The effect of demineralisation on characteristics and adsorption behaviour of activated carbons prepared from swine manure

L. Gonsalvesh[1*], A. Popova[2], S. P. Marinov[2], M. Stefanova[2], R. Carleer[3], J. Yperman[3]

[1] Central Scientific Research Laboratory, Assen Zlatarov University, Burgas 8000, Bulgaria
[2] Institute of Organic Chemistry with Centre of Phytochemistry, BAS, Sofia 1113, Bulgaria
[3] Hasselt University, CMK, Research group of Applied and Analytical Chemistry, Agoralaan – gebouw D, B-3590 Diepenbeek, Belgium

Dedicated to Acad. Ivan Juchnovski on the occasion of his 80th birthday

Activated carbons (ACs) from swine manure (SM), i.e. preliminary de-watered SM cake (Mc) and solid digestate (Md) were prepared by pyrolysis and water vapour activation. Demineralisation on obtained chars after carbonization was applied as well. Additionally, the adsorption capacity of demineralised ACs towards chromium in aqueous solutions was investigated and compared to non-demineralised ACs. Demineralisation caused a decrease in mineral matter content with more than 50% and affected characteristics and adsorption behaviour of these ACs. As a result, ACs with better developed porous texture were produced. Prepared ACs with reduced ash content demonstrated higher adsorption capacity toward Cr compared to non-demineralised ACs. The adsorption kinetics were investigated by applying two kinetic models, i.e. Lagergren pseudo-first order and pseudo-second order. The pseudo-second order kinetic model provided a better fit. Better fits are obtained for the Langmuir isotherm model and therefore a monolayer coverage chemisorption of the Cr(VI) on the ACs surface is suggested.

Key words: swine manure; activated carbons; demineralisation; adsorption; chromium ions

INTRODUCTION

Increasing awareness and environmental concern towards manure wastes impact on environmental contamination, reflecting in public health and biosystems life quality, determine the focus of scientific interest on minimization, re-use and recycling of these wastes into value added products. In this regard, thermochemical conversion technologies, i.e. pyrolysis, have been widely applied for successful manure valorisation. Pyrolysis results in high-energy-density volatile gases (condensable and non-condensable) that can be used as a fuel or chemical feedstock and a solid fraction (char) that could be applied as soil amendments [1,2]. Additionally, a profitable method for manure char utilization is the preparation of activated carbons (ACs) after char upgrade at higher temperature by means of physical or chemical treatment. Several studies on ACs preparation from manures and their usage for heavy metals remediation in aqueous solution have been reported. Recently, Lima and Marshall have prepared ACs from turkey manure by steam activation and used them for copper removal from aqueous solution [3]. They found that physical,

chemical and adsorptive properties were all dependent on the activation conditions, i.e. steam flow rate and activation time. Yields, surface area and Cu^{2+} adsorption up to 37 wt.%, 472 m^2 g^{-1} and 1.86 mmol g^{-1}, respectively, are achieved. Studied ACs were considered to have substantial potential in Cu^{2+} removal from water. Similar results were obtained for ACs prepared from broiler manure [4]. Poultry manure based ACs have shown excellent adsorption properties towards Cd and Zn as well [5]. Actually, their metal ion sequestering ability greatly exceeded characteristics of carbons made from conventional feedstocks, i.e. coal, coconut shell and wood, and of commercial ACs. Cattle-manure compost has been also efficiently converted to ACs [6,7]. Relatively high yields up to 47.5 wt.% and large surface area up to 2170 m^2 g^{-1} were obtained as a result of chemical activation by $ZnCl_2$. Cattle-manure compost based ACs have been successfully applied for removal of metal ions [8] and organic pollutants [9]. Swine manures have been also tested for activated carbons preparation [10,11]. Swine manure-based carbons demonstrated excellent adsorption abilities and a preference towards ions of copper, followed by zinc and cadmium. It is assumed that negatively charged phosphate groups attached to the carbon skeleton are responsible for their affinity towards positively

charged metal ions. In several investigations the effect of mineral matter removal on the characteristics of ACs has been examined. The removal of inorganic matter decreases char reactivity [12,13] and changes the surface area development of the carbons [14]. Similar behaviour has been observed for chars produced from six different lignites [15]. Fernandez-Morales and co-workers concluded that the demineralization process resulted in lowering the char reactivity and in an activation energy increase. For different rank coals, i.e. from lignite to anthracite, the effect of inorganic matter removal on surface area development, respectively adsorption behaviour, has been verified by Mahajan and Walker [16]. They found that inorganic matter removal by acid treatment resulted in random but significant changes in surface areas. It has been assumed that coal inorganic matter removal prior to carbonization affects the subsequent heating process and, hence, the surface area of the resultant material. The author admitted that surface area changes could be related to the inorganic matter removal from the orifice and to the displacement of insoluble inorganic species from the cavities, as well as to acid retention in the coal porous structure.

The aim of the present study is to elucidate the effect of demineralisation on the characteristics and adsorption properties of ACs produced from swine manures. Additionally, the adsorption capacity of prepared demineralised ACs towards chromium in aqueous solutions will be studied and compared to the non-demineralised ACs.

MATERIALS AND METHODS

Samples and treatments

In current research grounded, sieved (< 2 mm) and oven-dried at 110 ºC swine manure (SM) samples, preliminary de-watered SM cake (Mc) and solid digestate (Md), are under consideration. For activated carbon preparation, a two-steps process, comprising carbonization and physical activation in a stream of water vapour, is carried out. The carbonization of SM samples is performed in an inert atmosphere in a lab-scale pyrolysis reactor, described in a preliminary study [17]. The treatment has been performed by applying heating at a rate of 10 ºC min^{-1} up to a desired pyrolysis temperature of 500 ºC and kept isothermal for 1h. The obtained SM chars (20 g) were treated with 500ml of 5% HCl for 1h at 60ºC in order to reduce ash content. Subsequently, the acid-washed char

was extensively washed with hot distilled water till the lack of chloride ions and then dried. The demineralised chars are labelled as dc-Mc and dc-Md, while non-demineralised chars are marked as c-Mc and c-Md. Demineralised (dc-Mc and dc-Md) and non-demineralised (c-Mc and c-Md) chars were further subjected to activation by steam in a horizontal tubular reactor by applying the following experimental conditions: i) ~8g precursor materials; ii) heating rate of 35 ºC min^{-1} in an inert N$_2$ atmosphere (60 ml min^{-1}) up to activation temperature of 800 °C; iii) isothermal period at 800 ºC for 30 min; and iv) when the activation temperature is reached the inert atmosphere is replaced by a constant steam flow of 330 µL min^{-1}. Activated carbons obtained from demineralised chars are labelled as AC-dc-Mc and AC-dc-Md, while those obtained from non-demineralised chars are marked as AC-Mc and AC-Md.

Analyses

Determinations of proximate analysis (i.e moisture (W), volatile matter (VM), fixed carbon (C$_{fix}$) and ash contents) using DuPont Instrument 951 thermogravimetrical analyser and elemental analysis, i.e. C, H, N, S and O by difference using a Thermo Electron Flash EA1113 elemental analyzer are performed as described in Stals et al. [18]. In our study, pH*pzc* value of ACs is determined following the experimental procedure described by Moreno-Castilla et al. [19]. Porous texture characteristics of ACs are estimated by measuring nitrogen adsorption isotherms at -196 ºC on an automatic sorption apparatus Surfer (Thermo Scientific). The surface area S_{BET} is determined by the *BET* method using data from the adsorption isotherms in the range of relative pressures determined by the criteria of Rouquerol [20-21]. Total pore volume $V_{0.95}$ is determined based on the volume of adsorbate, recorded on the desorption branch of the adsorption isotherm at a relative pressure $P_i/P_o = 0,95$. The micropore volume ($V_{DR,micro}$) is calculated by using the Dubinin-Radushkevich equation up to $P_i/P_o \leq 0.15$ [22]. The pore size distribution and pore diameters L_0 are obtained by applying the Non Local Density Functional Theory (NLDFT) on N$_2$ adsorption data [23].

Adsorption experiments and modelling

The chromium adsorption experiments are performed in thermostatic water bath (25 °C) using 100 ml Erlenmeyer flasks containing 0.030 g of ACs and 50ml of Cr(VI) solutions with

concentrations varying in the range of 10 to 200 mg L^{-1}. The initial chromium solutions are prepared by dissolving $K_2Cr_2O_7$ (oven dried at 105 ºC for 1h) in *Milli-Q water*. The effect of pH of initial solution on Cr adsorption was studied by varying the pH in the range of 1 to 4. The initial pH of solutions is adjusted by adding 0.1N HCl or 0.1N NaOH and is not further altered during the adsorption experimental run. The exact total chromium (Cr$_{tot}$) concentrations of initial and equilibrium solutions are determined by Perkin Elmer Optima 3000 DV ICP AES device, while Cr(VI) concentrations are determined spectrophotometrically after complexing Cr(VI) with 1,5-diphenylcarbo-hydrazide according to the standard method ASTM D1687-92, Test Method A. The chromium adsorption capacities are calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad 1$$

where q_e is the adsorption capacity at equilibrium (mg g^{-1}), C_o and C_e are the Cr initial and equilibrium concentrations (mg L^{-1}), respectively, V is the volume of Cr solutions (L) and m is the weight of AC (g).

Two isotherm models, i.e. Freundlich and Langmuir, are applied to equilibrium adsorption data in order to clarify the mechanism of adsorption and to calculate estimates of adsorbent efficiency. The equilibrium data (experimental values) are fitted with linear forms of the Freundlich (Eq. 2) and Langmuir (Eq. 3) equations in order to determine the model parameters:

$$\log q_e = \frac{1}{n}\log C_e + \log K_F \qquad 2$$

where K_F and n are indicators of adsorption capacity and adsorption intensity, respectively;

$$\frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{K_L q_m} \qquad 3$$

where K_L (L mg^{-1}) and q_m (mg g^{-1}) are the Langmuir constants. K_L is the sorption equilibrium constant for distribution of adsorbate, while q_m is the maximum adsorption capacity which represents the mass of adsorbate adsorbed in a complete monolayer having one molecule thickness per mass of adsorbent. The adsorption kinetics are investigated by varying the contact time up to 72 h in the batch adsorption mode. In order to analyze the adsorption kinetics, two different models, i.e. Lagergren pseudo-first order and pseudo-second order are applied to the experimental data.

The pseudo-first order rate equation of Lagergren in its linear form is presented as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad 4$$

where q_e and q_t (mg g^{-1}) are the adsorption capacities at the equilibrium and at time t (min), respectively, and k_1 (min^{-1}) is the rate constant of the pseudo-first order adsorption. The plot of $\log(q_e-q_t)$ vs t should give a linear relationship in which the value of k_1 can be determined from the slope of the plot.

The pseudo-second order kinetic model can be expressed by the following linear equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad 5$$

where k_2 (g mg^{-1} min^{-1}) is the equilibrium rate constant for the pseudo-second order adsorption. The value of k_2 and adsorption capacity, q_e, can be obtained from the intercept and the slope of the plot of t/q_t vs. t, respectively. The initial adsorption rate, h, of pseudo-second order kinetic can be defined as:

$$h = k_2 q_e^2 \qquad 6$$

Beside the correlation coefficient, a real measure of the validity of pseudo-first (eq. (4)) and pseudo-second order (eq. (5)) kinetic models is the comparison between the experimentally determined q_e values and those obtained from the plots of $\log(q_e-q_t)$ vs. t and t/q_t vs. t, respectively

RESULTS AND DISCUSSION

The proximate and ultimate analyses as well as the char yields after demineralisation and ACs yields are summarised in Table 1. It is obvious that demineralisation with HCl acid results in a product yield of 66.4 wt.% and 69.6 wt.% for dc-Mc and dc-Md samples, respectively. Both samples are characterised by a high C$_{fix}$ content of ~70 wt.%, and an ash content of ~18 wt. %. In general, the ash in swine manures is associated with the pigs bedding material such as shredded corn stalks, different types of straw, wood chips and(or) shredded paper scattered on the floor which could be even not cemented but sandy. All these materials cannot effectively be separated from swine manures and contribute to the mineral matter content of manures. It is revealed that demineralisation treatment results in char's ash content decrease with about 65.5 wt.% for dc-Mc and 55.7 wt.% for dc-Md in comparison to not demineralised chars, c-Mc and c-Md, respectively. The decrease in ash content is mainly related to the removal of carbonates, sulphates, etc., while the remained ash is attributed to HCl acid insoluble inorganics, mainly silicates.

Table 1. Characteristics of samples under consideration.

Analysis	Samples			
	dc-Mc	AC-dc-Mc	dc-Md	AC-dc-MD
Yield (wt. %)	64.6*	48.0**	69.6*	50.0**
Proximate (wt.%)				
W^{ad}	1.7	1.0	1.7	0.7
Ash^{db}	17.7	26.9	17.5	25.1
VM^{db}	12.6	13.3	12.3	4.2
$C_{fix}{}^{db}$	69.7	59.8	70.2	70.7
Ultimate Analysis wt.%)^{db}				
C	66.0	65.2	70.5	62.6
H	2.1	0.3	1.6	0.6
N	3.6	2.0	1.6	0.6
S	0.9	0.8	1.3	1.0
O^{diff}	9.7	4.8	7.5	10.1
pH_{pzc}	-	8.6	-	8.2
Porous texture characteristics				
S_{BET} (m^2 g^{-1})	-	362	-	436
$V_{0.95}$ (cm^3 g^{-1})	-	0.260	-	0.276
$V_{DR,micro}$ (cm^3 g^{-1})	-	0.141	-	0.169
V_{meso} (cm^3 g^{-1})	-	0.119	-	0.106
L_0 (nm)	-	1.58	-	1.68

^{ad}- air dried; ^{db}-dry basis; *-product yield as a result of demineralisation procedure; **-activated carbon yield calculated based on demineralised char counterpart.

As a result of physical activation of demineralised chars with water vapour, ACs with product yield of about 50 wt.% are prepared. Although the yields of demineralised char based ACs are lowered with about 20 wt.% in comparison with the yield of non-demineralised char based ACs, the former possess lower ash content (≥ 50 % decrease) and higher C_{fix} content, hence, improved AC characteristics are expected. The removal of mineral matter is reflected in a change of pH_{pzc} value of AC-dc-Mc and AC-dc-Md samples as well. The pH_{pzc} value of AC-dc-Mc and AC-dc-Md samples are 8.6 and 8.2, respectively, while for non-demineralised char based ACs a pH_{pzc} of about 11 is found. Porous texture characteristics are also affected due to demineralization. N_2 adsorption isotherms of AC-dc-Mc and AC-dc-Md (Fig.1) similar to those of AC-Mc and AC-Md (not shown) represent a type I-IV hybrid shapes, according to the IUPAC classification [26]. This behaviour of the adsorption isotherms reveals that the porous structure of investigated carbons is characterized by both micro- and mesopores. However, the isotherms of AC-dc-Mc and AC-dc-Md compared to AC-Mc and AC-Md, respectively, display an increase in the adsorbed N_2. Consequently, higher S_{BET} and $V_{0.95}$, especially in the case of AC-dc-Mc, are calculated,

mainly related to the development of microporosity and to a lesser extent of mesoporosity increase.
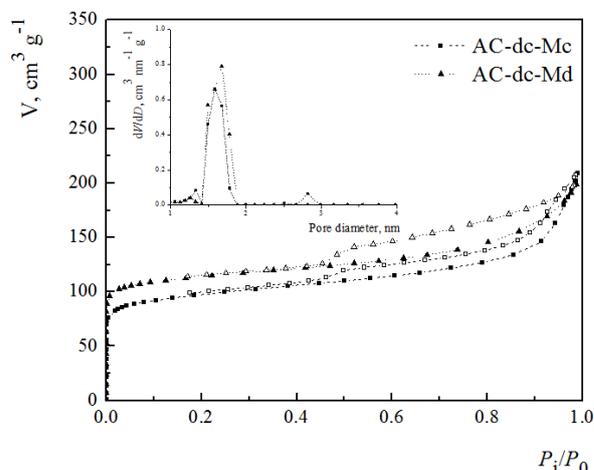

Fig. 1. N_2 adsorption isotherms of AC-dc-Mc and AC-dc-Md samples. Inset: Pore size distribution.

Apparently, physical activation of dc-Mc char by water vapour demonstrates a stronger gasification effect on carbons compared to the physical activation of c-Mc char, evoking a better developed porosity of AC-dc-Mc in comparison to AC-Mc. Nevertheless, from N_2 adsorption-desorption isotherms it can be revealed that dc-Md based AC demonstrates higher N_2 adsorption capacity, respectively larger surface area, than dc-Mc based

AC. This behaviour is again in accordance with ACs produced from not demineralised chars. S_{BET} values calculated for AC-dc-Mc and AC-dc-Md are 362 m^2 g^{-1} and 436 m^2 g^{-1}, respectively, while for AC-Mc and AC-Md 267 m^2 g^{-1} and 428 m^2 g^{-1} are noticed, respectively.
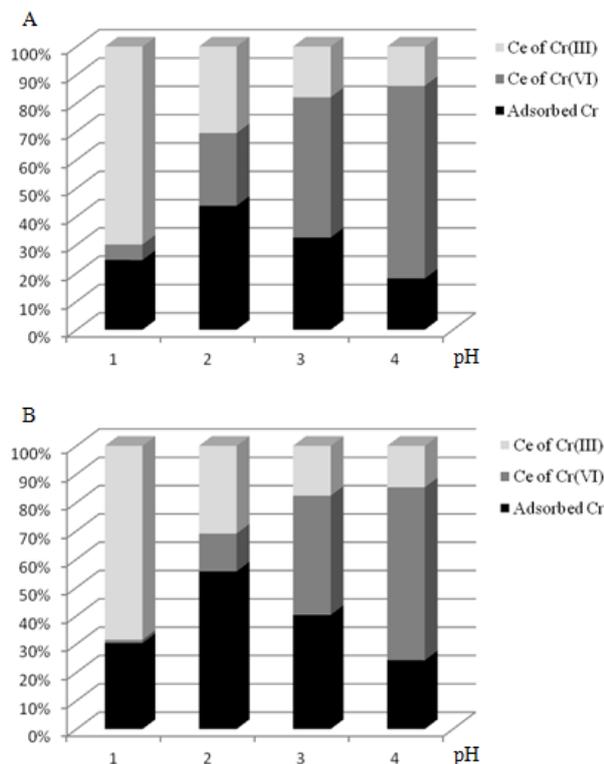

Fig. 2. Chromium distribution as a result of adsorption experiments on AC-dc-Mc (A) and AC-dc-Md (B) at different pH. Different colors of the columns represent adsorbed Cr_{tot} (black), C_e of Cr(III) in the solution (light grey) and C_e of Cr(VI) in the solution (dark grey). Experimental conditions: *m*= 0.030 g, *V*=50 ml, C_o=40 mg L^{-1}, *T*=25 °C, 48 h

The two oxidation states of chromium present in the environment are Cr(III) and Cr(VI). Trivalent chromium is considered to be less toxic than the hexavalent chromium, which is recognized as a carcinogenic and mutagenic agent. However, due to the possible oxidation of Cr(III) to Cr(VI), environmental legislation limits both, total and hexavalent chromium concentration in water [24]. It is well documented that Cr(VI) adsorption from aqueous solution by AC is favoured at low pH [25,26]. Therefore, the effect of pH on the removal of Cr(VI) by AC-dc-Mc and AC-dc-Md is investigated in a pH range of 1.0 to 4.0. Among existing Cr(VI) species, i.e. H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$ and $Cr_2O_7^{2-}$, the dominant form of Cr(VI) in this pH range is $HCrO_4^-$. Its adsorption by ACs can be explained by the following mechanisms

[24,26]: i) an electrostatic attraction with protonated acidic groups or protonated basic surface sites; and ii) AC oxidation by $HCrO_4^-$ in which Cr(VI) is reduced to Cr(III) and thus eventually adsorbed on AC external surface. The chromium distribution during Cr(VI) adsorption experiments on AC-dc-Mc and AC-dc-Md at different pH is assessed and is shown in Figure 2.

It is obvious that beside adsorption, reduction of Cr(VI) to Cr(III) takes place. The following peculiarities in Cr(VI) removal process by AC-dc-Mc and AC-dc-Md is depicted: i) the maximal Cr adsorption occurred at pH 2; and ii) the maximal reduction of Cr(VI) to Cr(III) appeared at pH 1. However, of utmost importance is the extent of total chromium (Cr_{tot}) removal. As mentioned earlier, Cr(III) is less toxic but in the environment oxidation of Cr(III) to Cr(VI) can occur. Consequently, it is advisable both Cr(VI) and Cr(III) to be removed by ACs. Therefore, the influence of initial solution pH on Cr_{tot} adsorption is assessed (Fig. 3). The results demonstrate that the optimal initial solution pH for Cr_{tot} adsorption by AC-dc-Mc and AC-dc-Md is pH 2. Similar results are observed for AC-Mc and AC-Md as well.
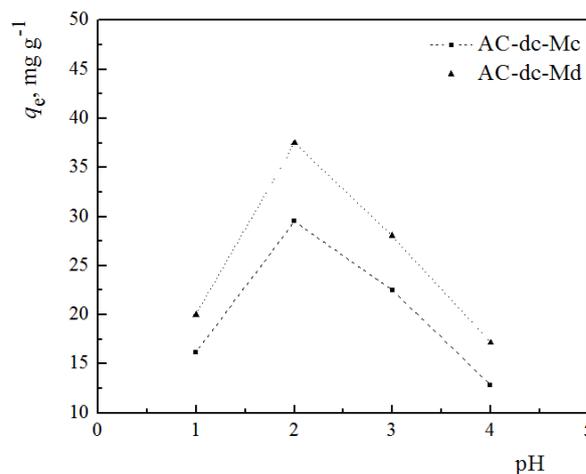

Fig. 3. Influence of initial solution pH on Cr_{tot} adsorption. Experimental conditions: *m* = 0.030 g, *V* = 50 ml, C_o = 40 mg L^{-1}, *T*= 25 °C, 48 h.

Freundlich and Langmuir isotherm models have been applied to Cr_{tot} equilibrium adsorption data obtained for AC-dc-Mc and AC-dc-Md at initial solution pH 2 (Fig. 4). Estimated parameters and correlation coefficients of isotherm modelling are presented in Table 2. In order to distinguish the influence of mineral matter content of studied ACs on Cr adsorption behaviour, data of isotherm modelling for AC-Mc and AC-Md are included as well. For all samples the Langmuir model describes better Cr_{tot} adsorption data at the studied

experimental conditions. Consequently, the applicability of a monolayer coverage chemisorption of Cr on the ACs surface could be considered. Calculated Langmuir monolayer adsorption capacity q_m demonstrates that higher Cr_{tot} adsorption is determined for AC-Md and AC-dc-Md. The observation could be explained by the higher surface of these ACs. Apparently applied demineralisation treatment also affects Cr_{tot} adsorption. Demineralised char based ACs reveal higher Cr_{tot} adsorption capacities. This is especially pronounced for AC-dc-Mc characterised by highly developed porous texture comparing to the non-demineralised counterpart.
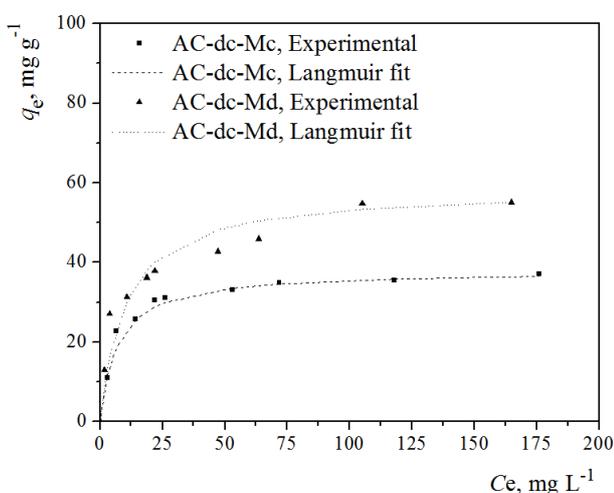

Fig. 4. Equilibrium Cr_{tot} adsorption isotherm for AC-dc-Mc and AC-dc-Md samples, i.e. experimental data and Langmuir fitting. Experimental conditions: initial Crtot solution pH = 2, m = 0.030 g, V = 50 ml, Co = 10-200 mg L-1, T= 25 °C, 48 h.

The adsorption of Cr_{tot} by the best ACs for Cr removal, i.e. AC-Md and AC-dc-Md, is studied as a function of contact time at the optimal initial solution pH as well (Fig. 5).
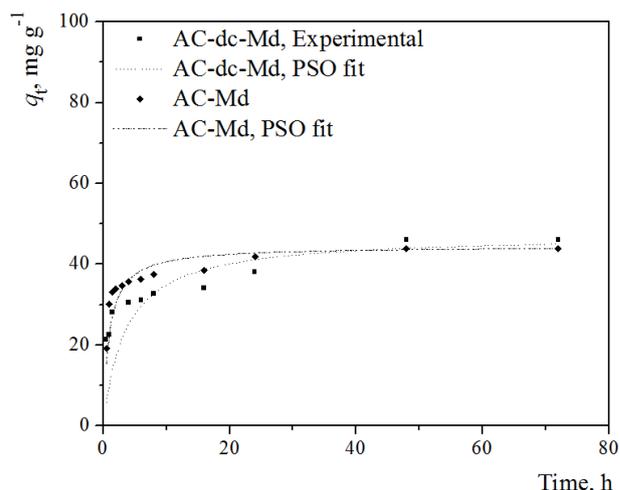

Fig. 5. Effect of contact time on adsorption of Cr_{tot} by AC-dc-Md and AC-Md. Experimental conditions: initial Cr_{tot} solution pH=2, m=0.030 g, C_0=40 mg L^{-1}, V=50 ml, T=25 °C.

In the first 3h adsorption for both samples increases rapidly, approaching slowly the equilibrium within 48 hour. Two reaction based kinetic models, *i.e.* pseudo-first and pseudo-second order (PSO) models, were applied to the experimental adsorption data. Calculated kinetic parameters as well as correlation coefficients of the models are presented in Table 3. Obviously, the PSO kinetic model provided a better fit, approved by the high correlation coefficient and better match for the experimental q$_{e(exp)}$ and the calculated one. This supports the assumption that the overall rate of Cr_{tot} adsorption might be controlled by a chemical process through sharing electrons or by oxidation/reduction reactions through exchanging of electrons between adsorbent and adsorbate. Calculated equilibrium rate constant for the pseudo-second order and the initial adsorption rate, *h*, are higher for AC-Md.

Table 2. Parameters and correlation coefficients of isotherm modelling

Sample	Langmuir			Freundlich		
	K_L L mg^{-1}	q_m mg g^{-1}	R^2	K_F mg g^{-1} (mg L^{-1})^n	n	R^2
AC-Mc	0.137	23.1	0.980	10.733	6.550	0.596
AC-dc-Mc	0.145	37.9	0.998	12.001	4.070	0.765
AC-Md	0.263	52.1	0.986	18.854	4.352	0.791
AC-dc-Md	0.099	58.5	0.991	14.649	3.510	0.890

Table 3. Parameters and correlation coefficients of kinetic modelling

	Parameter		AC-Md	AC-dc-Md
	$q_{e\,(exp)}$	(mg g^{-1})	43.9	46.1
Pseudo-first order	$q_{e\,(cal)}$	(mg g^{-1})	13.8	21.0
	k_1	(min^{-1})	0.6×10^{-3}	0.7×10^{-3}
	R^2		0.8345	0.8755
	$q_{e\,(cal)}$	(mg g^{-1})	44.4	47.2
Pseudo-second order	k_2	(g mg^{-1} min^{-1})	0.4×10^{-3}	0.1×10^{-3}
	h		0.79	0.22
	R^2		0.9993	0.9933

CONCLUSION

The present study demonstrates that the decrease in mineral matter content of manure based ACs influences their characteristics and adsorption behaviour. The HCl demineralisation of chars prior to physical activation decreases ash content with more than 50 %. The treatment affects the activation mechanism and ACs with better developed porous texture are prepared demonstrating higher adsorption capacity towards Cr compared to that of non-demineralised char based ACs. Among applied isotherm models to experimental adsorption data, better fits are depicted for the Langmuir model. Consequently, a monolayer coverage chemisorption of Cr on the ACs surface is in line with the obtained data

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ВЛИЯНИЕ НА ДЕМИНЕРАЛИЗАЦИЯТА ВЪРХУ ХАРАКТЕРИСТИКИТЕ И АДСОРБЦИОННОТО ПОВЕДЕНИЕ НА АКТИВНИ ВЪГЛЕНИ, ПОЛУЧЕНИ ОТ СВИНСКИ ТОР

Л. Гонсалвеш[1*], А. Попова[2], С. Маринов[2], М. Стефанова[2], Р. Карлеер[3], Я. Иперман[3]

[1]Централна научно-изследователска лаборатория, Университет „Асен Златаров“, Бургас 8000, България

[2]Институт по органична химия с Център по фитохимия, Българска академия на науките, София 1113, България

[3]Университет на Хаселт, Изследователска група по приложна и аналитична химия, Агора път - сграда Д, В-3590 Дийпенбек, Белгия

(Резюме)

Активни въглени (АВ[-ни]) от проби свински тор (СТ) бяха получени чрез пиролиз и активация с водна пара. Приложена също бе и деминерализация на получените след карбонизация въглени. Допълнително бе изследван адсорбционния капацитет на деминерализираните АВ[-ни] по отношение на съдържанието на хром във водни разтвори и бе сравнен адсорбционния им капацитет с този на АВ[-ни] получени от недеминерализираните въглени. Проведената деминерализационна обработка доведе до намаление съдържанието на минералната маса на АВ[-ни] с над 50% и до промяна в техните характеристики и адсорбционно поведение. Получените деминерализирани АВ[-ни] се характеризират с по-добре развита пориста текстура и по-висок адсорбционен капацитет по отношение на хрома в сравнение с недеминерализираните АВ[-ни]