

# Potential for using Cattle Hair from Hair-Saving Tanneries as Adsorbent for Crude Oil

by

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## Abstract

The oil cleanup potential of discarded cattle hair from tannery operations was investigated by batch adsorption experiments using two crude oils with different viscosities. The results illustrate that cattle hair exhibits higher adsorption capacity for crude oil with higher viscosity. The sorbent can adsorb 5 to 6 times its weight in the two crude oils. Maximum adsorption capacity of 8.72 g/g at 18°C is achieved with pulverized hair powder, and it is comparable to human hair. The sorption can fit better to Freundlich adsorption isotherm and shows the adsorption occurred on heterogeneous sites with a non-uniform distribution of energy. Desorption and reusability experiments confirmed reusability without significant reduction in sorption capacity. This investigation indicates that discarded cattle hair has potential as a low-cost and effective bio-sorbent for scavenging crude oil spillage.

## Introduction

Raw cattle hides are basic materials for the leather-making industry. They are processed in tanneries and the hairs in the hides are completely removed. The traditional leather-making process using hair-destruction technology leads to the hair being destroyed and useless. While the presently developed hair-saving unhairing technologies render the removed hair intact,<sup>1</sup> ensuring the utilization of the discarded hairs is feasible. What is more, the output of cattle hairs in tanneries is sizable due to the fact that 40 million pieces of cattle hides are processed in China every year, leading to more than  $4 \times 10^5$  tons discarded hair. Cattle hairs are often treated as solid waste or used for composting.<sup>2</sup> Thus the development of these discarded cattle hairs into appropriate products should be investigated to avoid problems such as waste of resources and environmental pollution.

Presently, with the development of offshore oil exploration and transportation, marine oil spill accidents have become increasingly serious, as shown by the January 2022 spillage of a tanker ship that released a huge amount of crude oil into the coast of Peru. Spillage demands urgent cleanup and regulatory sanctions to reduce environmental damage because spills spread rapidly and can cause significant ecological damage,<sup>3</sup> placing animal and human health at risk and destroying various natural resources.

Multiple cleanup strategies are applied including burning, usage of mechanical skimmers, chemical dispersants, and absorbents when oil spill occurs in marine environments. Among these methods, the use of sorbents is an attractive way due to their simplicity and relatively low cost.<sup>4</sup> Natural sorbents for the cleanup of oil spills have been considered due to their effectiveness, low cost, reusability and eco-friendliness. Several natural bio-sorbents for oil spillage removal have been reported.<sup>5</sup> These include plant fibers and protein fibers, such as cotton fiber, silk fiber, collagen fiber and keratin fiber. Keratin fibers such as wool,<sup>6</sup> yak hair and human hair,<sup>7-9</sup> have attracted great interest for oil spill remediation due to their effectiveness. Human hairs were often publicly called for as an emergency supply for cleanup during the recent oil spill incidents in Cayao (Peru) and Maracaibo Lake (Columbia). However, it is quite inconvenient to collect human hairs and the amounts are nowhere near enough as oil sorbents.

Cattle hairs are similar to human hairs in chemical components. They consist of medulla, cortex and cuticle made up of amino acids. The cuticle content makes hair water repellent and therefore, highly hydrophobic.<sup>10</sup> In addition, they have abundant peptide bonds and CO- as well NH- groups which form hydrogen bonds among the neighboring molecules on the hair surface and have a highly porous cortex.<sup>11</sup> The collection of cattle hair from tanneries is convenient and the cost is quite low. These make it possible for the cattle hair to be utilized as a new oil adsorbent.

The purpose of this paper is to investigate the adsorption capacity of discarded cattle hairs from tannery operations for oil spill cleanup under different conditions, and to provide a theoretical basis for the development and utilization of these cattle hairs in oil-adsorbing material.

## Experimental

### Reagents and materials

All chemicals used in the experiments were of analytical grade and purchased from Sinopharm Co. Ltd, Shanghai, China. Two light crude oils (No. 201# and 206#) were obtained from a petrochemical plant located in Ningbo City. The characteristics of the oils are outlined in Table I. Discarded cattle hair of 40-60  $\mu\text{m}$  used for the

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**Table I**  
Physical characteristics of used crude oils at temperature 18 °C

No. of Crude Oil	Density (g/cm <sup>3</sup> )	Rotary Viscosity (mPa-s)
201#	0.849	12.5
206#	0.853	26.0

adsorption experiments was collected from a tannery in Zhejiang province, and hair-saving technology was used in the unhairing process. Human hair of 30-70 µm used for comparison was obtained from a local hairdressing salon in Jiaying City. The human hair was sourced mainly from males and was original and free of dyes and dust.

#### Modification of the cattle hairs

Generally, the discarded cattle hairs from tanneries had been treated in lime solutions. These hairs are quite brittle if dried directly and inconvenient for use. Thus, the hairs were modified prior to use according to the following description. The hairs were first rinsed with 20 volumes of water containing HCl 0.01 mol/L for 30 min. After filtration, the hairs were immersed into 20 volumes of emulsifier solution containing 1% alkyl sulfonyl chloride (called M80) and treated in an ultrasonic bath with 40 Hz for 30 min. The hairs were then rinsed twice in warm water and dried at room temperature and were then ready for use.

#### Fiber surface morphology observation

The surface morphology of the hairs was examined after spraying gold to make the fibers conductive with a scanning electron microscope model of Phenom Pure from Phenom Scientific Co. Ltd Shanghai.

#### Adsorption experiments

Adsorption experiments were conducted in artificial seawater as described by Kester et al.<sup>12</sup> Crude oils (10-50 g, in Table I) were poured into separate 500 mL conical flask with 200 mL of seawater. Amounts of the sorbents (strands, 1-6 g) were added with a contact time (2-60 min) under a slight shaking action. All the experiments were conducted at the temperature 18±2°C approaching the average surface temperature of actual seawater.

Oil contents in the sorbent were measured based on EPA Method 1664 by hexane extraction.<sup>13</sup> The oil adsorption capacity (g/g) was calculated based on the weight of oil adsorbed in the hair and the weight of the hair before adsorption. The experiments were performed in triplicate with the average value and standard deviation (SD) calculated.

#### Effects of time on adsorption

The effects of contact time on the adsorption capacity were tested using the two types of oils (in Table I) separately. A dosage of 2 g adsorbent was used for the experiments. 20 g of crude oil were

subjected into 200 mL of seawater in a flask. Tests were carried out with samples withdrawn at intervals ranging from 2 to 60 min.

#### Effects of particle size on adsorption

The modified cattle hair and human hair were first cut into short fibers (< 3 mm) with electric scissors, and then pulverized with a precise grinder (Retsch ZM200, German). The particle sizes were checked with a Fiber Fineness Meter (Guoliang GL003, China), and the average sizes were almost at the range of 40-80 µm. A dosage of 2 g powder was added into the flask containing 20 g crude oil and 200 mL artificial seawater. The adsorption time was 60 min.

#### Effects of adsorbent dose on adsorption

This operation was the same as effects of time on adsorption described above, except that dosage of cattle hair strands ranged from 1 to 6 g, and the adsorption time was 60 min.

#### Sorption isotherm study

Batch adsorption isotherm studies were performed with dosage of 2 g hair strands used for the experiment. The operation was the same as effects of time on adsorption above, except that the adsorption time was 60 minutes. The experimental data obtained was analyzed using the Langmuir and Freundlich adsorption isotherm models separately.<sup>14-15</sup>

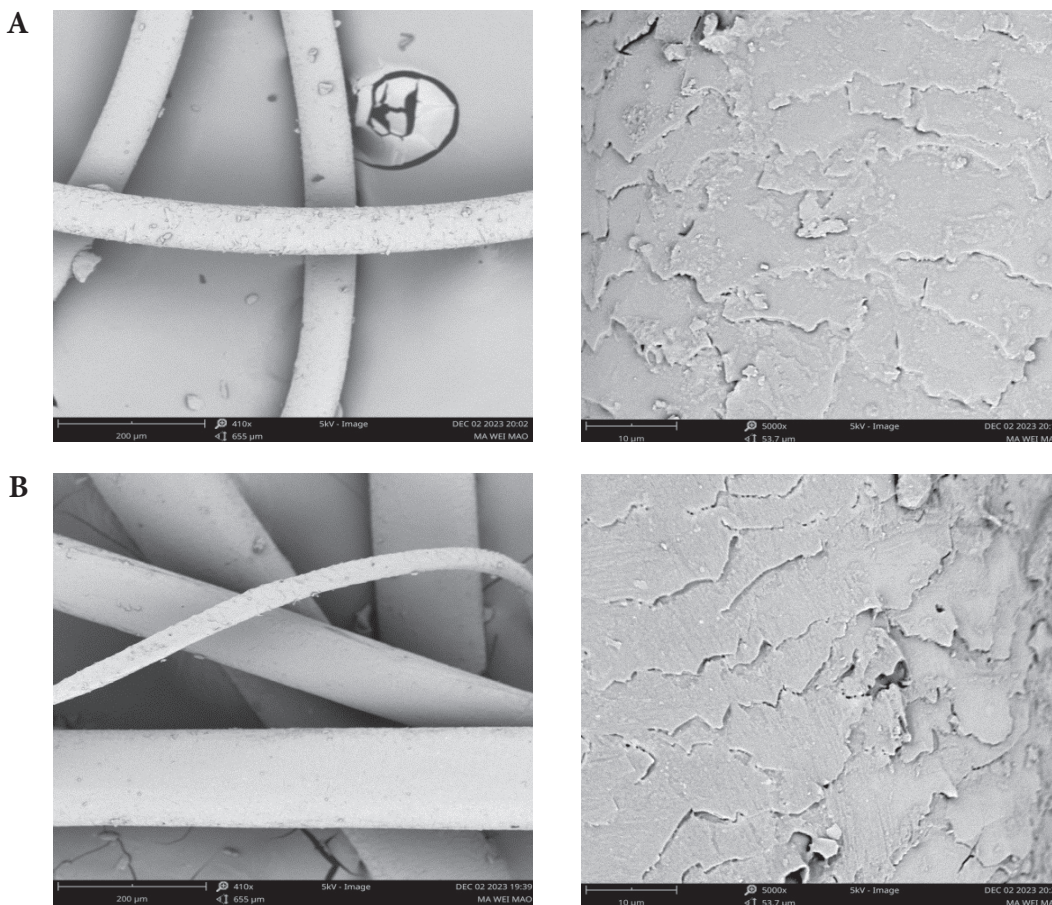
#### Reusability test

The hexane extraction method was used to recover the cattle hair for reuse, and the reusability of the sorbent for oil sorption was evaluated. The used cattle hairs were immersed into hexane and extracted for 60 min with ultrasonic assistance for desorption. The recovered hairs were then reused for the batch adsorption experiments in the following continuous cycles. Oils in the hexane were measured and the adsorption capacities were calculated.<sup>13</sup>

## Results and Discussion

#### Morphology of the hair

The surface morphology of the modified cattle hair was observed by scanning electronic microscopy (SEM). Human hair was also examined for comparison. As shown in Figure 1, the SEM images of cattle and human hair are quite similar. They have rough cuticles formed by many layers which look scaly. The cuticles are structural elements of individual hair strands, and they are more hydrophobic as water tends to bead on the hair strands. These contribute to the



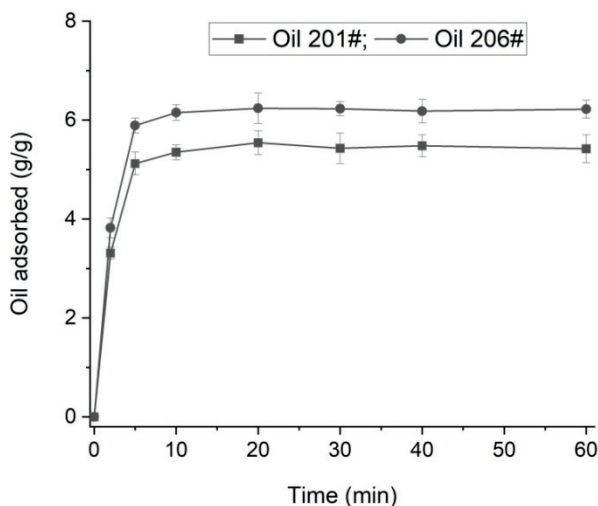
**Figure 1.** The surface morphology of cattle hair and human hair with magnification  $\times 410$  (left) and  $\times 5000$  (right).  
**A** - Cattle hair; **B** - Human hair.

action of the oil at the hair/oil interface and play a significant role in the sorption of oil by hair.

Both cattle hair and human hair are natural protein fibers, and their adsorption of oil is physical adsorption. It is mainly in the form of surface adhesion and adsorption, and the adsorption process is carried out on the surface of the fiber. For the two hairs with similar morphology and structure, their oil adsorption capacities should be comparable.

**Effects of time on adsorption**

The effects of contact time on the adsorption of cattle hair were tested by batch adsorption experiments at varying times of 2, 5, 10, 20, 30, 40, 60 min with other experimental variables kept constant. The results were illustrated in Figure 2. It was shown that there was a rapid increase in the sorption of the two crude oils in the first 5 minutes. From 5 to 20 min, the oil adsorption rate slowed and the oil adsorption capacities was close to saturation. After 20 min, the oil adsorption rate tends to zero and the oil adsorption capacities are



**Figure 2.** Adsorption rate of oil 201# and 206# on cattle hair strands at temperature 18°C. The hair dosage is 2 g and crude oil is 20 g. The bars represent standard deviation of the mean.

basically similar, which indicates that the sorption has reached the saturated oil adsorption capacities.

The initial high sorption rate might be attributed to the existence of bare sites available for adsorption on the surfaces of the hair. As most portions of these sites became occupied by the oil molecules with prolonged contact time, the adsorption rate decreased until the 20th minute, when there was no more obvious sorption of crude oils. The reasons should rely on the saturation of the surfaces of the hair with oil molecules, as well as the equilibrium between the adsorption and desorption processes that occur after saturation. Similar results were also obtained by other researchers regarding the use of yak hair<sup>8</sup> and human hair<sup>9-10</sup> for oil cleanup. Almost 90% of the total adsorbed oils took place in the first 5 min. These indicate that a certain contact time is necessary in possible field application of cattle hair for oil spill removal.

### Effects of particle size on adsorption capacity

Adsorption capacities of cattle hair in strands and powder forms were determined individually with the two crude oils 201# and 206# (as listed in Table I) by batch experiments, as shown in Figure 3. For cattle hair strands, the sorbents showed higher sorption capacity for oil 206# (6.28 g/g), and lower capacity for oil 201# (5.31 g/g), indicating that the hair has more affinity for oil 206# compared to

oil 201#. The better adsorption capacity for oil 206# might be due to its higher viscosity (Table I), which enhances the adherence of oils to the surface of the sorbents. The same phenomenon has been illustrated in other references.<sup>8,16</sup> For cattle hair powder with particle size of 40-80  $\mu\text{m}$ , the adsorption capacity improved to 7.63 and 8.49 g/g for oil 201# and 206#, respectively. The reason mainly relies on the enlarged surface area of the sorbents.

The adsorption capacities of human hair in strands and powder forms were also tested under the same adsorption conditions, as illustrated in Figure 3. It was found the cattle hair could compare favorably with the adsorption capacity of human hair, because the adsorption capacities of human hair strands were 5.41 g/g for oil 201# and 6.21 g/g for 206#, and the adsorption capacities of human hair powder were 7.95 g/g for oil 201# and 8.72 g/g for 206#. Considering that human hair has been recognized as a potential sorbent for oil cleanup by many researchers,<sup>8-9</sup> cattle hair can be another low-cost natural adsorbent used for oil spill cleanup.

### Effects of adsorbent dose on adsorption capacity

The effect of adsorbent dose (hair strands) on the adsorption efficiency was investigated, as shown in Figure 4. The adsorption efficiencies for the two oils increase with increasing mass of the

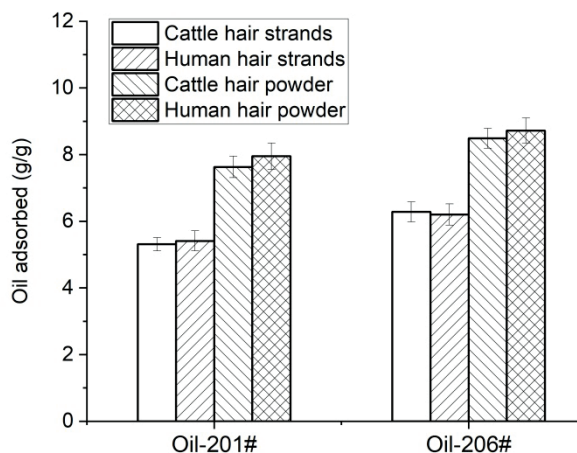


Figure 3. Adsorption capacities of cattle hair and human hair with strands and powder forms in crude oil 201# and 206# at temperature 18°C. The sorbent dosage is 2 g and crude oil is 20 g.

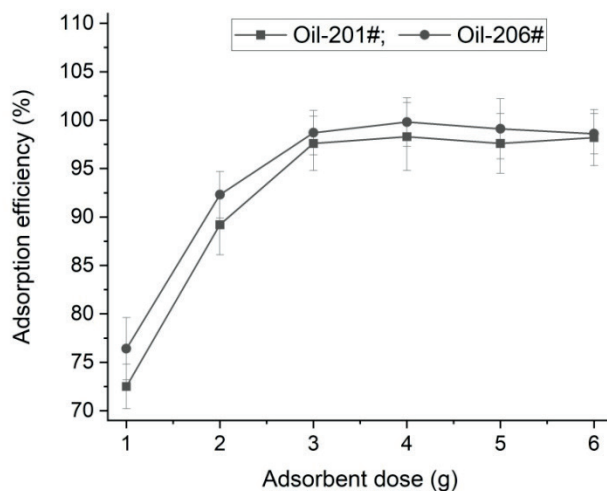


Figure 4. Dosage effect of cattle hair strands on the adsorption capacity in crude oil 201# and 206# at temperature 18°C.

adsorbent. The percentage uptake for oil 206# was found to be slightly higher than 201#. This might be related to the higher viscosity of 206#, as illustrated in Table I.

**Adsorption isotherms**

An adsorption isotherm helps to understand the interaction between the solute and the adsorbent, and also helps in modeling design parameters. Isotherms were depicted with equilibrium concentrations of the two oils (201# and 206#), as shown in Figure 5. The equilibrium data was further analyzed using the Langmuir and Freundlich adsorption isotherm models. The Langmuir model is often used for monolayer adsorption on a homogeneous surface with identical adsorption sites,<sup>14-15</sup> and is expressed as:

$$\frac{1}{Q_e} = \frac{1}{ab} \times \frac{1}{C_e} + \frac{1}{b}$$

where  $Q_e$  - the adsorption capacity at equilibrium (g/g),  $C_e$  - the concentration of oil remaining at equilibrium in mg/L, a, b - the constants, a is the coefficient, and b is the maximum amount of adsorbate. A plot of  $1/Q_e$  against  $1/C_e$  gives a straight line.

The empirical Freundlich model is appropriate for the adsorption on a heterogeneous surface,<sup>15</sup> which can be expressed as:

$$\log Q_e = \frac{1}{n} \log C_e + \log k_f$$

where  $Q_e$  - the adsorption capacity at equilibrium (g/g),  $C_e$  - the concentration of oil remaining at equilibrium in mg/L,  $n$  and  $k_f$  - constants derived from the adsorption isotherm by plotting  $Q_e$  against  $C_e$  on log-log paper which produces a straight line with a slope  $1/n$  while the y-intercept is  $k_f$ .

The Langmuir and Freundlich coefficients for single solute (crude oil) adsorption isotherms and their corresponding correlation coefficients are presented in Table II. The results illustrated a good fit of the Freundlich model ( $R^2 \approx 0.99$ ) to the experimental data. This fact is not rare as similar findings being previously reported.<sup>17-18</sup> This fact indicates that sites with non-uniform distribution of energy level rather than on a homogeneous site with uniform distribution of energy in cattle hair. In addition, the values of  $1/n$  were less than 1, indicating a favorable sorption of crude oil onto the cattle hair.<sup>19</sup>

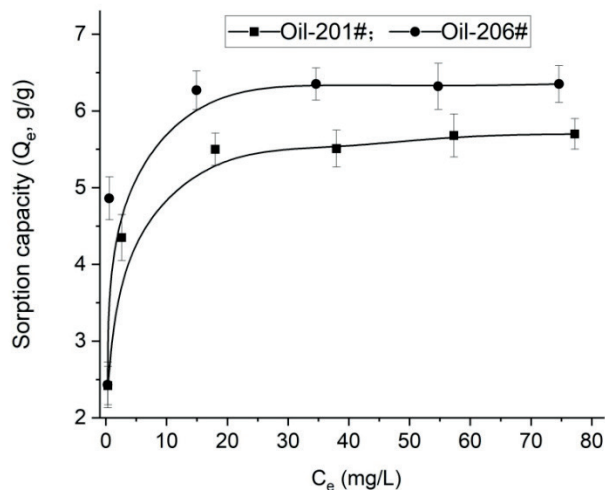


Figure 5. Adsorption isotherms of cattle hair strands to crude oils (201# and 206#) at temperature 18°C. The hair dosage is 2 g and crude oil is 20 g.

Solutes	Langmuir			Freundlich		
	<i>a</i>	<i>b</i>	<i>R</i> <sup>2</sup>	<i>1/n</i>	<i>k<sub>f</sub></i>	<i>R</i> <sup>2</sup>
Oil-201#	1.146	5.682	0.9689	0.1005	3.770	0.9879
Oil-206#	0.971	6.544	0.9669	0.1149	4.164	0.9892

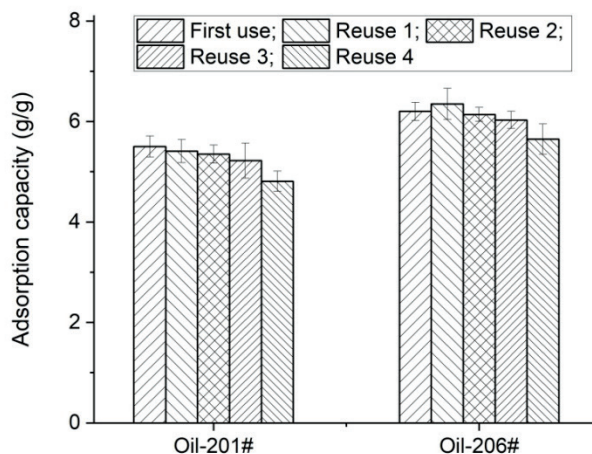


Figure 6. The reusability of the cattle hair strands at temperature 18°C

### Reusability of cattle hair sorbent

The recovered cattle hair by hexane extraction method was employed to evaluate the potential of reusing the sorbent without a significant decrease in performance over time. Figure 6 illustrated the results of the reusability test in the two crude oils (201# and 206#). It could be seen that there was no significant decrease in the adsorption capacity after five cycles of reuse. This is similar to other work of Ifeiebuegu et al<sup>8</sup> using human hair giving no obvious loss in its adsorption capacity after reusing four consecutive times, indicating the durability of this sorbent.

### Conclusion

The characteristics of discarded cattle hair obtained from a tannery adopting hair-saving unhairing technology were investigated to determine its potential for scavenging a crude oil spill. Two crude oils with different viscosities were used as adsorption targets. The results indicated that the cattle hairs exhibit higher adsorption ability for crude oil with higher viscosity, and the adsorption capacity reached 6.28 g/g at 18°C. It could be improved to a maximum of 8.72 g/g when the hair fiber was pulverized to fine powder, and its capacity was comparable to human hair. The sorption showed a better fit to the Freundlich adsorption isotherm, indicating the oil retention occurring on heterogeneous sites with a non-uniform distribution of energy. The sorbent could be reused in several cycles without significant deterioration in sorption characteristics, demonstrating its potential for use as a low-cost adsorbent for oil spill cleanup. Further studies for pilot experiments are underway in the lab.

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