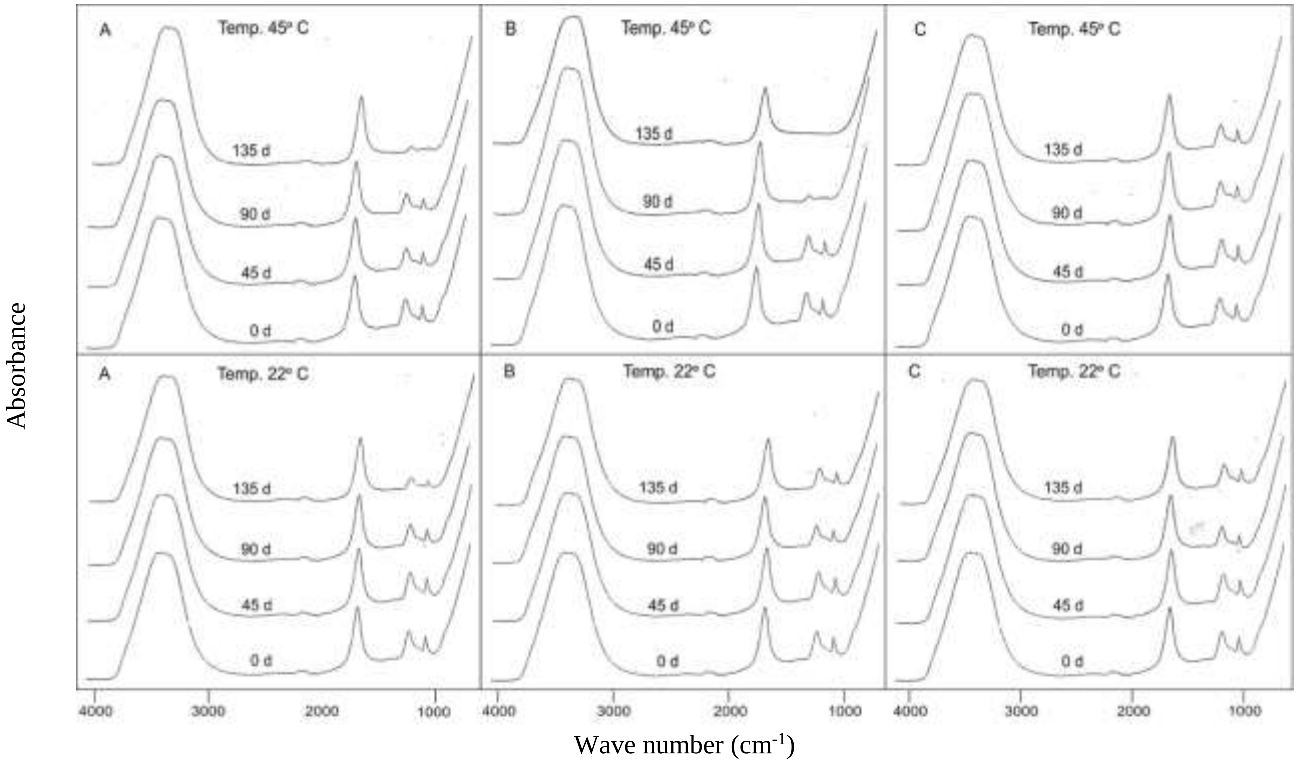
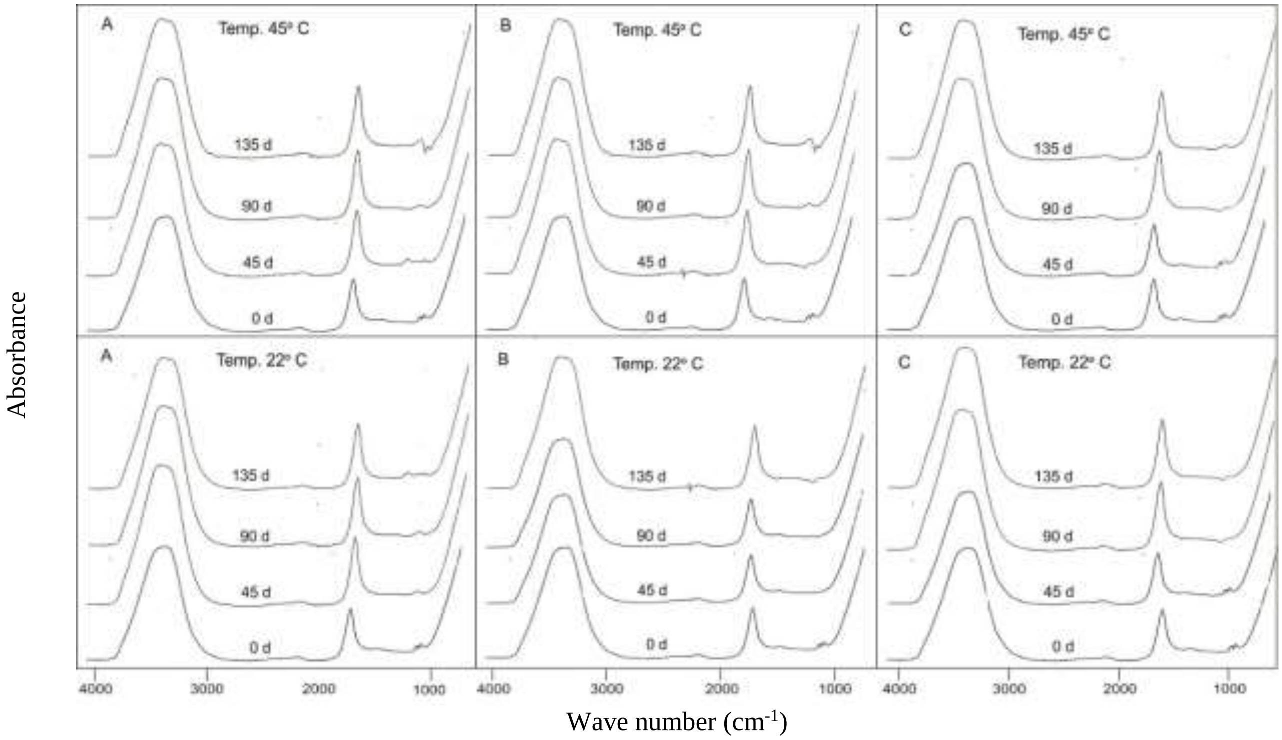


Figure 1. Fulvic acid transformation at varying temperature in soils amended with sewage sludge at 30 g kg^{-1} (A), 15 g kg^{-1} (B) and 0 g kg^{-1} (C).

Organic matter transformations during incubation at temperatures (22 and 45°C) were recorded in FTIR spectra of humic and fulvic acids. The initial interpretation of fulvic acid spectra of sewage sludge amended at 15 and 30 g kg^{-1} soil depicted four dominant regions of spectral absorbance (Fig. 1), i.e. (i) a broad band at 3400 cm^{-1} showed the occurrence of H-bonded N-H groups and H-bonded and non-bonded OH groups, (ii) a well-pronounced sharp peak at 1650



Figur 2. Humic acid transformation at varying temperature in soils amended with sewage sludge at 30 g kg^{-1} (A), 15 g kg^{-1} (B) and 0 g kg^{-1}.

cm^{-1} confirms the presence of aromatic and olefinic C=C bond, C=O bond in amide [I], ketone and quinine groups, (iii) a small peak at 1250 cm^{-1} showed the occurrence of amide [III], aliphatic alcohols, C-O stretch of aryl ethers / esters and organo-sulphur compounds, (iv) a small peak at 1040 cm^{-1} confirmed the presence of C-O and C-O-C stretch of polysaccharides and Si-O stretch of silicate impurities (Coates, 2000; Demyan *et al*., 2012). A distinct reduction of the bands assigned to polysaccharide region occurred at 1000 to 1500 cm^{-1} in sewage sludge amended soils at high temperature (45°C) (Fig. 1).

The initial interpretation of humic acid spectra of sewage sludge amended soil showed absorbance bands (Fig. 2) viz. a broad band at 3400 cm^{-1} assigned to the presence of H-bonded OH groups (alcohols, phenols, and organic acids) and NH groups, a sharp peak at 1600-1700 cm^{-1} owing to the presence of carboxylic acid and/or ketone C=O groups and C=C vibrations of alkenes and aromatic groups, while a weak band at 1050 cm^{-1} is generally attributed to the presence of aromatic ethers, polysaccharide-like substances, Si-O stretch of clay minerals, silicate (Si-O-Si) and mineral compounds (Coates, 2000; Demyan *et al*., 2012).

At high temperature (45°C), humic acid showed stability of bands around 3400 and 1650 cm^{-1} with a relative increase of absorbance intensity around 1050-1150 cm^{-1} (Fig. 2).

DISCUSSION

Organic matter decomposition and dissolution of soluble metal-humate complexes during incubation at 45°C favors progressive increase in exchangeable Cd fraction. Adekunle (2009) attributed increase in Cd availability due to increased OM decomposition at high temperature owing to which increase in exchangeable Cd fraction was 0.67 to 9.23%, as temperature increased from 10 to 80°C. Antoniadis and Alloway (2001) reported reflective influence of high temperature on Cd availability and carbon mineralization and observed more increase in exchangeable Cd fraction after incubation at 25°C than 15°C. The variations in humic and fulvic acids spectra (Fig. 1, 2) and increase in Cd availability in sewage sludge amended soil incubated at 45°C (Table 3), confirms the decomposition and dissolution of metal-humate complexes due to severe degradation and dehydration of easily decomposable functional groups like amino, alcoholic and carboxlic (El Fels *et al*., 2015).

Specific adsorption of Cd with soil constituents viz. hydrous oxides of Fe, Al and Mn and the humic substances caused a decrease in reducible Cd fraction in sewage sludge amended soils incubated at 45°C. Increased immobilization of reducible Cd fraction at high temperature (45°C) was ascribed due to rate limited kinetic sorption reactions (Feng *et al*., 2016). They also reported that ageing had major influence on the distribution of reducible Cd fraction. While He *et al.* (2016) reported a decrease in Cd bioavailability in sewage sludge amended soils incubated at high temperature (35°C) due to metal bioaccumulation by microorganisms (sequestration) and Cd adsorption on humate complexes. Moreover, elevated temperature (40°C) also enhanced metal activity and sorption reactions which favored decrease in potential availability of reducible Cd fraction (Azouzi *et al*., 2015).

The Cd adsorption on negative sites of humic and fulvic acids and precipitation with phosphates and sulphides affect a decrease in oxidizable Cd fraction (kulikowska *et al*., 2015). A decrease in oxidizable Cd fraction was attributed to increased precipitation of humic substances with Cd. Humic substances in OM possessed high surface area and large number of alcoholic, phenolic and carboxlic functional groups which generally favors these chelation and precipitation reactions (Sparks *et al*., 1997). Moreover, ageing promotes the progressive transfer of plant available metal forms (exchangeable and reducible) into non-available forms (oxidized and residual) most probably due to chelation reactions onto soil colloids and humate complexes. Organic matter decomposition also determines the composition of these chelate complexes through increased microbial activity and soil geochemical reactions (exchange reactions, chelation and redox reactions) at high temperature of 35°C (Golui, 2016).

Increased residual Cd fraction at high temperature (45°C) resulted in decreased Cd availability due to Cd adsorption on soil primary (mica and silicates etc.) and secondary (clay minerals, calcite, iron and aluminum oxides) minerals and forming stable inner-sphere metal complexes like $Cd(OH)_2$, CdO, $CdHPO_4$, $CdCO_3$ and $Cd(PO_4)_2$ etc (Sparks, 1997). It might also be due to the fact that land application of sewage sludge provides more surface area and sites for metal adsorption (McBride, 2003). Microbial activity and metal-humate complexes formation are also the major controlling factors in increasing residual Cd fraction during composting of sewage sludge at high temperature (Zhang *et al*., 2015) and probably incubation as well. Overall, it was inferred that Cd availability increased after initial decomposition of soluble OM substances (amino acids, carbohydrates, organic acids, polysaccharides and lignin) at high temperature (45°C) but with ageing Cd availability progressively decreased due to maturity and stabilization of OM derived humate complexes (Kulikowska *et al*., 2015).

Progressive changes in fulvic acid spectra at 1050 to 1150 cm^{-1} region were attributed to the formation of sulphur containing esters and increased poly condensation reactions which resulted in mature aromatic end products (Amir *et al*., 2010). This increase in aromatic character (showed by the stability of bands at 1645 and 3400 cm^{-1}) at high temperature (45°C) depicted fulvic acid in a much more condensed and complex form (Benlboukht *et al*., 2015). Fulvic acids being more rich in carboxylic, phenolic and alcoholic groups are natural polyelectrolytic organic compounds had more potential for specific adsorption with metals (Lehmann and Kleber, 2015; Stevenson, 1994). Boruvka and Drabek (2004) reported that ≈ 98% of oxidizeable Cd fraction in sewage sludge amended soils was related to fulvic acid fraction of OM that might be due to de-carboxylation and transformation of aliphatic to aromatic groups which help stabilize metal-humate complexes. High temperature treatment/incubation of fulvic acids during composting leads to decrease in aliphatic and carbohydrate groups and subsequent increase in stable carbonyl, alcoholic and phenolic groups (Yang *et al*., 2014).

The stability in humic acid structure at high temperature (45°C) occurred most probably due to de-carboxylation of labile aliphatic, carboxylic and amides functional groups, and increased proportion of oxidized and stable aromatic structures with ageing (Amir *et al*., 2010). High temperature (45°C) caused dehydration of hydrophilic groups (carboxylic, phenolic, protein and polysaccharides), reduction in acidic groups and increase in hydrophobic groups, which resulted in maturity and more stability in humate complexes for metal adsorption (Yang *et al*., 2014).

There was less transformation in humic acid spectra compared to that of fulvic acid at high temperature (45°C). Piccolo (2001) referred stability in humic substances due to additional chemical bonding (C-O and C-C bonds) with main hydrogen bonds through van der Waal's forces. Stevenson (1994) also reported more stability in humic acid structure than fulvic acid during degradation of OM. They found fulvic acid derived complexes mostly to exhibit initial stages of humification, while humic acid showed final stages of humification which leads to increased metal retention of final humate products in soils.

Conclusions: The results showed that sewage sludge application under higher temperature (45°C) conditions (like the summer in Pakistan) enhanced the release of exchangeable Cd fraction. However, ageing of compost or soils could decrease Cd mobility due to a decrease in available Cd fractions. Fulvic acid showed higher degradation due to the higher contents of easy-to-degrade labile amino, alcohols, carbohydrates and carboxylic groups which usually result in increased Cd release. The humic acid underwent less transformation and exhibited higher aromacity with ageing that decreased Cd availability. Since immobilization and redistribution pattern of metal fractions significantly changes with ageing and temperature, it is concluded that sewage sludge should not repeatedly be applied at higher rates (particularly to cereal crops, vegetables whose leaves or roots are consumed by human beings) to avoid health risks associated with sludge borne Cd.

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