REMOVAL OF ARSENIC AND LEAD FROM GOLD MINING WASTEWATER BY ADSORPTION USING CATLLE MANURE ACTIVATED CARBON IN MONGOLIA

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1. Introduction

Mongolia has many rivers and lakes, among them, the Selenge River is considered the largest. It is a significant water source for over half the country's population. It is where most of the country's agricultural and mining activities, the largest industries in Mongolia, are located. The high concentration level of arsenic and lead in surface water, groundwater, and wells is mainly generated by gold mining activity. Gold minerals and bedrock contain high quantities of arsenic and lead that during the gold extraction and washing process, the toxic chemicals are released to the environment. Batbayar, G. revealed that large levels of arsenic have been discovered in artificial ponds used in gold mining for processing water as well as in the mine effluents [1]. In addition, a mining site called Bor Tolgoi had a maximum arsenic concentration of 2.82 $\times\ 10^{-3}$ kg m^{-3} in the mining wastewater ponds and the effluent discharge, which exceeded the limit of World Health Organization's (WHO) arsenic in drinking water level which is 10^{-5} kg m^{-3} [1,2]. Ulziikhishig showed that the blood lead concentration of children who participated in the survey recorded a high geometric average of 7.42 $\times\ 10^{-5}$ kg m^{-3}, which is higher than the blood lead reference value of 3.5 $\times\ 10^{-5}$ kg m^{-3} [3,4]. The children have high blood lead concentration because their residence is near the mine and being exposed to it. Thus, when the gold mining wastewater contains this high amount of toxic chemicals, as well as in the mining effluents, it could cause danger to the people living near the gold mining site and area, increasing the demand to treat the wastewater.

The annual livestock of Mongolia in 2023 is reported as 64.7 million, with 5.47 million from cattle [5]. Then, due to the enormous number of livestock, manure is produced massively. However, the manure management is underdeveloped, and it could cause harm to the soil and water bodies. Hence, livestock manure should be managed properly.

There are several methods for the removal of heavy metals from water. Among them, adsorption is frequently used, and activated carbon is often used as sorbents, where they are prepared from various materials including manure. There are studies on using manure to adsorb heavy metals, but there are very few on adsorption of the arsenic and lead.

The objective of the study was to remove arsenic and lead by adsorption using cattle manure activated carbon (CMAC) for the treatment of gold mining wastewater in Mongolia. CMAC was prepared from dried cattle manure and its yield, properties were studied. Then batch adsorption experiments of model wastewater were conducted with CMAC to determine the performance. Lastly, material balance of the treatment of gold mining wastewater in Mongolia was discussed based on the CMAC yield and adsorption performance obtained in the above.

2. Experimental

2.1. Production and characterization of CMAC

Cattle manure was obtained from two different places, a farm in Satsuma Sendai city, Kagoshima prefecture, and a farm in Fujisawa city, Kanagawa prefecture. The cattle manure was stored in the refrigerator and before the experiments, it was thawed, dried, ground, and screened. The prepared dried cattle manure was characterized by a CHN elemental analyzer and was provided to CMAC production.

Figure 1 shows the schematic diagram of the thermal treatment reactor [6]. The specific amount of dried cattle manure was put on a sample boat and the boat was placed into the tubular reactor. Then, the reactor was sealed and filled with nitrogen gas for about 0.17 hours. After that, the heating was started and when the temperature inside the reactor reached 473 K, steam was started to be supplied to the device. Then, at 1 hour of thermal treatment time, the heating and steam supply were stopped. When the reactor was naturally cooled down to room temperature, CMAC was taken out from the reactor and weighed.

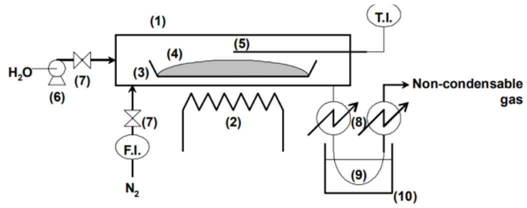


Fig. 1 Thermal treatment reactor
(1) tubular reactor; (2) electric tubular furnace; (3) sample boat; (4) feed product; (5) NiCr-Constantan thermocouple; (6) micro-plunger pump; (7) valves; (8) condensers; (9) liquid product trap; (10) iced bath; [6]

After washing and drying, CMAC was provided to the characterization in terms of specific surface area and pore size distribution. Table 1 shows the experimental condition for the thermal treatment process.

Table 1 Experimental conditions of thermal treatment

Feed	Dried cattle manure
Mass of feed, W_0 [kg]	0.013
Atmosphere	N_2; H_2O
Flow rate [$m^3\ h^{-1}$]	4.8×10^{-3}, 9×10^{-3} (N_2); 4×10^{-3} (H_2O)
Temperature, T_{TT} [K]	873 – 1273
Thermal treatment time [h]	1

2.2. Batch adsorption of model wastewater

The conditions of batch adsorption runs are given in Table 2. The model wastewater was the aqueous solutions of $Na_2HAsO_4\cdot7H_2O$ and/or lead $Pb(NO_3)_2$ with deionized water. The commercial activated carbon, CAC, and CMAC were the adsorbents. CAC was crushed and screened by a commercial sieve of 425×10^{-6} m apertures. Specified amounts of model wastewater and activated carbon in flask were shaken in a constant temperature shaker to be contacted for a specified time.

Table 2 Experimental conditions of batch adsorption

Feed		Aqueous solution of As and/or Pb
Mass, L_0	[kg]	0.025
Concentrations of solutes, $C_{i,0}$ (i=As, Pb)		
$C_{As,0}$	[kmol m^{-3}]	1.72×10^{-5} - 0.003
$C_{Pb,0}$	[kmol m^{-3}]	6.94×10^{-5} - 0.014
Adsorbent		CAC, CMAC
Mass ratio to feed, S_0/L_0	[–]	0.02
Contacting time, t_{AD}	[h]	1 - 1824
Contacting temperature, T_{AD}	[K]	300

Liquid phases were analyzed by ICP-OES to determine the concentration of solutes.

3. Results and discussions

3.1. Production and characterization of CMAC

Table 3 shows the elemental composition of dried cattle manure.

Table 3 Elemental composition of dried cattle manure

Origin	C	H	N	Ash
Kagoshima	0.385	0.056	0.025	0.165
Kanagawa	0.425	0.058	0.024	0.091

The content of H, N were similar for both samples while the content of C was higher in sample from Kanagawa prefecture. The ash content of sample from Kagoshima prefecture was high with 0.165, almost twice of the other one. The cattle manure from Kanagawa had high carbon and low ash content.

The fractional yield of CMAC, Y_{CMAC}, was defined by,

$$Y_{CMAC} = W_f\ /\ W_0 \tag{3.1}$$

Table 4 summarizes the effect of nitrogen flow rate on the yield, Y_{CMAC}. The Y_{CMAC} decreased with N_2 flow rate.

Table 4 Effect of nitrogen flow rate on yields of CMAC

N_2 Flow rate [m^3h^{-1}]	Y_{CMAC}
4.8×10^{-3}	0.33
9×10^{-3}	0.28

Figure 2 shows the effect of thermal treatment temperature on the fractional yields of CMAC. The yield of CMAC decreased with thermal treatment temperature, T_{TT}. This could be due to the increased reaction rates of activating agents and removal of the carbon materials. In addition, the ash content present in the dried cattle manure could be lost at higher temperatures.

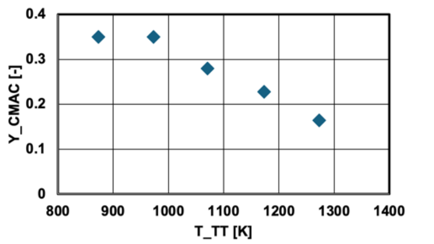


Fig. 2 Effect of thermal treatment temperature on yield

Figures 3 and 4 shows the specific surface area, BET plot, and pore size distribution, BJH plot, of CMAC.

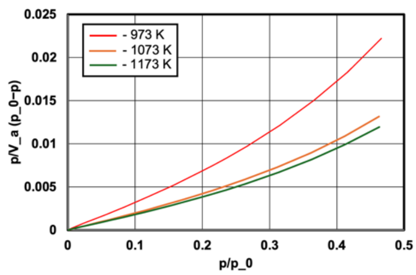


Fig. 3 BET-Plot

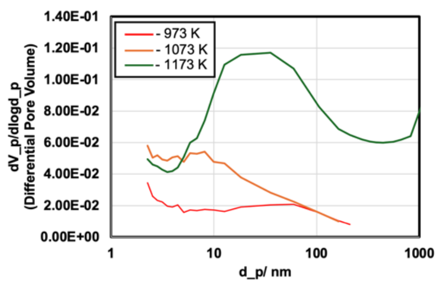


Fig. 4 BJH-Plot

Table 5 shows the specific surface area of CMAC. The specific surface area increased with the increasing temperature.

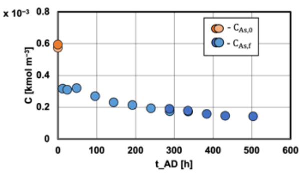
Table 5 Specific surface area of CMAC

T_{TT} [K]	S_{BET} $[m^2 g^{-1}]$
973	1.4×10^2
1073	2.2×10^2
1173	2.4×10^2

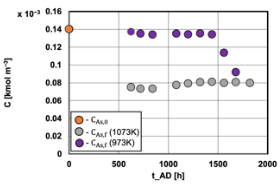
The increase in specific surface area could be caused by the creation of pores at higher temperature from the removal of volatile matters and enhancement of reaction between the steam activating agent and carbon materials. Then from the BJH method, the pores with larger diameters were formed at higher thermal treatment temperatures. CMAC produced at 973 K had high micropore and low mesopore volume. At 1073 K, the distribution of micropores and mesopores was broad. At 1174 K, high mesopore and low macropore volumes were present.

3.2. Batch adsorption of model wastewater

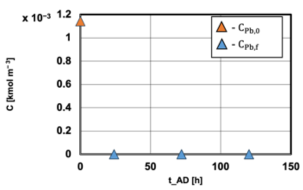
The time course of the solute concentrations, C_{As}, C_{Pb}, by CAC and CMAC are shown in Figures 5(a)-(f).



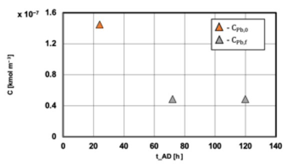
(a) As by CAC

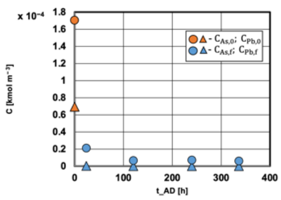


(b) As by CMAC



(c) Pb by CAC


(d) Pb by CMAC


(e) As and Pb by CAC

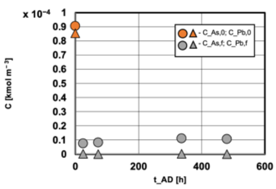

(f) As and Pb by CMAC

Fig. 5 The time course of the solute concentrations, C_{As}, C_{Pb}, by CAC and CMAC

The CMAC could remove both arsenic and lead from the model wastewater in single and binary systems. The single component adsorption of arsenic by CAC and CMAC reached equilibrium at 432 and 624 hours. On the other hand, the single component adsorption of lead by CAC and CMAC reached equilibrium at 24 and 72 hours, much faster compared to the arsenic ions. In addition, the system reached equilibrium faster with up to 72, 120 hours by CMAC and CAC, respectively in the binary system. This could be due to the lower initial concentration of the model wastewater and increased competition for the adsorption sites.

Then, the fractional removal of arsenic by CAC was higher than that of CMAC that they were all above 0.5. In the case of lead by CMAC, the initial concentration of the model wastewater varied up to 5×10^{-3} kmol m^{-3}. In this region, the fractional removal rate was all above 0.99, higher than that of CAC. For binary adsorption system, the adsorbed amount of heavy metal ions was high with fractional removal of above 0.9 for both activated carbons.

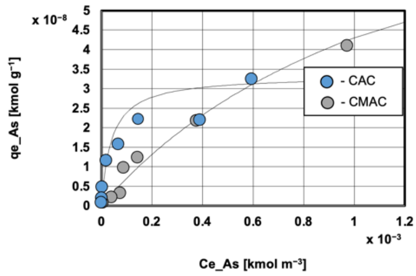
The material balance relation in the adsorption run is represented by,

$$V_0 C_{i,0} = V_0 C_i + S_0 q_i \quad (3.2)$$

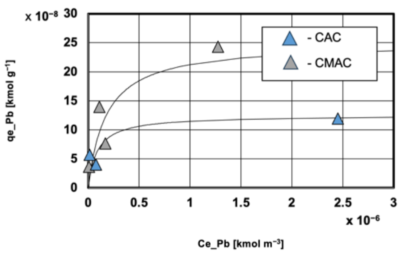
By this equation, the adsorbed amount, q_i, was calculated. The adsorption isotherms were studied using Langmuir model,

$$q_{i,e} = q_{i,max} K_{i,L} C_{i,e} / (1 + K_{i,L} C_{i,e}) \quad (3.3)$$

Figures 6 (a) and (b) shows the adsorption isotherms of single component adsorptions of arsenic and lead. In all cases, the adsorptions followed the Langmuir model.



(a) Adsorption isotherm of arsenic



(b) Adsorption isotherm of lead

Fig. 6 Adsorption isotherms of single component adsorptions of As and Pb

Table 6 shows the Langmuir isotherm values for the single component adsorptions of arsenic and lead.

Table 6 Langmuir isotherm values

Single component adsorption	Activated Carbon	$q_{i,max}$ $[kmol\ g^{-1}]$	$K_{i,L}$ $[m^3\ kmol^{-1}]$
As	CAC	3.3×10^{-8}	2.5×10^4
	CMAC	1×10^{-7}	7.6×10^2
Pb	CAC	2.5×10^{-7}	3.5×10^3
	CMAC	2.5×10^{-7}	5.6×10^5

The maximum adsorption capacity of arsenic by CMAC was higher than that of by CAC. In the case of lead, it was the same. Although the Langmuir constant of arsenic on CAC was higher than that on CMAC, that of lead on CMAC was higher than on CAC.

3.3. The gold mining wastewater treatment by CMAC in Mongolia

Table 7 shows the heavy metal concentration in gold mining wastewater. The flow rate of 10000 m^3 per day, from the wastewater treatment plant in Darkhan City, Mongolia, is used [8].This is because the data of gold mine effluent flow rate couldn't be found. This wastewater treatment plant is said to be bigger than the average wastewater pond of gold mine in Mongolia.

Table 7 Heavy metal concentration in gold mining wastewater

Heavy metal	Metal concentration in mine effluent [$kmol\ m^{-3}$]	Metal concentration discharged per year [kmol]
Arsenic	3.764×10^{-5}	1.37×10^{2}
Lead	-	-

Table 8 shows the amount of heavy metal ions that can be adsorbed from the gold mine effluent. The data of annual cattle amount in Mongolia and manure generated per day by cattle in Japan are used. [5,7]

Table 8 Treatment of gold mining wastewater

Definition	Amount
Cattle in Mongolia	5.47 million
Feces generated by cattle per day [kg]	58.9
Cattle manure generated per year [kg]	1.17×10^{11}
Possible CMAC production [kg]	3.06×10^{10}
Arsenic ion that can be adsorbed [kmol]	3.06×10^{6}
Lead ion that can be adsorbed [kmol]	7.64×10^{6}

In real life scenario, the amount of arsenic ion discharged from the mine effluent is lower than the amount of arsenic ion that can be adsorbed by the CMAC. In addition, the lead ion that can be adsorbed is more than twice of that of arsenic. Then as the concentration of arsenic in gold mine is generally higher than that of lead, the amount of lead ion discharged from the mine effluent would be lower than the amount of lead ion that can be adsorbed by the CMAC. Thus, dried cattle manure can be utilized to remove the arsenic and lead from gold mining wastewater and solve the problems occurring in Mongolia.

4. Conclusion

Activated carbon could be produced from dried cattle manure through thermal treatment under nitrogen and steam activation. The yield of CMAC was around 0.3.

In the batch adsorption runs, CMAC successfully removed arsenic and lead from the model wastewater in both single and binary component adsorptions. The adsorption of the metals followed the Langmuir model.

The study of CMAC production, its adsorption capacity, and removal of arsenic and lead ion in the real gold mining wastewater scenario suggested that CMAC could reduce the concentration of heavy metals significantly. In conclusion, the study was proposed as a feasible method to treat the gold mining wastewater and to reduce the cattle manure in Mongolia.

Nomenclature

W_0 : Initial mass of dried cattle manure [kg], W_f : Mass of CMAC [kg], T_{TT} : Thermal treatment temperature, $C_{i,o}$: Concentration of solutes in feed solution [$kmol\ m^{-3}$], $C_{As,o}$: Concentration of $As(V)$ in feed solution [$kmol\ m^{-3}$], $C_{Pb,o}$: Concentration of $Pb(II)$ in feed solution [$kmol\ m^{-3}$], L_0 : Mass of feed [kg], S_0 : Mass of adsorbent [kg], t_{AD} : Contacting time [h], T_{AD} : Contacting temperature [K], Y_{CMAC} : Yield of activated carbon produced from thermal treatment [-], S_{BET} : Specific surface area [$m^2\ g^{-1}$], V_0 : Volume of liquid [m^3], $C_{i,e}$: Equilibrium concentration [$kmol\ m^{-3}$], $q_{i,e}$: The amount of arsenic adsorbed at equilibrium [$kmol\ g^{-1}$], $q_{i,max}$: The maximum adsorption capacity [$kmol\ g^{-1}$], $K_{i,L}$: The Langmuir constant [$m^3\ kmol^{-1}$]

References

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