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Coal fly ash for the recovery of nitrogenous compounds from wastewater: Parametric considerations and system design

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Abstract The use of coal fly ash for nutrient recovery in wastewater treatment offers a potential win–win scenario as it simultaneously utilizes and re-channels two wastes – coal fly ash and wastewater. This study investigated the adsorptive recovery of urea from synthetic urine using fly ash. Equilibrium experiments revealed that 1.5 g ash loading, initial urea concentration of 13.5 g L⁻¹, urine pH = 6.0, sorption temperature = 30 °C and 150 rpm shaker speed were the optimal process parameters and maximum adsorption capacity was 410 mg g⁻¹. Proof of concept to the use of synthetic urine was conducted by performing adsorption with real human urine which validated the experimental findings. Comparative analysis and non-linear optimization of nine isotherm models through comprehensive error analysis revealed that Flory–Huggins and Redlich–Peterson equations best described the adsorption. Process thermodynamics suggested that Van der Waal's and electrostatic interactions occur between urea molecules and the surface of fly ash particles; besides, the sorption was found to be exothermic, spontaneous and physical in nature. Kinetic studies pointed toward a pseudo-second-order kinetic fit with contributions from intra-particle diffusion. Further,

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Nomenclature

R^2	coefficient of determination	K_S	sips isotherm model constant ($L g^{-1}$)
A	Temkin equilibrium binding constant ($L g^{-1}$)	K_T	toth isotherm constant ($mg g^{-1}$)
A_{KC}	Koble–Corrigan isotherm constant ($L^n mg^{1-n} g^{-1}$)	LoD	limit of detection ($mg L^{-1}$)
A_{RP}	Redlich–Peterson isotherm constant (mg^{-1})	LoQ	limit of quantitation ($mg L^{-1}$)
B	Temkin isotherm constant ($J mol^{-1}$)	m	amount of fly ash per unit volume of urea-free adsorbate (g)
B_{KC}	Koble–Corrigan isotherm constant ($L mg^{-1-n}$)	ND	Normalized Deviation
B_{RP}	Redlich–Peterson isotherm constant ($L g^{-1}$)	n_{FH}	Flory–Huggins isotherm model exponent
C_0	amount of urea at $t = 0$ in the sorbate ($mg L^{-1}$)	n_{FR}	Freundlich isotherm adsorption intensity
C_e	amount of urea at equilibrium in the sorbate ($mg L^{-1}$)	NSD	Normalized Standard Deviation
C_t	amount of urea at any time ‘ t ’ in the sorbate ($mg L^{-1}$)	q, q_t	amount of urea adsorbed at time t ($mg g^{-1}$)
D_i	effective diffusivity coefficient	q_∞	urea adsorption at infinite time
E_A	activation energy ($kJ mol^{-1}$)	q_e	amount of urea adsorbed at equilibrium ($mg g^{-1}$)
Err_{AR}	Average Relative Error	$q_{e \text{ exp, pred}}$	experimental and predicted urea uptake at equilibrium ($mg g^{-1}$)
Err_{CF}	Composite Fractional Error Function	q_m	maximum monolayer urea sorption ($mg g^{-1}$)
Err_{MPSD}	Derivative of Marquardt’s Percent Standard Deviation	q_s	Dubinin–Radushkevich theoretical maximum sorption capacity ($mg g^{-1}$)
Err_{SA}	Sum of Absolute Errors	Q_s	sips theoretical isotherm saturation capacity ($mg g^{-1}$)
Err_{SS}	Sum of Squares of Errors	q_t	urea adsorption at time t ($mg g^{-1}$)
E_s	mean sorption energy ($kJ mol^{-1}$)	Q_t	toth theoretical isotherm saturation capacity ($mg g^{-1}$)
F	fraction of urea adsorbed ($mg g^{-1}$)	R	gas constant ($8.314 J mol^{-1} K^{-1}$)
g	Redlich–Peterson isotherm exponent	R_L	Langmuir separation factor
h	initial rate of urea adsorption	S_S	surface to volume ratio (cm^{-1})
K	dimensionless parameter estimated from the Langmuir isotherm model constants	t	time (min)
K_0	Arrhenius factor	T	temperature ($^{\circ}C$)
k_1	first order rate constant (min^{-1})	V	sorbate volume (L)
k_2	second order rate constant ($g mg^{-1} min^{-1}$)	W, W_1, W_2, \dots, W_N	amount of coal fly ash (g)
K_a	Flory–Huggins isotherm constant ($L g^{-1}$)	β_L	mass transfer coefficient
K_{ad}	Dubinin–Radushkevich isotherm constant ($mol^2 kJ^{-1}$)	ΔC	change in initial urea concentration
K_F	Freundlich isotherm constant ($mg g^{-1} (L mg^{-1})^{1/n}$)	ΔT	change in sorption temperature
k_{id}	intra-particle diffusion rate constant ($mg g^{-1} min^{-0.5}$)	ΔW	change in fly ash dosage
K_L	Langmuir isotherm constant ($L mg^{-1}$)	ε	Polanyi potential
		θ	degree of surface coverage

the rate of mass transfer was seen to be controlled and limited by film diffusion of urea which featured stronger than its pore diffusion. To design a multistage batch adsorber, a mathematical model unique to the sorption system was derived that minimized the total amount of fly ash required for 90% removal of urea from different volumes of influent synthetic urine solutions.

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1. Introduction

The provisioning of electricity is undoubtedly a prerequisite for national development as prosperity (measured as per capita GNP) is strongly correlated with the per capita electricity generation capacity of a nation (Beér, 2013). In this regard, coal power, historically as well as in the present times, plays a pivotal role by fueling nearly 41% of the global electricity supply (World Bank, 2016). Despite the high level of environmental consciousness in the world today and concerted efforts

to decarbonize the global economy by promoting renewable energy production (Young et al., 2006), it is widely acknowledged that coal-based power generation will likely be the dominant source for global electricity generation, at least in the first half of the twenty first century (Luderer et al., 2012; Beér, 2013). In particular, emerging economies such as India, China and South Africa where coal accounts for 72.8, 75.4 and 93.7% of the electricity production, respectively, are expected to continue their reliance on coal power (World Bank, 2016; Wu et al., 2016).

However, the disposal and/or efficient utilization of coal combustion products and residues, of which the majority is fly ash (500 million tons per year globally), continues to be an economical problem with potentially severe environmental consequences if left unresolved (Ahmaruzzaman, 2010). As Iyer and Scott (2001) remark, despite the utilization of fly ash in various applications such as cement and brick manufacturing (Koukouzas et al., 2011), zeolites production (Itskos et al., 2010), adsorption and soil amendment, the rate of reutilization is far less than the amount of ash being produced annually. In India, there has been sustained increase in fly ash utilization from 6.6 mt yr^{-1} in 1996–97 to 102.5 mt yr^{-1} in 2014–15; as of 2015, the utilization of ash stood at 55.7% vis-à-vis an ambitious target of 100% utilization of fly ash stipulated by the Indian Ministry of Environment and Forests and Climate Change (MoEFCC) (Central Electricity Authority, 2015). This increase can be attributed to the shift of the regulatory status of coal fly ash from 'hazardous industrial waste' to 'waste material', thus making it a saleable 'useful commodity' on the market (Dhadse et al., 2008; Central Electricity Authority, 2015). Although this progress is encouraging, since coal power generation across India's 145 thermal plants is expected to grow at a rate of 8–10%, attaining the MoEFCC's target of complete utilization of ash in a time-bound phased manner would be a 'challenging task' as 'utilization of fly ash is not commensurate with fly ash generation' (Central Electricity Authority, 2015; Chattopadhyay, 2015).

The utilization of coal combustion products has been reviewed elsewhere and does not require further elaboration here (Iyer and Scott, 2001; Kumar et al., 2007; Wang, 2008; González et al., 2009; Ahmaruzzaman, 2010; Blissett and Rowson, 2012; Yao et al., 2015). In another review Jala and Goyal (2006) point toward the agronomic benefits of applying fly ash as a soil conditioner or amender. Hence, the focus of the present study was on the potential utilization of fly ash in the inter-related sectors of agriculture and wastewater treatment (reclamation). Fly ash has been utilized as an adsorbent for the removal of polychlorinated biphenyls (Nollet et al., 2003), industrial dyes (Wang et al., 2005; Jedidi et al., 2009), gaseous organics (Wang and Wu, 2006; Bandura et al., 2016), heavy metals (Cho et al., 2005; Itskos et al., 2010; Javadian et al., 2015) and organics such as phenols (Sarkar and Acharya, 2006), pesticides (Gupta and Ali, 2001), detergents (Bhargava et al., 1974), oxalic acid (Jain et al., 1980) and remediation of oil spills (Bandura et al., 2015). To the best of our knowledge, fly ash has not been utilized for the 'recovery' of nutrients from wastewater streams such as human urine. At the other end of the spectrum of the developmental agenda in India lies the persistent and seemingly insurmountable issue of municipal waste management; the use of fly ash as an adsorbent for the removal and recovery of nutrients from wastewater could potentially offer a win-win scenario; it would allow simultaneous utilization and re-application of two waste resources – coal fly ash and wastewater.

Hence, in the present study, an initiative was taken to investigate the potential of coal fly ash toward the recovery of urea from human urine as urea constitutes 85% of its tot-N (Kirchmann and Pettersson, 1994). The principal aim in the study was to establish the isothermal, kinetic, and mass transfer mechanisms for the adsorptive separation of urea from urine solutions mediated by the use of ash. It is acknowledged that the results from the study are of pertinence to N recovery from source-separated urine and not domestic wastewater per se, wherein concurrent adsorption of other compounds is likely to occur.

2. Methods and materials

Synthetic urine was prepared according to guidelines of Ciba-Geigy (1977) and Burns and Finlayson (1980) with modifications from Pronk et al. (2006) and Ganesapillai et al. (2015) (Supplementary Information, Table S1(a)). Fresh human urine was collected from male volunteers (18–22 years) immediately after excretion and stored in sterile, air-tight containers. The

Table 1 Chemical composition and physical properties of coal fly ash.

Component	% Dry weight	Property	Value
SiO ₂	57.6	Moisture (%)	5.50
Al ₂ O ₃	31.6	pH _{1:5} ^a	8.08
Fe ₂ O ₃	2.88	Bulk density (g cm ⁻³)	0.82
CaO	0.82	Specific gravity (g cm ⁻³)	2.45
K ₂ O	1.72	Loss on ignition (%)	0.96
TiO ₂	2.40	Surface area (m ² g ⁻¹)	5.59
Na ₂ O	0.72	Particle size (μm)	74 < φ < 88
MgO	1.05		
Loss on Ignition	1.21		

^a pH determined through a 1:5 fly ash:deionized water suspension.

urine was characterized for its components (Table S1(b)) as described elsewhere (Pillai et al., 2014); the initial urea concentration was 13.5 and 12.7 mg L^{-1} in synthetic urine and human urine, respectively. While all experiments were performed using synthetic urine solutions, as a proof of concept and validation, an additional set of experiments was also carried out with human urine wherein the sorption system was designed with identified (optimum) values of the process parameters. Coal fly ash (ASTM Class F) was obtained from the Ennore Thermal Power Plant in Chennai, India. The physical and chemical properties of the fly ash have been summarized in Table 1. All reagents and chemical used were of analytical grade and purchased from SD Fine Chemicals, Mumbai, India.

2.1. Urea adsorption experiments

The effect of process parameters viz., initial urea concentration in urine (3.375, 6.75, 10.125 and 13.5 g L^{-1}), adsorbent loading (0.5–2.5 g), solution temperature (30–40 °C), pH (5.6–7.0) and incubator shaker speed (100–200 rpm) was investigated using an incubator shaker (Orbitek LT, Scigenics Biotech, India). Solutions of different urea concentrations were prepared by diluting the prepared synthetic urine with deionized water; pH was adjusted using HCl (0.1 M) or NaOH (0.1 M). For every experimental module involving the effect of a process parameter, all others were held constant. In each experimental run, 100 mL synthetic urine of known concentration was mixed with a fixed quantity of fly ash; pH of the mixture was adjusted and kept in the incubator shaker at a constant temperature and shaker speed until the establishment of equilibrium. At predetermined intervals of time, 5 mL aliquots were withdrawn, centrifuged (REMI Instruments, AUCI-5230, India) and filtered through a Ministat filter (0.45 μm; Sartorius Stedim Biotech GmbH, Germany). Spectrophotometric determination (Shimadzu UV-1601, Japan) of urea was done by observing change in absorbance ($\lambda_{\text{max}} = 430 \text{ nm}$) (With et al., 1961). The aliquots were returned to the adsorption system after the spectrophotometric determination. pH of the adsorbate was adjusted using HCl or NaOH. The adsorptive urea recovered or urea removed (q_e ; mg g^{-1}) was

calculated using Eq. (1); here, C_0 and C_t (mg L^{-1}) represent the amount of urea at $t = 0$ and at any time 't' in the sorbate, V is the sorbate volume (L) while W is the amount (g) of fly ash used in the experimental run.

$$q_e = \frac{(C_0 - C_t) \times V}{W} \quad (1)$$

To validate the experimental findings for synthetic urine solutions, additional experiments were performed using human urine with an average urea concentration of 12.7 g L^{-1} and pH of 6.1. The sorption system was set up by using 100 mL human urine and 1.5 g ash with the incubator shaker kept at 30°C and 150 rpm.

2.2. Isotherm, mass transfer and kinetic analysis

To understand the distribution of urea between the sorbate and the adsorbent (fly ash) as well as to gain insights into the adsorptive performance of the sorption system, experimental data were analyzed against several well-known model equations. With the aim of identifying the best isotherm equation, we analyzed two parameter models (Langmuir, Freundlich, Dubinin–Radushkevich, Temkin and Flory–Huggins) in their linearized form and three parameter models (Redlich–Peterson, Sips, Toth and Koble–Corrigan) through non-linear optimization (Supplementary Information, Eq. (s1)–(s9)). In this regard, a review by Foo and Hameed (2010) is particularly helpful in understanding the various model equations, their fundamental characteristics and significance. In Section 2.3, the methodology followed for identifying and selecting the best model equation has been detailed.

Process kinetics was evaluated by using the Lagergen's pseudo-first-order model (Acemioğlu, 2004), Ho and McKay's (1999) pseudo-second-order model as well as Weber and Morris's (1963) intra-particle diffusion model. Mass transfer of urea was investigated according to procedure detailed elsewhere (McKay et al., 1981; Eq. (2)); the dimensionless parameter K was estimated from the Langmuir isotherm model constants, S_s is the surface to volume ratio (cm^{-1}) and represents the area available for urea transfer (assuming fly ash particles to be spherical) and m is the amount of fly ash per unit volume of urea-free adsorbate.

$$\ln \frac{C_t}{C_0} - \frac{1}{1+mK} = \ln \frac{mK}{1+mK} - \frac{1+mK}{mK} \times \beta_L S_s t \quad (2)$$

2.3. Statistical analysis

Spectrophotometric measurements of urea absorbance were performed with 10 scans per measurement with a photometric accuracy of ± 0.002 Abs, repeatability of ± 0.001 Abs and noise level of 0.002 Abs. The standard deviation over the adsorption experiments carried out in triplicate was $< 5\%$, and mean values have been quoted in the illustrations. For the two parameter linearized isotherm models, coefficient of determination (R^2), Normalized Deviation (ND; Eq. (3)) and Normalized Standard Deviation (NSD; Eq. (4)) were calculated to evaluate the goodness of fit.

$$ND = \frac{100}{n} \sum \left| \frac{q_{e, \text{exp}} - q_{e, \text{pred}}}{q_{e, \text{exp}}} \right| \quad (3)$$

$$NSD = 100 \sqrt{\frac{\sum (q_{e, \text{exp}} - q_{e, \text{pred}})^2 / q_{e, \text{exp}}^2}{n}} \quad (4)$$

For error analysis of the three parameter isotherm models, the procedure detailed by Ho et al. (2002, p.10) was followed. Five different error functions viz., Err_{SS} – Sum of Squares of Errors, Err_{CF} – Composite Fractional Error Function, Err_{MPSD} – Derivative of Marquardt's Percent Standard Deviation, Err_{AR} – Average Relative Error and Err_{SA} – Sum of Absolute Errors were evaluated (Eq. (5)–(9)) with the model parameters determined for each function and a 'sum of normalized error' was calculated for each parameter set. The parameter set that yielded the minimum sum of normalized error was considered optimal. Statistical analysis was performed using Microsoft® Excel 2010/XLSTAT© Pro 11 (v. 7.5, Addinsoft Inc., NY, USA).

$$Err_{SS} = \sum_{i=1}^p (q_{e, \text{exp}} - q_{e, \text{pred}})_i^2 \quad (5)$$

$$Err_{CF} = \sum_{i=1}^p \left[\frac{(q_{e, \text{exp}} - q_{e, \text{pred}})^2}{q_{e, \text{exp}}} \right]_i \quad (6)$$

$$Err_{MPSD} = \sum_{i=1}^p \left(\frac{q_{e, \text{exp}} - q_{e, \text{pred}}}{q_{e, \text{exp}}} \right)_i^2 \quad (7)$$

$$Err_{AR} = \sum_{i=1}^p \left| \frac{q_{e, \text{exp}} - q_{e, \text{pred}}}{q_{e, \text{exp}}} \right|_i \quad (8)$$

$$Err_{SA} = \sum_{i=1}^p |q_{e, \text{exp}} - q_{e, \text{pred}}|_i \quad (9)$$

3. Results and discussion

3.1. Effect of fly ash loading and initial concentration

For a fixed amount of the target compound that needs to be adsorbed, there exists an optimal dosage of the adsorbent that maximizes its uptake capacity at equilibrium. To identify the ideal amount of fly ash to be utilized in the sorption system, a series of experiments were conducted with varied fly ash loading (0.5–2.5 g) (Fig. 1). It was evident that the urea sorption was high ($> 380 \text{ mg g}^{-1}$) at ash loadings $\leq 1.5 \text{ g}$ which is possibly due to the availability of sorption sites on the ash surface. When dosage exceeds 1.5 g, the equilibrium adsorption capacity decreases and this is presumably because the number of sorption sites is far more than the amount of urea present in the solution. With increase in ash loading from 0.5 to 2.5 g causes the removal of urea to also increase from 27 to 91%. However, the increase in urea recovered is insignificant ($< 5\%$) for ash dosage greater than 1.5 g; hence, 1.5 g ash loading was considered to be the optimal dosage for urea recovery from 100 mL of synthetic urine.

Using a fixed adsorbent loading of 1.5 g, the initial urea concentration in the synthetic urine was varied by dilution with deionized water to investigate the effect of concentration on the sorption (Fig. 2). The strong influence of concentration is clearly evident with urea uptake capacity of the ash

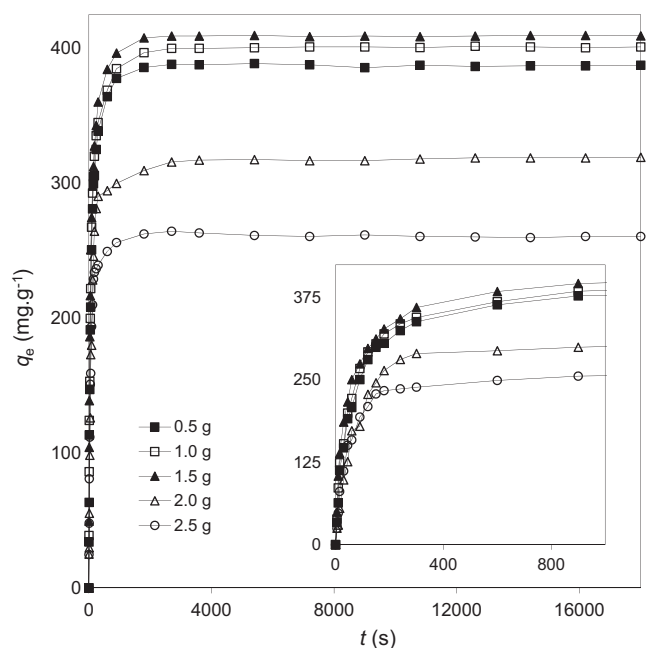


Fig. 1 Urea recovery from synthetic urine investigated at various fly ash dosages and $[\text{CO}(\text{NH}_2)_2] = 13.5 \text{ g L}^{-1}$, 30°C , 125 rpm and $\text{pH} = 6.5$.

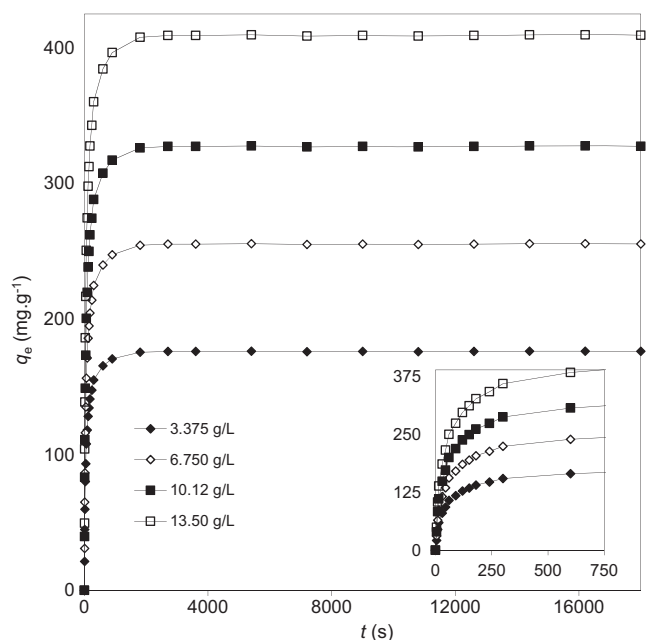


Fig. 2 The adsorption profile of urea investigated at various initial concentrations of urea with 1.5 g ash loading, 30°C , 100 rpm and $\text{pH} = 6.0$.

increasing from 176.2 to 409.3 mg g^{-1} as concentration varies from 25 to 100%. Further, urea recovery was seen to be $>80\%$ for all concentrations suggesting that initial urea concentration affects only the quantity of the urea recovered at equilibrium. Furthermore, at fixed adsorbate concentration of 3.375 g L^{-1} and adsorbent loading of 1.5 g, the effect of shaker speed (100–200 rpm) was observed to be insignificant and

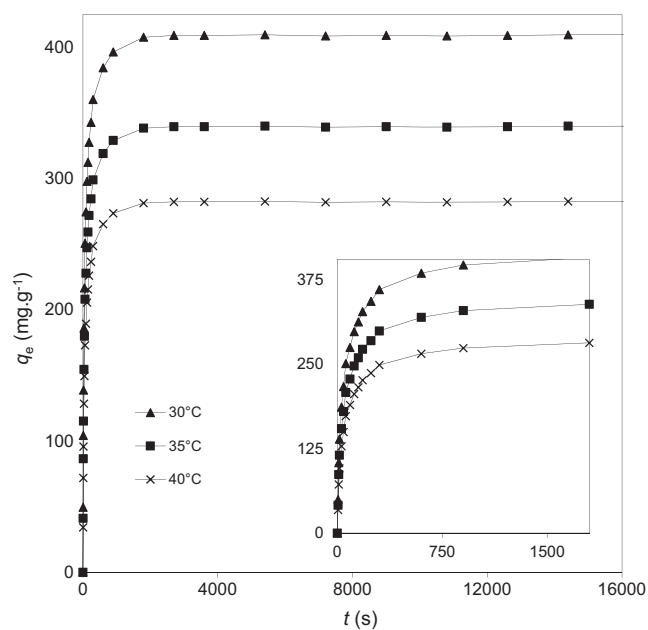


Fig. 3 Effect of sorption temperature on the uptake of urea by coal fly ash investigated at $[\text{CO}(\text{NH}_2)_2] = 13.5 \text{ g L}^{-1}$, 1.5 g ash dosage, 150 rpm and $\text{pH} = 6.5$.

hence, an average value of 150 rpm was selected for use in further experiments (Fig. S3).

3.2. Effect of sorption temperature

Experiments were performed at three different incubator temperatures while fly ash loading, initial concentration, shaker speed and pH were held constant at 1.5 g , 13.5 g L^{-1} , 150 rpm and 7.0 respectively (Fig. 3). Results indicated that urea removal from urine over ash could be exothermic in nature as adsorption capacity decreased in the order, $30^\circ\text{C} > 35^\circ\text{C} > 40^\circ\text{C}$; urea uptake capacity decreased from 409.3 to 282.4 mg g^{-1} as temperature increased from 30 to 40°C . At low temperatures, the average molecular energy is low; hence, the interaction of urea and fly ash is higher which resulted in enhanced adsorption. An observation contrary to this trend has been made in the case of industrial dye sorption where higher temperatures are seen to be favorable (Sarkar and Acharya, 2006); however, the exothermic nature of sorption of organic compounds has been noted by Gupta and Ali (2001) who investigated the removal of pesticides using bagasse fly ash. In any case, small variations in sorption temperature should not significantly affect the adsorptive separation of solute from the solution.

3.3. Effect of urine pH

The variation in urea uptake capacity of fly ash was also investigated under different synthetic urine pH (Fig. 4). In these experiments the pH was varied between 5.5 and 7.5 considering the variability of pH of human urine from person-to-person as well as different dietary preferences. In any case, the effect of pH was not considerably significant as urea was the dominant molecule in the solution across the range of pH

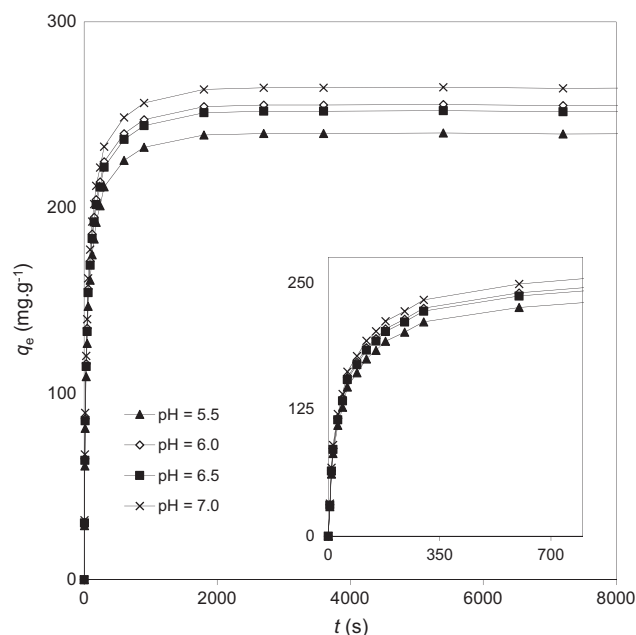


Fig. 4 Influence of urine pH on the urea adsorption capacity of coal fly ash studied at 1.5 g ash loading, $[\text{CO}(\text{NH}_2)_2] = 6.75 \text{ g L}^{-1}$, 30 °C and 150 rpm.

examined. Maximum urea adsorption was observed to occur at a synthetic urine pH of 7. It could be quite possible that urea adsorption onto fly ash is governed by non-electrostatic interactions and thus, to increase its removal from urine, either the pore volume of the ash has to be augmented or the molecular size of the solute has to be increased through agglomeration. Alternatively, increasing ionic strength has also been advocated as a suitable option for improving adsorption capacity at a given pH (Newcombe and Drikas, 1997). Radovic et al. (1997) recorded similar observations in their study involving nitrobenzene adsorption onto activated carbon.

3.4. Experiments with human urine

The average maximum adsorption capacity of coal fly ash for adsorption of urea from human urine studied in triplicate was

found to be 388.3 mg g^{-1} which agreed well ($\delta = 5.12$) with that observed in experiments with synthetic urine (409.3 mg g^{-1}). In all experiments, $\geq 90\%$ removal of urea was recorded. Although not tested in this study, in order to facilitate urea desorption from the fly ash and allow fly ash re-use, the methodology for regeneration suggested by Ganesapillai et al. (2016) can be followed; deionized water of a pre-determined volume based on the fly ash adsorption capacity could allow recovery of urea as an aqueous concentrated solution for subsequent use in agriculture as a crop fertilizer. Alternatively, fly ash adsorbed with urea can be used as such for crop fertilization especially for the amendment and conditioning of acidic soils (Yadav et al., 2016) given the alkaline nature of the fly ash ($\text{pH}_{1:5} \sim 8$).

3.5. Contact time and adsorption kinetics

It is evident from Figs. 1–4 that the sorption was rapid as the time required for establishment of equilibrium was observed to be $\sim 3600 \text{ s}$. Majority ($>95\%$) of the sorption was seen to occur in $t < 70 \text{ min}$ across all the experimental conditions investigated. Besides, the adsorption profile revealed three distinct sections: swift urea removal from urine was observed for $t < 500 \text{ s}$, gradual removal for $500 \text{ s} < t < 2500 \text{ s}$ and slow uptake at $t > 2500 \text{ s}$. Such behavior has been observed elsewhere in studies involving the adsorption of organics (Brás et al., 2005).

Tables 2–4 summarize the results of the kinetic experiments. When experimentally derived sorption data were tested against the three kinetic models it was observed that, using the coefficient of determination as the selection criteria for goodness of fit yielded the pseudo-second-order equation as the best fit (Ho and McKay, 1998). This was a consistent observation ($R_2^2 > 0.99$) throughout all the investigated experimental modules – concentration (C ; g L^{-1}), temperature (T ; °C) as well as fly ash loading (W ; g). Likewise, the predicted urea adsorption capacity at equilibrium (q_2) was very close to observed values. In contrast, $\log(q_e - q_t)$ versus t plots (not shown) for the pseudo-first-order model indicated the deviation between predicted and experimental data, especially in the initial portion of the adsorption ($t < 500 \text{ s}$). The pseudo-second order rate constant (k_2) was found to increase with concentration and

Table 2 Process kinetics for adsorption of urea onto fly ash at different initial concentrations.

C (g L^{-1})	R_1^2	k_1	q_1	R_2^2	k_2	q_2	h	R_t^2	k_{id}
3.375	0.9286	0.00128	88.61	0.9999	5.46587	176.68	170,622	0.9421	21,737
6.750	0.9286	0.00128	128.42	0.9999	7.92740	255.75	518,516	0.9423	31,503
10.125	0.9286	0.00129	164.64	0.9999	10.18845	327.87	1,095,246	0.9423	40,389
13.500	0.9287	0.00130	208.93	0.9999	12.71387	409.84	2,135,534	0.9426	50,486

Table 3 Process kinetics for adsorption of urea onto fly ash at different sorption temperatures.

T (°C)	R_1^2	k_1	q_1	R_2^2	k_2	q_2	h	R_t^2	k_{id}
30	0.8247	0.00070	257.04	0.9999	7.54E-05	410.34	12.69	0.9426	50,486
35	0.8003	0.00068	208.93	0.9999	5.06E-05	340.60	5.87	0.9425	41,903
40	0.8097	0.00069	112.20	0.9999	1.09E-05	283.13	0.87	0.9426	34,835

Table 4 Process kinetics for adsorption of urea onto fly ash at different ash loadings.

W (g)	R_1^2	k_1	q_1	R_2^2	k_2	q_2	h	R_i^2	k_{id}
0.5	0.9175	0.00129	204.38	0.9999	7.38E-05	387.60	11.09	0.9428	47,757
1.0	0.8727	0.00130	200.35	0.9999	7.69E-05	401.61	12.40	0.9426	49,462
1.5	0.9286	0.00138	325.55	0.9999	7.92E-05	409.84	13.30	0.9426	50,488
2.0	0.6971	0.00098	154.77	0.9999	6.62E-05	319.49	6.76	0.9415	39,303
2.5	0.8416	0.00031	107.67	0.9999	1.94E-05	261.10	1.32	0.9435	32,118

Table 5 Mass transfer coefficient and effective diffusivity coefficient determined at various process conditions.

W (g)	β_L	D_i	C (g L ⁻¹)	β_L	D_i	T (°C)	β_L	D_i
0.5	2.93E-08	3.37E-12	3.375	1.30E-08	7.09E-13	30	7.99E-08	1.77E-11
1.0	7.31E-08	4.96E-12	6.750	2.28E-08	1.29E-12	35	7.77E-08	2.66E-12
1.5	7.99E-08	1.77E-11	10.125	4.75E-08	2.36E-12	40	6.52E-08	1.60E-12
2.0	7.69E-08	1.54E-12	13.500	7.99E-08	1.77E-11			
2.5	2.20E-08	8.10E-13						

ash dosage (≤ 1.5 g) and decreased with sorption temperature. An Arrhenius type relationship ($R^2 > 0.9$) was seen between k_i (k_1 , k_2 or k_{id}) and temperature as seen through Eq. (10) with the activation energy (E_A) calculated to be < 22 kJ mol⁻¹; R (8.314 J mol⁻¹ K⁻¹) is the gas constant, T (K) is the temperature and k_0 is the Arrhenius factor. This is consistent with values reported in literature where Nolle et al. (2003) provided similar observations for fly ash in experiments involving the adsorptive separation of PCBs. The low energy of activation also suggested that diffusion processes featured strongly in determining the rate and that, the sorption was physical in nature (Dogán et al., 2009). Besides, it can also be advocated that Van der Waal's and electrostatic interactions occur between urea (polar compound) and the surface of fly ash particles. The initial rate of urea adsorption displayed an inverse relationship with temperature; such experimental findings have been reported by others where the suggestive explanation for such behavior is that, adsorbate-adsorbent forces of attraction tend to be weak for exothermic processes (Ofomaja and Unuabonah, 2013).

$$\ln k_i = \ln k_0 - \frac{E_A}{RT} \quad (10)$$

While intra-particle diffusion also plays a part in determining the kinetics of urea removal from synthetic urine, it is not the primary factor in controlling the sorption rate. The sorption is likely to be described through a complex mechanism where, the rate is controlled by both surface and pore diffusion (Chaturvedi et al., 1988). This was confirmed through q_t versus $t^{0.5}$ plots (Fig. S4) which did not pass through the origin. k_{id} was observed to decrease with sorption temperature. Also, intercepts of the intra-particle diffusion plots that provided an estimation of the thickness of the boundary layer decreased with temperature which in part, helps explain the lower sorption capacity at higher temperatures. In addition, it is known that the solubility of urea in water increases with temperature (Pinck and Kelly, 1925); as Chiou et al. (1979) note, decreased sorption is to be expected with increasing temperatures for compounds whose solubility exhibits a direct positive relationship with temperature. The results are in agreement with studies conducted elsewhere involving phenols (Gupta et al.,

1998; Sarkar et al., 2003) and other organic micropollutants (Hulscher and Cornelissen, 1996).

3.6. Mass transfer and rate determination

Linear plots based on Eq. (2) were obtained and used for the estimation of the mass transfer coefficient using the method of slopes (Fig. S5). As seen in Table 5, the mass transfer analysis again confirmed the significant contribution of fly ash loading and initial solute concentration in determining the extent and rate of urea adsorption. To determine and distinguish the mechanism governing the transfer and/or diffusion of urea molecules, the procedure detailed by Boyd et al. (1947), Reichenberg (1953) and Helfferich (1962) was followed (Eqs. (11) and (12)). F is calculated as the ratio of q_t to q_∞ , i.e. the fraction of urea adsorbed (mg g⁻¹) with respect to urea adsorption at infinite time (in this study, 5 h). Bt versus time plots were linear ($R^2 > 0.86$) for $t < 300$ s but did not pass through the origin (Fig. 5). Ignoring the surface adsorption of urea that can be assumed to be spontaneous and thus, no n-rate-controlling, it can be suggested here that film diffusion of urea features stronger than its pore diffusion and thus, is rate determining. The estimated coefficient of diffusion values are provided in Table 5 and were found to vary between 7.07×10^{-13} and 1.77×10^{-11} cm² s⁻¹.

$$F = 1 - \frac{6}{\pi^2} \exp(-Bt) \quad (11)$$

$$Bt = -0.498 - \ln \left(1 - \frac{q}{q_e} \right) \quad (12)$$

3.7. Linear and non-linear isotherm analysis

Isotherm analysis was conducted by testing sorption data from experiments involving the change in concentration (ΔC), ash dosage (ΔW) and temperature (ΔT) against 9 isotherm models. Initially, regression of the data against linearized two parameter equations was performed and results are summarized in Table 6. The favorability of the sorption process investigated was confirmed by the estimated separation factor

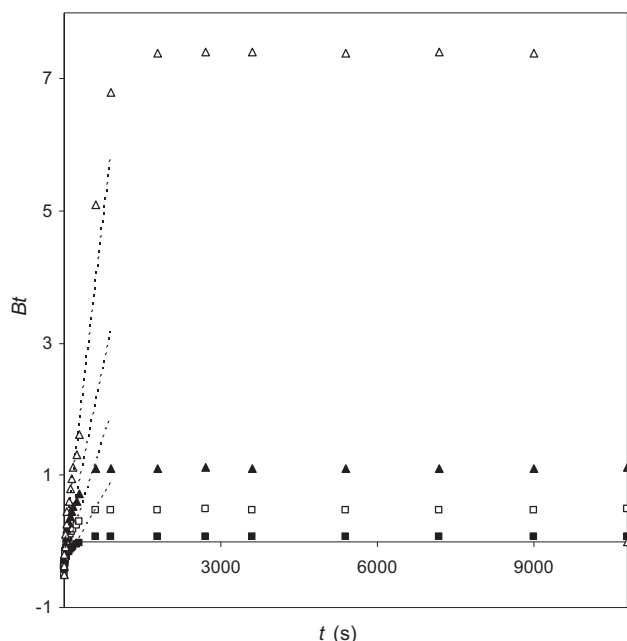


Fig. 5 Bt versus t plots for urea adsorption with 1.5 g ash loading, 30 °C, 100 rpm and pH = 6.0 at various initial concentrations: 3.375 g L⁻¹ (■), 6.75 g L⁻¹ (□), 10.125 g L⁻¹ (▲) and 13.5 g L⁻¹ (○).

($0 < R_L < 1$) as well as the Freundlich adsorption intensity ($n_{FR} > 2$). Thermodynamic parameters were evaluated using the Eyring equation (Doğan et al., 2009) and found to be as follows $-\Delta H^*$: -75.4 kJ mol⁻¹, ΔS^* : +0.19 kJ mol⁻¹ and ΔG^* varied as -129 to -132 kJ mol⁻¹. In addition, the average free energy (E_s) calculated using the Dubinin-Radushkevich model constant was found to be <8 kJ mol⁻¹ affirming that the process was indeed physical. Utilizing a criterion of high R^2 , low ND and low NSD indicated that, the Flory-Huggins isotherm was seen as an appropriate choice of linearized isotherm model equation. This indicated that that urea adsorption onto coal fly ash was a spontaneous process and that, the removal of urea from urine followed the mechanism of physisorption.

Results of the non-linear regression and error analysis performed as per the guiding notes of Ho et al. (2002, p.10) are presented in Tables 7-9. For every model equation, the parameter set that resulted in the least Err_{SN} was considered the optimal solution and was used to further evaluate the correlation between experimental and predicted adsorption capacity of fly ash as investigated under various process conditions. For example, as seen in Table 7 for the Toth model, minimum Err_{SN} was 4.8 suggesting the model parameters Q_t , K_t and t_t were 401, 2.5 and 3, respectively. Considering the overall analysis (four isotherms and three modules) where the optimization objective was to minimize Err_{SN} , Err_{SS} and Err_{MPSD} provided the best parameters sets across eight systems. Moreover, the

Table 6 Linear analysis of two parameter isotherm models for urea sorption.

Isotherm model	Parameter	ΔC	ΔW	ΔT
Langmuir Isotherm	R^2	0.6725	0.8436	0.8336
	q_m	203.66	434.78	277.78
	K_L	0.0015	0.0037	0.0024
	R_L	0.0458	0.0191	0.0290
	ND^a	17.6893	6.2982	5.6171
	NSD^b	19.1382	7.6347	5.8886
Freundlich Isotherm	R^2	0.8548	0.5440	0.9470
	K_f	7474	156	2376
	n_{FR}	2.506	9.285	4.063
	ND	11.4378	8.9060	3.1528
	NSD	12.0186	11.3696	3.4294
	Flory-Huggins	R^2	0.8854	0.9872
Ka		1.3E-05	2.5E-05	3.8E-05
ND		13.7433	1.8813	0.3682
NSD		16.9989	2.1091	0.3962
Dubinin-Radushkevich	R^2	0.6809	0.8367	0.8714
	q_s	202.73	423.56	270.75
	K_{ad}	0.3607	0.0792	0.2025
	E_s	1.1774	2.5126	1.5713
	ND	15.4855	5.1833	33.9692
	NSD	18.1836	6.7256	38.3323
Tempkin	R^2	0.9295	0.5376	0.9689
	B	-114.719	35.453	85.204
	A	2.1E-05	12.424	2.8531
	ND	8.4046	8.7402	2.5868
	NSD	9.6657	11.2877	2.8538

^a ND : Normalized Deviation.

^b NSD : Normalized Standard Deviation.

Table 7 Three parameter isotherm analysis at various fly ash loadings.

	Err_{SS}	Err_{CF}	Err_{MPSD}	Err_{AR}	Err_{SA}
<i>Redlich-Peterson</i>					
A_{RP}	94.016	154.232	40.769	90.001	9.799
B_{RP}	0.256	0.420	0.111	0.256	0.026
g	0.990	0.990	0.990	0.984	0.990
Err_{SS}	489.577	475.242	541.257	645.723	884.162
Err_{CF}	1.230	1.193	1.356	1.619	2.201
Err_{MPSD}	0.003	0.003	0.003	0.004	0.005
Err_{AR}	0.079	0.079	0.084	0.090	0.104
Err_{SA}	31.643	31.552	33.445	35.909	41.436
Err_{SN}	3.434	3.452	3.471	4.211	4.199
<i>Sips</i>					
Q_s	399.261	399.058	398.853	401.039	401.039
K_s	3.585	4.000	4.000	6.000	2.000
$1/n$	4.256	5.000	5.000	3.000	2.499
Err_{SS}	242.119	242.244	242.619	251.600	251.600
Err_{CF}	0.611	0.611	0.611	0.640	0.640
Err_{MPSD}	0.002	0.002	0.002	0.002	0.002
Err_{AR}	0.059	0.060	0.060	0.055	0.055
Err_{SA}	23.567	23.770	23.975	21.789	21.789
Err_{SN}	4.889	4.863	4.837	4.805	4.792
<i>Toth</i>					
Q_t	399.262	399.058	398.853	401.039	401.039
K_t	413.974	25.000	2.500	1.200	2.500
t_t	1.533	3.000	3.100	3.800	3.000
Err_{SS}	242.119	242.244	242.619	251.600	251.600
Err_{CF}	0.611	0.611	0.611	0.640	0.640
Err_{MPSD}	0.002	0.002	0.002	0.002	0.002
Err_{AR}	0.059	0.060	0.060	0.055	0.055
Err_{SA}	23.565	23.770	23.975	21.789	21.789
Err_{SN}	4.889	4.863	4.837	4.805	4.792
<i>Koble-Corrigan</i>					
A_{KC}	45.680	23.726	21.158	2.208	8.591
B_{KC}	0.114	0.059	0.053	0.006	0.021
n_{KC}	3.727	3.052	2.505	2.267	5.000
Err_{SS}	242.119	242.245	242.599	251.726	251.599
Err_{CF}	0.611	0.611	0.611	0.640	0.640
Err_{MPSD}	0.002	0.002	0.002	0.002	0.002
Err_{AR}	0.059	0.060	0.060	0.055	0.055
Err_{SA}	23.567	23.771	23.965	21.797	21.789
Err_{SN}	4.890	4.863	4.837	4.807	4.794

Bold values indicate minimum value for an error function.

Redlich–Peterson model, using parameters derived from Err_{MPSD} and Err_{SS} , was able to adequately capture the sorption process across all the systems (Table S6). Since the Redlich–Peterson model is derived from a combination of the Freundlich and Langmuir isotherm model relations, the fit of the experimental data is expectedly better than either of them; further, this is also indicative of surface heterogeneity of the fly ash in providing the active sites for urea adsorption.

3.8. System design

The design of a batch adsorption system can be carried out using the results of the isotherm analysis which indicated that as far as the three parameter models are concerned, the relationship between q_e and C_e can be adequately described by the Redlich–Peterson equation (Eq. (13)). Assuming that the

fly ash does not adsorb any water from the solute, the adsorbate balance can be expressed as in Eq. (14). Simultaneously solving Eqs. (13) and (14) yields the amount of fly ash required (Eq. (15)) to result in a predetermined extent of reduction/removal of the target compound.

$$q_e = \frac{A_{RP}C_e}{1 + B_{RP}C_e^g} \quad (13)$$

$$W = \frac{V(C_0 - C_e)}{q_e} \quad (14)$$

$$W = \frac{V(C_0 - C_e) \cdot (1 + B_{RP}C_e^g)}{A_{RP}C_e} \quad (15)$$

Since a multistage adsorber reduces the amount of adsorbent required to effect the same reduction in the target compound vis-à-vis single stage adsorption, let us consider a

Table 8 Three parameter isotherm analysis at various sorption temperatures.

	Err_{SS}	Err_{CF}	Err_{MPSD}	Err_{AR}	Err_{SA}
<i>Redlich-Peterson</i>					
A_{RP}	188.671	22.130	37.614	112.117	21.056
B_{RP}	0.549	0.603	1.738	0.373	5.150
G	1.000	0.733	0.672	0.985	0.454
Err_{SS}	8131.302	33961.232	41852.358	9225.291	66788.550
Err_{CF}	24.029	89.208	108.126	26.439	186.054
Err_{MPSD}	0.073	0.240	0.285	0.078	0.536
Err_{AR}	0.391	0.734	0.807	0.395	1.037
Err_{SA}	131.442	262.962	292.286	134.931	359.544
Err_{SN}	2.395	2.332	2.263	3.244	3.285
<i>Sips</i>					
Q_s	343.784	336.007	328.505	346.037	339.712
K_s	15.115	0.250	1.207	0.997	5.000
$1/n$	27.440	25.000	2.376	0.492	1.001
Err_{SS}	8073.463	8254.926	8773.851	8824.717	8129.507
Err_{CF}	23.872	23.332	23.835	25.314	23.468
Err_{MPSD}	0.073	0.068	0.067	0.075	0.070
Err_{AR}	0.389	0.380	0.394	0.387	0.373
Err_{SA}	130.965	130.557	138.059	131.998	126.916
Err_{SN}	4.766	4.733	4.700	4.936	4.770
<i>Toth</i>					
Q_t	343.786	336.003	328.538	339.691	339.691
K_t	5.853	1.200	4.431	1.000	5.318
t_t	2.036	2.531	2.364	3.000	13.552
Err_{SS}	8073.463	8255.115	8770.745	8123.714	8123.713
Err_{CF}	23.872	23.332	23.830	23.453	23.453
Err_{MPSD}	0.073	0.068	0.067	0.070	0.070
Err_{AR}	0.389	0.380	0.393	0.373	0.373
Err_{SA}	130.967	130.561	138.026	126.873	126.873
Err_{SN}	4.714	4.940	4.767	4.850	4.733
<i>Koble-Corrigan</i>					
A_{KC}	211.244	184.555	134.891	54.996	87.291
B_{KC}	19.000	40.000	10.000	15.000	32.000
n_{KC}	0.050	0.050	0.100	0.195	0.129
Err_{SS}	11516.085	11730.433	16663.276	24406.391	18150.403
Err_{CF}	33.549	32.805	44.409	67.818	50.735
Err_{MPSD}	0.101	0.095	0.122	0.195	0.147
Err_{AR}	0.462	0.444	0.525	0.624	0.541
Err_{SA}	156.646	153.621	186.137	216.541	187.326
Err_{SN}	3.379	3.381	3.384	4.162	4.158

Bold values indicate minimum value for an error function.

two stage adsorber wherein the amount of fly ash required in each stage can be estimated by Eqs. (16) and (17). With the objective of minimization of the total ($M_1 + M_2$) amount of fly ash required (Eq. (18)), an expression for the intermediate concentration (C_1 in this case) as a function of initial and equilibrium adsorbate concentration can be found (Eq. (19)). By simultaneously considering Eqs. (16), (17), and (19), an expression unique to the investigated system was found for multistage adsorption involving N stages (Eq. (20)).

$$W_1 = \frac{V(C_0 - C_1) \cdot (1 + B_{RP}C_1^g)}{A_{RP}C_1} \quad (16)$$

$$W_2 = \frac{V(C_1 - C_e) \cdot (1 + B_{RP}C_e^g)}{A_{RP}C_e} \quad (17)$$

$$\frac{\partial(W_1 + W_2)}{\partial C_1} = \frac{\partial}{\partial C_1} \left\{ \frac{V(C_1 - C_e) \cdot (1 + B_{RP}C_e^g)}{A_{RP}C_e} \right\} = 0 \quad (18)$$

$$C_1 = (C_0 \cdot C_e)^{1/2} \quad (19)$$

$$\sum W_1 + W_2 + \dots + W_N = \frac{V \cdot (1 + B_{RP}C_e^g)}{A_{RP}} \left\{ \left(\frac{C_0}{C_e} \right)^{N-1} - 1 \right\} \quad (20)$$

Under the experimental conditions of pH = 6.0, sorption temperature of 30 °C, shaker speed of 150 rpm and initial urea concentration as 13.5 g L⁻¹, the minimum amount of fly ash required for 90% removal of urea from different volumes of influent synthetic urine solutions was calculated and is enlisted

Table 9 Three parameter isotherm analysis at various initial concentrations.

	Err_{SS}	Err_{CF}	Err_{MPSD}	Err_{AR}	Err_{SA}
<i>Redlich-Peterson</i>					
A_{RP}	200.536	200.000	250.017	250.000	200.530
B_{RP}	0.792	0.843	1.124	0.730	0.674
G	0.990	0.990	0.990	0.161	0.254
Err_{SS}	11446.979	12191.951	14263.185	12758.935	12605.282
Err_{CF}	50.425	47.286	50.084	56.886	56.210
Err_{MPSD}	0.242	0.201	0.188	0.275	0.272
Err_{AR}	0.673	0.693	0.712	0.704	0.700
Err_{SA}	153.635	169.388	184.262	159.641	158.675
Err_{SN}	5.019	4.586	4.279	4.889	4.481
<i>Sips</i>					
Q_s	253.003	237.250	222.363	255.382	255.382
K_s	5.000	5.009	2.000	2.000	1.890
$1/n$	5.356	2.758	3.000	4.000	3.500
Err_{SS}	11439.137	12183.638	14255.582	11456.118	11456.118
Err_{CF}	50.396	47.258	50.061	51.415	51.415
Err_{MPSD}	0.242	0.201	0.188	0.250	0.250
Err_{AR}	0.672	0.693	0.712	0.669	0.669
Err_{SA}	153.579	169.332	184.219	151.200	151.200
Err_{SN}	4.264	4.873	4.520	4.797	4.394
<i>Toth</i>					
Q_t	253.003	237.229	222.363	417.076	450.031
K_t	250.002	277.458	149.994	24.998	25.028
t_t	3.138	1.044	2.192	0.194	0.185
Err_{SS}	11439.137	12185.592	14255.575	14455.273	14764.362
Err_{CF}	50.396	47.258	50.061	63.978	65.285
Err_{MPSD}	0.242	0.201	0.188	0.308	0.314
Err_{AR}	0.672	0.693	0.712	0.747	0.755
Err_{SA}	153.579	169.353	184.219	169.985	171.798
Err_{SN}	4.545	4.243	3.989	4.742	4.608
<i>Koble-Corrigan</i>					
A_{KC}	34.205	50.464	45.006	40.001	44.800
B_{KC}	0.135	0.213	0.202	0.157	0.175
n_{KC}	3.643	3.500	4.000	2.500	3.000
Err_{SS}	11439.137	12183.579	14255.583	11456.117	11456.119
Err_{CF}	50.396	47.258	50.061	51.415	51.415
Err_{MPSD}	0.242	0.201	0.188	0.250	0.250
Err_{AR}	0.672	0.693	0.712	0.669	0.669
Err_{SA}	153.579	169.331	184.219	151.200	151.200
Err_{SN}	5.306	4.873	4.520	4.797	4.394

Bold values indicate minimum value for an error function.

Table 10 Estimation of the total amount of fly ash required for 90% removal of urea from different volumes of synthetic urine.

N	Volume [L] of solution containing $[\text{CO}(\text{NH}_2)_2]$: 13.5 g L^{-1}									
	1	5	10	25	50	100	300	750	1000	5000
1	53.03	265.13	530.26	1325.66	2651.31	5302.63	15907.88	39769.71	53026.28	265131.41
2	12.74	63.70	127.40	318.49	636.99	1273.97	3821.92	9554.80	12739.73	63698.64
3	6.80	34.01	68.02	170.04	340.09	680.17	2040.51	5101.28	6801.71	34008.54
4	4.59	22.93	45.85	114.64	229.27	458.55	1375.64	3439.11	4585.47	22927.37
5	3.45	17.23	34.46	86.15	172.30	344.61	1033.82	2584.56	3446.08	17230.40
6	2.76	13.78	27.56	68.90	137.81	275.62	826.86	2067.14	2756.18	13780.92
7	2.29	11.47	22.95	57.37	114.74	229.48	688.45	1721.12	2294.83	11474.17
8	1.97	9.83	19.65	49.13	98.25	196.50	589.51	1473.78	1965.04	9825.22
9	1.72	8.59	17.18	42.94	85.89	171.78	515.33	1288.32	1717.75	8588.77
10	1.53	7.63	15.26	38.14	76.28	152.55	457.66	1144.15	1525.54	7627.70

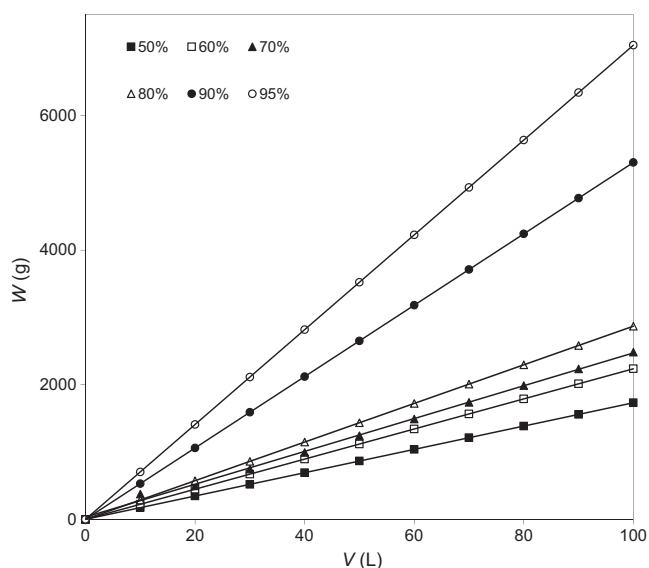


Fig. 6 Estimation of amount of fly ash (g) required to treat a given volume of wastewater (synthetic urine in this study) under various removal (%) of urea scenarios.

in Table 10. It is evident that increasing the number of stages decreases the total fly ash required while increasing the volume of urine necessitates higher ash dosages (Fig. 6).

4. Conclusions

The present study demonstrated the potential of utilizing untreated coal fly ash in wastewater treatment by using adsorptive recovery of urea from synthetic urine solutions as the case study. While pH and shaker speed have insignificant interactive effects on the sorption, high initial concentration and low temperatures at an ideal fly ash dosage (1.5 g) resulted in a maximum urea adsorption capacity of 410 mg g^{-1} . Flory–Huggins (two parameter; linear analysis) and Redlich–Peterson (three parameter; non-linear analysis) isotherm models were found to best represent the experimental data. In addition to the evaluation of process mass transfer and kinetic mechanisms, a mathematical basis for system design was advocated by estimating the minimum fly ash dosage required under various scenarios for single and multistage adsorption.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabjc.2016.11.013>.

References

- Acemioğlu, B., 2004. Adsorption of Congo red from aqueous solution onto calcium-rich fly ash. *J. Colloid Interface Sci.* 274 (2), 371–379.
- Ahmaruzzaman, M., 2010. A review on the utilization of fly ash. *Prog. Energy Combust. Sci.* 36 (3), 327–363.
- Bandura, L., Franus, M., Józefaciuk, G., Franus, W., 2015. Synthetic zeolites from fly ash as effective mineral sorbents for land-based petroleum spills cleanup. *Fuel* 147, 100–107.
- Bandura, L., Panek, R., Rotko, M., Franus, W., 2016. Synthetic zeolites from fly ash for an effective trapping of BTX in gas stream. *Microporous Mesoporous Mater.* 223, 1–9.
- Beér, J., 2013. CO₂ reduction and coal-based electricity generation. In: Malhotra, R. (Ed.), *Fossil Energy: Selected Entries from the Encyclopedia of Sustainability Science and Technology*. Springer, New York, pp. 475–488. http://dx.doi.org/10.1007/978-1-4614-5722-0_13.
- Bhargava, R., Mathur, R.P., Khanna, P., 1974. Removal of detergent from wastewater by adsorption on fly ash. *Indian J. Environ. Health* 16 (2), 109–120.
- Blissett, R.S., Rowson, N.A., 2012. A review of the multi-component utilisation of coal fly ash. *Fuel* 97, 1–23.
- Boyd, G.E., Adamson, A.W., Meyers, L.S., 1947. The exchange adsorption of ions from aqueous solution by organic zeolites II, kinetics. *J. Am. Chem. Soc.* 69, 2836.
- Brás, I., Lemos, L., Alves, A., Pereira, M.F.R., 2005. Sorption of pentachlorophenol on pine bark. *Chemosphere* 60 (8), 1095–1102.
- Burns, J.R., Finlayson, B., 1980. A proposal for a standard reference artificial urine in in vitro urolithiasis experiments. *Invest. Urol.* 18 (2), 167.
- Central Electricity Authority, 2015. Report on fly ash generation at coal/lignite based thermal power stations and its utilization in the country for the year 2014–15. Printed by Government of India Press. Published by the Controller of Publications, New Delhi, India. URL: <http://cea.nic.in/reports/others/thermal/tcd/fly-ash_final_1415.pdf> .
- Chattopadhyay, G.C., 2015. Issues in utilization of ash by Thermal Power Plants in the country. *J. Gov. Audit Acc.* 3. Available at: <http://www.cag.gov.in/sites/default/files/cag_pdf/august-2015/home.html> .
- Chaturvedi, A.K., Pathak, K.C., Singh, V.N., 1988. Fluoride removal from water by adsorption on china clay. *Appl. Clay Sci.* 3 (4), 337–346.
- Chiou, C.T., Peters, L.J., Freed, V.H., 1979. A physical concept of soil–water equilibria for nonionic organic compounds. *Science* 206 (4420), 831–832.
- Cho, H., Oh, D., Kim, K., 2005. A study on removal characteristics of heavy metals from aqueous solution by fly ash. *J. Hazard. Mater.* 127 (1), 187–195.
- Ciba-Geigy (Ed.), 1977. *Wissenschaftliche Tabellen Geigy. Teilband Körperflüssigkeiten*, Basel.
- Dhadse, S., Kumari, P., Bhagia, L.J., 2008. Fly ash characterization, utilization and government initiatives in India – a review. *J. Sci. Ind. Res.* 67 (1), 11–18.
- Doğan, M., Abak, H., Alkan, M., 2009. Adsorption of methylene blue onto hazelnut shell: kinetics, mechanism and activation parameters. *J. Hazard. Mater.* 164 (1), 172–181.
- Foo, K.Y., Hameed, B.H., 2010. Insights into the modeling of adsorption isotherm systems. *Chem. Eng. J.* 156 (1), 2–10.
- Ganesapillai, M., Simha, P., Desai, K., Sharma, Y., Ahmed, T., 2016. Simultaneous resource recovery and ammonia volatilization minimization in animal husbandry and agriculture. *Resour.-Eff. Technol.* 2 (1), 1–10.
- Ganesapillai, M., Simha, P., Zabaniotou, A., 2015. Closed-loop fertility cycle: realizing sustainability in sanitation and agricultural production through the design and implementation of nutrient recovery systems for human urine. *Sustain. Prod. Consum.* 4, 36–46.

- González, A., Navia, R., Moreno, N., 2009. Fly ashes from coal and petroleum coke combustion: current and innovative potential applications. *Waste Manage. Res.* 27 (10), 976–987.
- Gupta, V.K., Ali, I., 2001. Removal of DDD and DDE from wastewater using bagasse fly ash, a sugar industry waste. *Water Res.* 35 (1), 33–40.
- Gupta, V.K., Sharma, S., Yadav, I.S., Mohan, D., 1998. Utilization of bagasse fly ash generated in the sugar industry for the removal and recovery of phenol and p-nitrophenol from wastewater. *J. Chem. Technol. Biotechnol.* 71 (2), 180–186.
- Helfferich, H., 1962. *Ion-Exchange*. McGraw-Hill, New York.
- Ho, Y.S., McKay, G., 1998. Sorption of dye from aqueous solution by peat. *Chem. Eng. J.* 70 (2), 115–124.
- Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption processes. *Process Biochem.* 34 (5), 451–465.
- Ho, Y.S., Porter, J.F., McKay, G., 2002. Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems. *Water Air Soil Pollut.* 141 (1–4), 1–33.
- Hulscher, T.E., Cornelissen, G., 1996. Effect of temperature on sorption equilibrium and sorption kinetics of organic micropollutants—a review. *Chemosphere* 32 (4), 609–626.
- Itskos, G., Koukouzas, N., Vasilatos, C., Megremi, I., Moutsatsou, A., 2010. Comparative uptake study of toxic elements from aqueous media by the different particle-size-fractions of fly ash. *J. Hazard. Mater.* 183 (1), 787–792.
- Iyer, R.S., Scott, J.A., 2001. Power station fly ash—a review of value-added utilization outside of the construction industry. *Resour. Conserv. Recycl.* 31 (3), 217–228.
- Jain, K.K., Prasad, G., Sinha, V.N., 1980. Application of Langmuir isotherm for oxalic adsorption by fly ash and activated carbon. *Ind. J. Chem. Sect. A – Inorg. Bio-Inorg. Phys. Theor. Anal. Chem.* 19, 154–156.
- Jala, S., Goyal, D., 2006. Fly ash as a soil ameliorant for improving crop production—a review. *Bioresour. Technol.* 97 (9), 1136–1147.
- Javadian, H., Ghorbani, F., Tayebi, H.A., Asl, S.H., 2015. Study of the adsorption of Cd (II) from aqueous solution using zeolite-based geopolymer, synthesized from coal fly ash; kinetic, isotherm and thermodynamic studies. *Arab. J. Chem.* 8 (6), 837–849.
- Jedidi, I., Saïdi, S., Khmakem, S., Larbot, A., Elloumi-Ammar, N., Fourati, A., Charf, A., Amar, R.B., 2009. New ceramic microfiltration membranes from mineral coal fly ash. *Arab. J. Chem.* 2 (1), 31–39.
- Kirchmann, H., Pettersson, S., 1994. Human urine—chemical composition and fertilizer use efficiency. *Fertil. Res.* 40 (2), 149–154.
- Koukouzas, N., Ketikidis, C., Itskos, G., Spiliotis, X., Karayannis, V., Papapolymerou, G., 2011. Synthesis of CFB-coal fly ash clay bricks and their characterisation. *Waste Biomass Valoriz.* 2 (1), 87–94.
- Kumar, R., Kumar, S., Mehrotra, S.P., 2007. Towards sustainable solutions for fly ash through mechanical activation. *Resour. Conserv. Recycl.* 52 (2), 157–179.
- Luderer, G., Bosetti, V., Jakob, M., Leimbach, M., Steckel, J.C., Waisman, H., Edenhofer, O., 2012. The economics of decarbonizing the energy system – results and insights from the RECIPE model intercomparison. *Climatic Change* 114 (1), 9–37.
- McKay, G., Allen, S.J., McConvey, I.F., Otterburn, M.S., 1981. Transport processes in the sorption of colored ions by peat particles. *J. Colloid Interface Sci.* 80 (2), 323–339.
- Newcombe, G., Drikas, M., 1997. Adsorption of NOM onto activated carbon: electrostatic and non-electrostatic effects. *Carbon* 35 (9), 1239–1250.
- Nollet, H., Roels, M., Lutgen, P., Van der Meeren, P., Verstraete, W., 2003. Removal of PCBs from wastewater using fly ash. *Chemosphere* 53 (6), 655–665.
- Ofomaja, A.E., Unuabonah, E.I., 2013. Kinetics and time-dependent Langmuir modeling of 4-nitrophenol adsorption onto *Mansonia* sawdust. *J. Taiwan Inst. Chem. Eng.* 44 (4), 566–576.
- Pillai, M.G., Simha, P., Gugalia, A., 2014. Recovering urea from human urine by bio-sorption onto microwave activated carbonized coconut shells: equilibrium, kinetics, optimization and field studies. *J. Environ. Chem. Eng.* 2 (1), 46–55.
- Pinck, L.A., Kelly, M.A., 1925. The solubility of urea in water. *J. Am. Chem. Soc.* 47 (8), 2170–2172.
- Pronk, W., Palmquist, H., Biebow, M., Boller, M., 2006. Nanofiltration for the separation of pharmaceuticals from nutrients in source-separated urine. *Water Res.* 40 (7), 1405–1412.
- Radovic, L.R., Silva, I.F., Ume, J.I., Menendez, J.A., Leon, C.L.Y., Scaroni, A.W., 1997. An experimental and theoretical study of the adsorption of aromatics possessing electron-withdrawing and electron-donating functional groups by chemically modified activated carbons. *Carbon* 35 (9), 1339–1348.
- Reichenberg, D., 1953. Properties of ion-exchange resins in relation to their structure III, kinetics of exchange. *J. Am. Chem. Soc.* 75, 589–592.
- Sarkar, M., Acharya, P.K., Bhattacharya, B., 2003. Modeling the adsorption kinetics of some priority organic pollutants in water from diffusion and activation energy parameters. *J. Colloid Interface Sci.* 266 (1), 28–32.
- Sarkar, M., Acharya, P.K., 2006. Use of fly ash for the removal of phenol and its analogues from contaminated water. *Waste Manage.* 26 (6), 559–570.
- Wang, S., 2008. Application of solid ash based catalysts in heterogeneous catalysis. *Environ. Sci. Technol.* 42 (19), 7055–7063.
- Wang, S., Wu, H., 2006. Environmental-benign utilisation of fly ash as low-cost adsorbents. *J. Hazard. Mater.* 136 (3), 482–501.
- Wang, S., Boyjoo, Y., Choueib, A., Zhu, Z.H., 2005. Removal of dyes from aqueous solution using fly ash and red mud. *Water Res.* 39 (1), 129–138.
- Weber, W.J., Morris, J.C., 1963. Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div.* 89 (2), 31–60.
- With, T.K., Petersen, T.D., Petersen, B., 1961. A simple spectrophotometric method for the determination of urea in blood and urine. *J. Clin. Pathol.* 14, 202–204.
- World Bank, 2016. World Development Indicators – Electricity production from coal sources (% of total). URL: <<http://data.worldbank.org/indicator/EG.ELC.COAL.ZS>>.
- Wu, X.D., Xia, X.H., Chen, G.Q., Wu, X.F., Chen, B., 2016. Embodied energy analysis for coal-based power generation system—highlighting the role of indirect energy cost. *Appl. Energy*. <http://dx.doi.org/10.1016/j.apenergy.2016.03.027>.
- Yadav, A., Ansari, K.B., Simha, P., Gaikar, V.G., Pandit, A.B., 2016. Vacuum Pyrolysed Biochar for Soil Amendment. *Resource-Efficient Technologies* (in press). <http://dx.doi.org/10.1016/j.refitt.2016.11.004>
- Yao, Z.T., Ji, X.S., Sarker, P.K., Tang, J.H., Ge, L.Q., Xia, M.S., Xi, Y.Q., 2015. A comprehensive review on the applications of coal fly ash. *Earth Sci. Rev.* 141, 105–121.
- Young, O.R., Berkhout, F., Gallop, G.C., Janssen, M.A., Ostrom, E., Van Der Leeuw, S., 2006. The globalization of socio-ecological systems: an agenda for scientific research. *Glob. Environ. Change* 16 (3), 304–316.